Developments in Paleoenvironmental Research 18

Jules M. Blais
Michael R. Rosen
John P. Smol *Editors*

Environmental Contaminants

Using natural archives to track sources and long-term trends of pollution

Springer

Developments in Paleoenvironmental Research

Volume 18

Series Editor
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Aims and Scope:

Paleoenvironmental research continues to enjoy tremendous interest and progress in the scientific community. The overall aims and scope of the Developments in Paleoenvironmental Research book series is to capture this excitement and document these developments. Volumes related to any aspect of paleoenvironmental research, encompassing any time period, are within the scope of the series. For example, relevant topics include studies focused on terrestrial, peatland, lacustrine, riverine, estuarine, and marine systems, ice cores, cave deposits, palynology, isotopes, geochemistry, sedimentology, paleontology, etc. Methodological and taxonomic volumes relevant to paleoenvironmental research are also encouraged. The series will include edited volumes on a particular subject, geographic region, or time period, conference and workshop proceedings, as well as monographs. Prospective authors and/or editors should consult the Series Editor John P. Smol for more details. Any comments or suggestions for future volumes are welcomed.

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This book is dedicated to Professor David W. Schindler, in recognition of his tireless work dealing with environmental issues. We wish him well in his "retirement".

Preface

The Developments in Paleoenvironmental Research book series has thus far covered a wide spectrum of paleoenvironmental subjects, some of which have included examples of studies using natural archives of contaminants. However, given the growing interest and development of approaches used in this area, we believed it was an opportune time to collate summaries of some of these sub-disciplines into a single volume.

This book aims to provide a review of recent developments in the study of natural archives to resolve the timing and magnitude of environmental contaminants. Natural archives have tremendous potential to resolve the human footprint on the environment, but experience has shown that these archives must be examined with an understanding of the processes that may shape and modify the historical record. We have asked all contributing authors to bring these issues to bear, and we devote several chapters to discuss how external and internal processes may modify the historical record in sediments, specifically focusing on hydrology, geochemistry, and physical turbulence.

Our intent with this book was to provide a review of sufficient breadth and depth to serve both seasoned practitioners of the field, as well as newcomers. We strived to make the writing accessible to a general audience that could serve as a text for graduate courses as well as a reference for those actively participating in the field. The vast literature that utilizes natural archives to determine the timing and magnitude of pollutants spans a broad spectrum, including cores collected from ice, peat, lake and marine sediments, to sclerontological archives and museum specimens spanning centuries. This book spans this full range of natural archives, and will hopefully be useful to those who are curious about recent developments in these related fields. Ultimately, a strong proof of concept for the use of natural archives is to determine the concordance of separate lines of evidence as recorded in different kinds of archives, and this book aims to provide a platform to facilitate those kinds of comparisons.

Many people helped with the planning, development, and final production of this book. We would like to acknowledge the hard work and professionalism of our many reviewers, who provided constructive comments on earlier drafts of the manuscripts. We would also like to acknowledge the assistance we received from our publishers, and especially the efforts and encouragement from our main Springer colleagues—Judith Terpos and Sherestha Saini. Thanks are also due to our host institutions and our funding sources, which helped facilitate our academic endeavours. We also gratefully acknowledge a variety of publishers and authors who allowed us to reproduce previously published figures. Foremost, we would like to thank the authors for their hard work.

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About the Editors

Jules M. Blais is Professor of Biology and Environmental Toxicology at the University of Ottawa. He has published over 120 scientific articles on environmental chemistry and toxicology dealing especially with the behavior and fate of environmental contaminants and their impacts on lakes and northern communities. He is currently leading several projects on the effects of warming temperatures and resource extraction on freshwaters in Canada's north, and is also working closely with federal regulators to investigate risks to northern populations by exposure to environmental contaminants from northern traditional diets and contaminated soils. He was recently named Environmental Scientist of the Year by the Royal Canadian Geographical Society (2008), and is co-recipient of the 2013 Brockhouse Canada Prize for outstanding contributions to interdisciplinary research, awarded by the Natural Sciences and Engineering Research Council of Canada. He is Associate Editor of Environmental Reviews, and serves on the editorial board of other journals. He founded and co-directs the Laboratory for the Analysis of Natural and Synthetic Environmental Toxicants, a major laboratory for the analysis of organic and metallic contaminants at the University of Ottawa. He is currently President of the Society of Canadian Limnologists, which is committed to the advancement of aquatic science and water issues in Canada.

Michael R. Rosen is Water Quality Specialist for the Western United States within the Water Science Field Team of the U.S. Geological Survey. He has been a research scientist with the U.S. Geological Survey since 2001. Before this, he was the Groundwater Quality Programme Leader at the Institute of Geological and Nuclear Sciences (now known as GNS Science), New Zealand, a research scientist at CSIRO, Australia, the Limnological Research Center, University of Minnesota, and Curtin University of Technology, Western Australia. He has published more than 175 journal articles and reports on topics ranging from limnogeology and limnology of lakes, groundwater and lake pollution, geothermal water chemical evolution and sinter formation, and tufa formation. He has also edited three books on groundwater in New Zealand, limnogeology of playas, and the ecosystem and limnology of Lake Mead. He has been an associate editor for the journals Ground Water and Sedimentology and currently is the editor of the Journal of the Nevada Water Resources Association and serves on the Board of Directors. He was elected as a fellow of the Geological Society of America in 2010.

John P. Smol is professor of biology (cross-appointed with the School of Environmental Studies) at Queen's University (Kingston, Ontario), where he also holds the Canada Research Chair in Environmental Change. He founded and co-directs the Paleoecological Environmental Assessment and Research Lab (PEARL), a group of ~30 students and other scientists dedicated to the study of long-term global environmental change, and especially as it relates to lake ecosystems. He has authored ~500 journal publications and chapters since 1980, as well as completed 20 books. He was the founding Editor of the international Journal of Paleolimnology (1987–2007) and is the current Editor of the journal Environmental Reviews. Since 1990, he has been awarded over 45 research and teaching awards and fellowships, including the 2004 NSERC Herzberg Gold Medal as Canada's top scientist or engineer. Recently, he was named an Officer of the Order of Canada, the country's highest civilian honour. He is currently Chair of the International Paleolimnology Association (IPA).

Using Natural Archives to Track Sources and Long-Term Trends of Pollution: An Introduction

Jules M. Blais, Michael R. Rosen and John P. Smol

Abstract This book explores the myriad ways that environmental archives can be used to study the distribution and long-term trajectories of contaminants. The volume first focuses on reviews that examine the integrity of the historic record, including factors related to hydrology, post-depositional diffusion, and mixing processes. This is followed by a series of chapters dealing with the diverse archives available for long-term studies of environmental pollution.

Keywords Environmental archives · Sediments · Contaminants · Pollution · Metals · Mercury · Persistent organic pollutants · Long-term trends

We live in a constantly changing environment. Some changes are natural, but many can be closely linked to human activities such as urban, mining, agriculture, and other aspects of industrial development. Throughout most of human history, our population was too small, scattered and technologically undeveloped to markedly influence our local environment. However, as our technological skills and tools developed and population size increased, so also did our influence on ecological systems. As Crutzen and Stoermer (2000) noted, the human footprint is now everywhere, so much so that the designation of a new geological epoch, the Anthropocene or the period of human-dominated Earth history, appears to be appropriate.

One of the biggest challenges faced by environmental scientists and their efforts to provide evidence-based recommendations to policy-makers is the lack of long-term monitoring information or the lack of understanding of pre-disturbed conditions. Much like arriving at the scene of an accident after-the-fact, environmental

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studies are usually initiated only *after* an environmental problem has been recognized. Fortunately, all around us, there are natural archives of environmental change (e.g., sediments, growth rings, ice and peat cores) that are passively documenting the environment for us. For example, many of the volumes in the *Developments in Paleoenvironmental Research* (*DPER*) book series deal with various aspects of these historic records. Much has been gained from these paleoenvironmental perspectives, helping researchers disentangle natural from anthropogenic changes within the complex world we live in.

This *DPER* volume focuses on the tremendous library of information available in environmental archives for the study of contamination. Ever since humans harnessed fire and began agricultural practices, we began producing and affecting the transport and fate of pollutants. All environmental problems have a history, and this history is often critical to understand for effective ecosystem management. For example, due to the lack of direct monitoring data, it is often difficult to assess if in fact environmental conditions have changed, and if so, how much, when, and why? Can the influence of humans be detected, or are the changes due to natural processes? What are natural or baseline (reference) conditions and how much improvement can be expected upon contaminant remediation? Each of these questions has a temporal component associated with it but, because of the limited availability of monitoring data, we must make use of indirect, proxy methods, such as those summarized in this book.

The volume consists of 17 chapters, broadly encompassing three main subject areas. Following this short introduction, the first cluster of reviews consists of three chapters related to the integrity of the historic record in sediment profiles. The responsible use and interpretation of natural archives must be done with an understanding of how external and internal processes may modify the historic record. This section devotes attention to these important issues with chapters emphasizing the effects of hydrology, post-depositional diffusion, and physical mixing on the sediment record.

The second portion of the book contains eight chapters that review recent developments in the use of sedimentary archives to resolve: the effect of contaminants released during the Permian Extinction on marine life preserved in sedimentary deposits over 250 million years ago; temporal and spatial distribution patterns of metals in pre-industrial era sediments; temporal changes in metal accumulations from post-industrial mining and other industrial activities; temporal changes in organic pollutants caused by changes in the use of these pollutants; the distribution and source of contaminant particles such as fly ash; and the pathways for long-range transport of contaminants to the Arctic and mountain regions.

The third cluster of reviews contains five chapters that expand the scope of the historic environmental records to include natural archives that are not necessarily derived from sediment including peat cores, sclerochronological archives, ice cores, museum specimens, and contaminant transport by migratory animals, or biovectors.

We conclude the book with a short chapter summarizing some final thoughts on future avenues of research.

The continued success of research into the historic record preserved in natural archives will depend on interdisciplinary approaches to investigate the potential use and reliability of natural deposits to record historic events over the span of years to millennia and beyond. This book is intended to provide an overview of recent developments to both experienced researchers and to those new to the field. We hope that the book will inspire continued cutting-edge dialogue into this important line of inquiry.

References

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The Influence of Hydrology on Lacustrine Sediment Contaminant Records

Michael R. Rosen

Abstract The way water flows to a lake, through streams, as runoff, or as groundwater, can control the distribution and mass of sediment and contaminants deposited. Whether a lake is large or small, deep or shallow, open or closed, the movement of water to a lake and the circulation patterns of water within a lake control how and where sediment and contaminants are deposited. Particle-associated contaminants may stay close to the input source of contamination or be transported by currents to bathymetric lows. A complex morphology of the lake bottom or shoreline can also affect how contaminants will be distributed. Dissolved contaminants may be widely dispersed in smaller lakes, but may be diluted in large lakes away from the source. Although dissolved contaminants may not be deposited in lake sediments, the impact of dissolved contaminants (such as nitrogen) may be reflected by the ecosystem. For instance, increased phosphorus and nitrogen may increase organic content or algal biomass, and contribute to eutrophication of the lake over time. Changes in oxidation-reduction potential at the sediment-water interface may either release some contaminants to the water column or conversely deposit other contaminants to the sediment depending on the compound's chemical characteristics. Changes in land use generally affect the hydrology of the watershed surrounding a lake, providing more runoff if soil binding vegetation is removed or if more impervious cover (roads and buildings) is increased. Groundwater inputs may change if pumping of the aquifer connected to the lake occurs. Even if groundwater is only a small portion of the volume of water entering a lake, if contaminant concentrations in the aquifer are high compared to surface water inputs, the mass of contaminants from groundwater may be as, or more, important than surface water contributions.

Keywords Hydrology · Lake sediments · Contaminants · Surface water · Groundwater · Organic pollutants · Inorganic pollutants

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Introduction

Contamination of sediments (both marine and lacustrine) can cause chronic health issues or can be toxic to aquatic organisms and animals that feed on aquatic organisms (Malins et al. 1984; Adams et al. 1992; Long et al. 1995). This can be caused by bioaccumulation through the foodweb, or by directly ingesting contaminated sediment while feeding. Where contaminated sediment comes to rest in a lake is largely the result of hydrological processes that contribute sediment to the lake. Yet, the role that natural or human-induced hydrologic changes in a lake basin plays in the development of the contaminant history of lake systems is often only indirectly assessed through analysis of mass accumulation rates, sediment focusing, or changes in land use. Seasonal or long-term changes in hydrology (changes in circulation patterns, sediment input from rivers, lake levels, or stratification), either natural or human caused, may impact contaminant concentrations in lakebed sediments and may change distribution patterns of contaminants spatially within a lake. Although sedimentary archives of lakes are often used to understand regional or local climate change, evidence of hydrological changes are often preserved that can be used to determine changes in inflow, lake level, precipitation, or groundwater input (i.e. Bradbury et al. 1989; Benson et al. 1991; Arnaud et al. 2005). These changes can be used to track locally derived pollution in the watershed (Spliethoff and Hemond 1996), diagenesis of metals deposited with the sediment (Callender 2000), and constrain interpretations of pollution from outside local areas (Blais 2005; Mahler et al. 2006; Chalmers et al. 2007).

Contaminant deposition in lake sediments can vary depending on the hydrology of the lake and the chemistry of the contaminants (Fig. 1). Local or regional input from rivers and groundwater, or regional to global input from atmospheric sources, may be able to be differentiated in lake deposits with careful observation. Some contaminants, such as nitrates or pharmaceuticals, are more water soluble (hydrophilic) than other contaminants that bind to organic matter or sediment (particle-associated, hydrophobic, or lipophilic). Both particle-associated and hydrophilic contaminants are able to move through groundwater depending on pore-throat sizes of the aquifer material and the redox condition of the water, and enter lakes as non-point source pollutants. Some metals that are soluble under anaerobic conditions in the groundwater may precipitate in nearshore areas of the lake as the groundwater interacts with the oxygenated lake water and the precipitates coat the sediment (Rosen et al. 2002). Hydrophilic compounds may not be directly present in the sedimentary record. However, contaminants such as nitrate may stimulate algal production in the lake, increasing organic nitrogen content of the sediments (Herczeg et al. 2003). Increased algal production due to nutrient inputs may lead to deposition of different species of diatoms (Fritz 1989; Hall and Smol 2010) or other algae, and ultimately lead to eutrophication of the lake. Increased nutrient concentrations may then be represented as increased biogenic silica concentrations in the lakebed sediment, or increased total organic carbon or total nitrogen concentrations in the sediment.

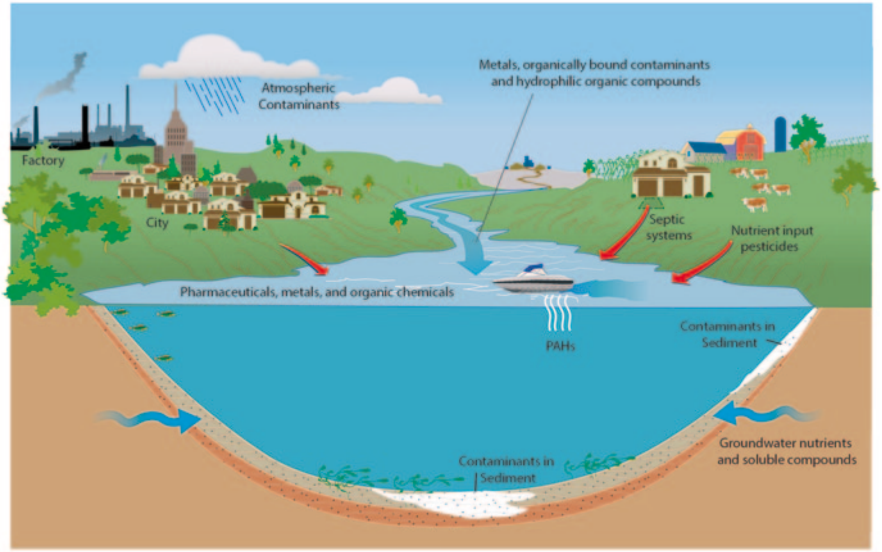

Fig. 1 Diagram of possible important hydrological sources of contaminants to a lake. Surface runoff from cities can be due to paved surfaces and buildings, improperly impounded construction sites, or overflowing sewers. Direct discharge may be from industrial sites or treated municipal wastewater. Groundwater contaminants may accumulate near the discharge point or may circulate throughout a lake if the contaminant is water soluble. Some contaminants may originate from activities on the lake, such as boat traffic

The role that different hydrologic processes play in lake systems, such as groundwater input, seasonal changes in watershed river flows, or human influences on the hydrologic system, is controlled by many factors including the size of the lake and watershed, the regional or local climate, the degree to which the basin is hydrologically open or closed, and the urbanization of a lake's watershed. All of these factors may change over time and be reflected vertically and spatially in the contaminant archive preserved in the lake sediments. Therefore, except perhaps for lakes that receive uniform inputs, spatially distributed sediment cores are likely to enhance the interpretation of contaminant archives in lakes by providing information on the hydrology of contaminant inputs. However, it has been demonstrated in man-made reservoirs of various sizes that sediment distributions appear to be mostly controlled by tributary inputs of sediments of different geologic origin (Abraham et al. 1999). The overall variability in geologic source material and human-derived contaminants implies that the uniform distribution of contaminants in a lake is unusual rather than typical in all lakes. This chapter examines many of these hydrological influences on contaminant records in lakes and illustrates how to utilize this information to enhance interpretations of contaminant histories in lake sediments.

Hydrologic Processes in Lake Systems

Hydrologic processes in lake systems vary in importance for the deposition of contaminants depending on climatic factors, relief of the basin, geology, and watershed and lake area (Fig. 2). In large, deep lakes[1], river inputs generally dominate volumetrically over groundwater inputs (e.g. Schouten 1983; Quinn and Guerra 1986). This pattern is observed because the flow needed to maintain large lake systems must arrive quickly or lake levels would decline. Groundwater, which usually moves slowly (feet per day to much longer time spans), generally is not capable of sustaining deep lakes except in fractured rock or karst terrains where groundwater flow is similar in volume to riverine input (Soler et al. 2007). During drought conditions, most large lakes will shrink even though the flux of groundwater input may actually increase during these times because the elevation between the groundwater table and the lake becomes steeper (Winter 1999).

Although the volume of water entering a lake may be vastly greater from rivers and overland flow in large lake systems, the mass of contaminants entering a lake from groundwater flow may be important because concentrations in the groundwater may be much higher than in the surface water. In Lake Taupo, New Zealand, for example, the volume of inflow from almost 30 rivers entering the lake and direct rainfall onto the lake accounts for approximately 95 % of the water input (Schouten 1983). Yet, the mass of sodium and chloride in the lake is significantly lower in the inflow than in the outflow from the lake, indicating an additional source of these elements that is not included in the dominant freshwater inflows. Lake Taupo was formed from volcanic eruptions and flows, and still has an active volcanic center. Evidence of continued geothermal input to the bottom of the lake has been documented by sampling the deepest parts of the lake bottom (de Ronde et al. 2002). Upward fluxes of Na, Cl and other constituents such as Hg, Sb, Au and S in current and paleo-vent structures into the bottom of the lake indicates that geothermal fluids contribute a large mass of constituents into the lake (Jones et al. 2007), even though the water volume of the geothermal fluids has been calculated to be less than 1 % of the total inflow to the lake (Schouten 1983). In addition, cold groundwater has been calculated to comprise less than 5 % of the water inflow to Lake Taupo (Schouten 1983), yet the mass of nitrogen entering the lake from groundwater has been estimated to be 20–30 % of the total (Rosen 2002). Changes in land use from forestry and natural habitats to sheep and dairy farming since 1960 have been linked to declines in water clarity in the Lake, and a potentially large portion of this decrease in clarity is likely to have come from groundwater nutrient inputs (Hadfield et al. 2001; Rosen 2002).

Conversely small and shallow (or deep) lakes may be dominated or highly influenced by groundwater input (Winter 1976, 1999). Australian shallow coastal lakes may be almost exclusively fed by groundwater (von der Borch 1975; Warren 1982;

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[1] No attempt is made to quantify the terms large, deep, small or shallow lakes. This is because the degree to which a hydrologic process is important will vary depending on the combination of these measures of size.

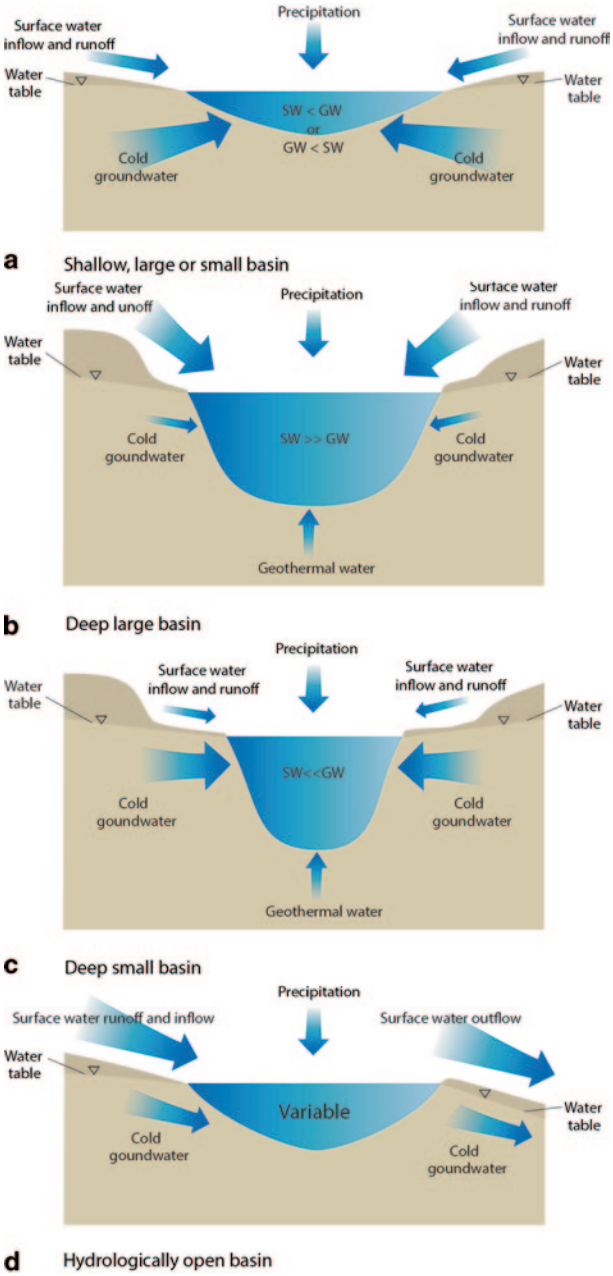


Fig. 2 Schematic of different hydrologic situations in lakes where groundwater or surface water may dominate (relative magnitude of input is indicated by *arrow* size). In shallow closed basins (**a**), large or small, groundwater may be the dominant water source, partly because if constant surface water is entering a lake, the lake will either get deeper or overflow. Groundwater can also dominate shallow hydrologically open basins. In deep large basins (**b**) either hydrologically -open or closed, surface water almost always dominates over groundwater. This is because groundwater flow is generally not fast enough to keep a large deep basin filled. Deep basins that are small (**c**) can be dominated by groundwater where porous rocks or fractures allow swift inflow of groundwater (see text). In hydrologically open basins (**d**) groundwater may be dominant but generally surface water controls water balances and is a greater part of the hydrologic budget than groundwater. Exceptions to all of these generalizations occur and this diagram is intended as a guide

Rosen et al. 1996), and some deep (>50 m) but spatially small maar lakes around the world are also supported mostly by groundwater (e.g. Russell 1885; Kebede 2013). In these types of lakes, water soluble contaminants (i.e. nutrients, major ions, some metals, and organic compounds with low octanol-water partition coefficients (K_{ow}) of less than 3, may be transported through the groundwater (Burne and Moore 1987; Rosen et al. 1996; Vroblesky et al. 1991) or may come from regional atmospheric inputs. Karst lakes may be dominated by regional or local groundwater flow that may travel long distances before reaching a lake (Katz et al. 1995).

Steep watershed topography (the topography of the area surrounding the lake that contributes runoff to the lake) or steep slopes of the lake basin (the slope of the lake bottom) are likely to result in accelerated sediment accumulation rates compared to more gently sloping areas. This may contribute particular architecture to the sediment cores, such as turbidite intervals caused by severe storms or seismic activity, or homogenites caused by rapid groundwater influx after heavy rainfall (Osleger et al. 2009; Twichell et al. 2005; Valero-Garcés et al. 2014). Steep topography can contribute sediment from less human-impacted areas of the watershed that may dilute contaminant concentrations as it enters the lake. Therefore, knowledge of the mass accumulation rates and potential for sediment focusing (see below) need to be taken into account when assessing contaminant contributions from different sources.

Differences in Sedimentation Between Natural Lakes and Reservoirs

Lakes and reservoirs have sometimes been considered to be synonymous because processes such as internal mixing, redox reactions, nutrient cycling, and primary production occur in both lakes and reservoirs (Thornton 1984). However, the variables driving these processes for lakes and reservoirs may not be identical so the response of these two systems may be different. For example, the stream channel up-gradient of the reservoir is likely to aggrade for some distance above the reservoir because of backwater effects on sediment transport. The formation and growth of deltas accelerate and extend the process even farther upstream. Thus channel gradients become flatter, channel cross sections become smaller, flooding occurs more frequently, and drainage of floodplain lands is slowed due to reservoir sedimentation (Glymph 1973). Other factors that distinguish sedimentation in reservoirs versus natural lakes is that reservoirs often have greater drainage area (DA) to surface area (SA) ratios, greater mean and maximum depths, greater shoreline development, and larger areal water loads than natural lakes. The greater DA/SA ratio in particular allows a potential for greater hydrologic and sediment (and contaminant) transport and loading to reservoirs (Thornton 1984). The greater areal water load leads to shorter hydraulic residence time of reservoirs, and allows faster input of contaminants and the potential for greater accumulation (Thornton 1984). For example, at Lake Mead, USA, sedimentation rates were high enough near Hoover Dam at Lake Mead that another reservoir was constructed upstream near Page, Arizona (Lake Powell) to control sedimentation rates in Lake Mead (Rosen and Van Metre 2010).

Many reservoirs, particularly large reservoirs, have been established in major incised river valleys. Another example from Lake Mead illustrates this point. Lake Mead was established by damming the well-entrenched Colorado River that had formed deep canyons in the bedrock (including the Grand Canyon upstream of Lake Mead). After the establishment of Hoover Dam, most of the sediment that had flowed down the entrenched river course began accumulating in the reservoir near the dam (Smith et al. 1960). However, sediment from the surrounding watershed that was washed into the lake became focused into the deep paleo-river channels (Twichell et al. 2005), with less than 1 m of sediment accumulating outside of the deep paleo-channels (Turner et al. 2012). Therefore, sediment deposition in the lake is non-uniform and leads to variable sedimentation patterns and thicknesses in the reservoir. This may be important to consider for contaminant deposition in any reservoir that dams a well-entrenched river.

In smaller reservoirs, sedimentation rates may be variable, with some annual depositional rates that are at the high end for natural lakes (Einsele 2000). Sedimentation rates can be high even in areas with low topographic gradients in the watershed. Measurement of sedimentation rates in eight small reservoirs with watershed areas less than 52 km^2 in Kansas, USA, exhibited sedimentation rates between 0.14 and 9.7 mm/year (Juracek 2004). The topographic gradients in these watersheds are relatively low and smaller watershed areas generally having the higher sedimentation rates. Some of these reservoirs were half-filled with sediment at the time of the measurements, so some of these reservoirs are filling relatively quickly. Not all small reservoirs have high sedimentations rates, but in many cases, reservoirs are located in climatic areas where natural lakes don't exist (Thornton 1984). This may lead to high sedimentation rates because rivers in high topographic gradient regions may carry high sediment loads, particularly during flood conditions. In low gradient areas, watersheds with highly erodible sediment that would naturally have been carried downstream would be trapped behind dams.

Land Use Change as a Surrogate for Hydrology

Changes in land use within a lake's watershed can dramatically affect the hydrology of a lake. Yet, there are relatively few papers that specifically set out to determine hydrologic changes in a watershed caused by human development over time, and without continuously recorded flow information, it is difficult to make this type of assessment. However, changes in land use over time can be used as a surrogate for changes in hydrology. Deforestation of a watershed (Fritz 1989) and changes in agricultural practices (Jacob et al. 2009) can lead to more erosion and runoff entering a lake and will also likely increase stream flow as well (Glade 2003). Irrigation for crops in arid areas may lead to a rise in the water table and increase groundwater flow to a lake (Hutchinson 1937; Rush 1972). The development or growth of cities in a watershed will likely increase runoff due to pavement and runoff from roof tops (Lindström 2001; Chalmers et al. 2007). The use of stream flow or groundwater for drinking water supplies or irrigation may reduce water flow to lakes (Paul and Meyer 2001; Liu and Chen 2006).

The implementation of more sustainable land management practices in agricultural or urban areas may subsequently decrease flows and contaminant inputs to lakes (Makarewicz et al. 2009). Lakes that may have become larger due to increased runoff or groundwater input, may shrink if land use practices change (Scott et al. 2011), potentially impacting wildlife that have grown accustomed to the additional open water. Therefore, it is important to consider the potential impact that various land use changes (for better or for worse) may have on the sediment input to a lake and how the hydrologic character of the lake may have changed independently of climate.

Sources of Contaminants

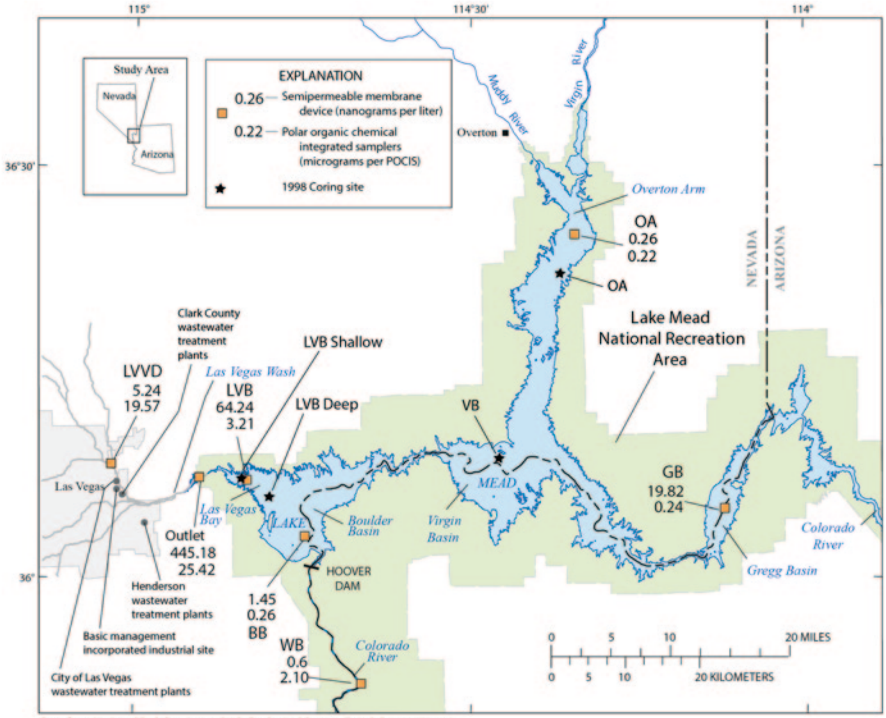
There may be multiple hydrologic sources of contaminants to a lake from rivers, groundwater, biologic transportation to a lake, or atmospheric inputs. In this chapter, only direct hydrologic inputs, surface water (including rivers, runoff and point sources) and groundwater will be considered. Point sources, such as factories, leaking pipelines, road runoff, wastewater discharge, and leaking landfills, as well as non-point sources, such as agricultural chemical use, closely spaced septic systems, regional smoke stack emissions, and land use change (Fig. 1) may deliver contaminants to lakes somewhat uniformly or in certain areas of lakes. Large lakes with complex basin structure and shorelines and multiple riverine inputs will likely have non-uniform contaminant inputs (e.g. Rosen and Van Metre 2010); whereas, atmospheric contaminants may show relatively uniform distributions in lake sediments (e.g. Heyvaert et al. 2000; Yang et al. 2002). In the following sections, examples of different hydrological inputs are shown as well as post-depositional hydrological changes that may change where sediments are located in lake basins. Contaminant inputs from dry or wet fallout from atmospheric sources are not considered in this chapter but are discussed in Korosi et al. (this volume), Kirk and Gleason (this volume), Catalan (this volume), Gabrielli and Vallelonga (this volume) and Kallenborn (this volume). This is because the majority of rainfall will enter lakes through watershed hydrologic process (runoff, rivers, and groundwater) except in those basins that have extremely limited catchments. Where catchment size is exceptionally small, groundwater may be the main source of water to the lake.

River Inputs and Localized Sources

The most obvious way for contaminants to enter lakes is through runoff to rivers or from direct point-source releases to rivers or lakes from industrial or municipal wastewater. These types of releases may result in more localized sediment contamination than atmospheric inputs because particulate-associated contaminants may not cover the entire lake floor in large lakes. Large lakes and lakes with complex shoreline morphology and multiple river inputs may also help to localize contaminant inputs because of uneven or variable lake bathymetry (e.g. Gewurtz et al. 2008; Rosen and Van Metre 2010). Particulate-bound contaminants entering Lake Mead, USA, from urban runoff, historical industrial complexes, and municipal wastewater are generally confined to one bay (Las Vegas Bay) in the lake (Fig. 3) due to the complex shape of the lake, circulation pattern, and relatively narrow passages between sub-basins. Although dissolved contaminants travel farther into the lake than particulate-bound contaminants (Rosen et al. 2010), the highest concentrations of particle-associated contaminants are found in Las Vegas Bay (Rosen and Van Metre 2010). For example, concentrations of DDE (dichlorodiphenyldichloroethylene), a metabolite of DDT (dichlorodiphenyltrichloroethane), were found in cores from Las Vegas Bay, but not in other areas of the lake (Rosen and Van Metre 2010). The peak in concentration is later than in most areas because DDT was not used in Las Vegas but was manufactured there close to Las Vegas Wash. Leaking holding ponds and careless disposal of waste after the plant closed led to DDT entering Las Vegas Wash. Concentrations declined after cleanup of the site in 1980 rather than after it was banned from use in the early 1970s (Fig. 4).

In Lake Ontario, PCB concentrations were uniformly distributed in deeper subbasins of the lake, and lower concentrations were found in nearshore areas and areas outside of these deep basins (Oliver et al. 1989). Earlier studies done when many of the PCB generating industries were still operating showed the opposite trend, with higher concentrations in the nearshore areas close to where the contaminants were discharging from rivers. This change was attributed to the fact that these deeper basins accumulate the long-term sediment and contaminant loads and the nearshore loads may be ephemeral or perhaps buried. In addition, lake-wide circulation patterns in morphologically simple large lakes, such as Lake Erie, may redistribute local river inputs long distances from their source (Smirnov et al. 1998).

Industrial complexes may also release contaminants into localized areas of lakes that are reflected in sediment cores near the source. Given enough time and sufficient contaminant releases, these local inputs may affect the entire hydrology of the lake (Rowell 1996). These changes may include changing the timing and duration of stratification in a lake (Owens and Effler 1989) and changes in dissolved oxygen content at the sediment-water interface due to differences in oxygen consumption and release from the sediment over time (Matthews and Effler 2006). High ionic strength wastes from an alkali plant that was located on the shores of Lake Onondaga in New York State, USA, from 1880 to 1986, increased the salinity of the lake, prevented the lake from turning over in some years, and caused it to stay stratified longer each year than it would have naturally (Owens and Effler 1989). Sediment



Base from National Park Service and U.S. Geological Survey digital data, 1:675,000
Universal Transverse Mercator projection, Zone 11
North American Datum 1983

Fig. 3 Map of Lake Mead showing 1998 coring sites from Rosen and Van Metre (2010) and surface water total organic compound concentrations collected by semipermeable membrane devices (hydrophobic compounds) and polar organic chemical integrative samplers (hydrophilic) reported by Rosen et al. (2010). The greatest concentration of organic compounds is coming from Las Vegas Wash downstream of the industrial complexes and wastewater treatment plants. Note that both the hydrophilic and hydrophobic compounds extend more than 10 km out into the lake. The relatively high concentration of hydrophobic compounds in Gregg Basin (*GB*) is likely from boating traffic on the lake at that time

cores taken in the north and south of the lake show similar patterns of calcium carbonate increases caused by the influx of salts from the alkali plant located on the western shore of the lake. In addition, metal and Hg contaminant patterns from urbanization and steel manufacturing also show similar patterns throughout the lake even though the dominant urbanization and industrial activities occur in the south near the city of Syracuse (Rowell 1996). Although Onondaga Lake has two sub-basins divided near the middle of the lake by a 2–3 m high sill, the outlet of the lake is at the north end. This may explain why contaminant profiles in both sub-basins are similar.

Direct hydrological change can lead to rapid eutrophication of the lake. Mathewes and D'Auria (1982) used a combination of lake coring (metal and pollen analysis), sediment trap data, and historical records to outline the contaminant history

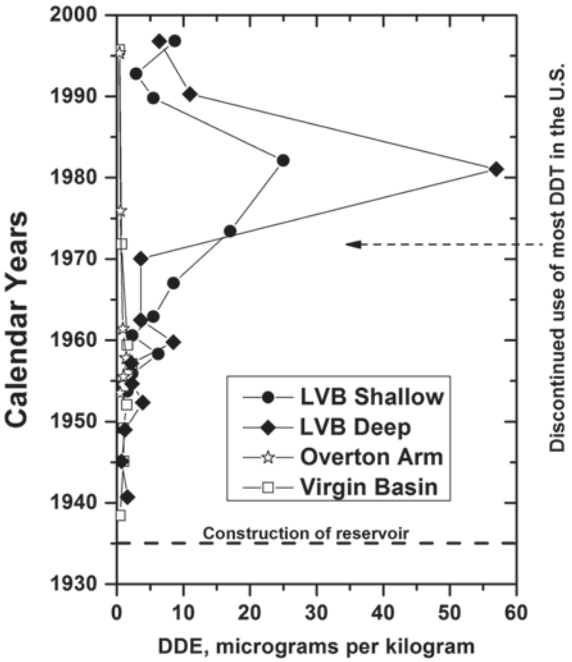


Fig. 4 Patterns of *DDE* (dichlorodiphenyldichloroethylene) a metabolite of *DDT* (dichlorodiphenyltrichloroethane) from 4 cores taken in Lake Mead in 1998. The highest concentrations occur in the early 1980's more than 8 years after DDT was banned in the United States. This is because the DDT was manufactured near Las Vegas Wash and it wasn't until clean up processes were in place that concentrations fell. The cores from other parts of the lake show very low concentrations or non-detects of DDT and DDE, indicating that these compounds are not circulating throughout the lake. Sediment core locations are shown in Fig. 3. (Figure is modified from Rosen and Van Metre (2010))

of Deer Lake, British Columbia, Canada. They determined that initial disturbance to the lake in the late 1800's was caused by deforestation and agriculture, although this was relatively minor compared to the change in hydrology caused by rapid urbanization since the 1960's. Lead concentrations increased markedly during this period. The increase in lead was attributed to increasing automobile traffic. Sedimentation rates also more than doubled during this time period. Sewage discharge (a completely human-caused hydrological change) directly into the lake since the 1920's caused eutrophication. In addition, lime and copper sulfate apparently were added to the lake water in 1957 in an attempt to curtail algal growth. The addition of copper sulfate to the lake is reflected in a distinct peak in copper and sulfur concentrations in lake cores at about this time.

In a study of Lake Vesijärvi in Finland, Honkonen and Rantalainen (2013) showed that the sediment concentrations of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) tended to decrease as a function of distance from the urban shore and stormwater outlets entering the lake. Their results indicated that the impact of the urban area on the contamination of Lake Vesijärvi is limited to approximately 500 m from the shore. Concentrations of these compounds where suburban settings were the dominant land use did not impact the lake. Although urban areas contributed significant local sources of PAHs, regional atmospheric input (coal burning power plants) and boating on the lake also contributed PAHs to the lake as a whole. The finding that boating is a significant source of PAHs to lakes is similar to the findings in Lake Mead (Lico and Johnson 2007) and Lake Tahoe (Lico 2004) that showed that PAHs particularly from inefficient 2-stroke

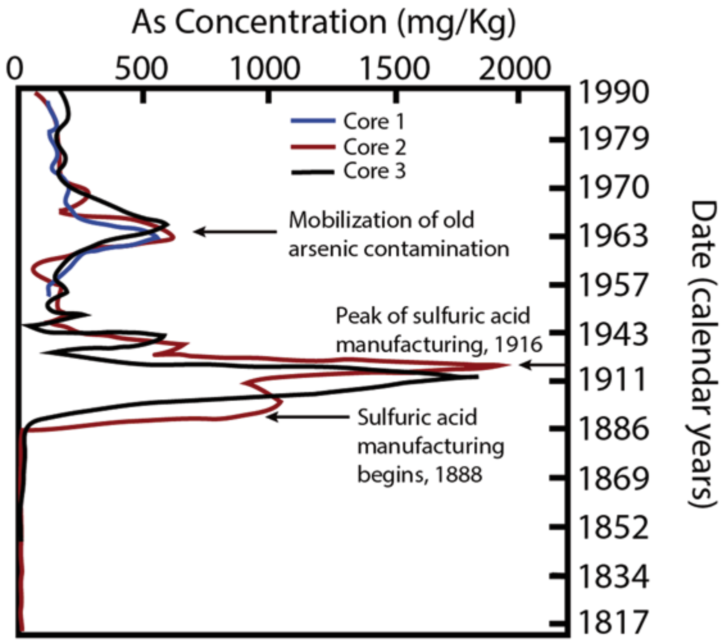


Fig. 5 Arsenic concentrations from three basin center cores from Upper Mystic Lake, Massachusetts, USA. The major peak occurred during industrial manufacturing near the lake at the turn of the twentieth century. However, a later peak occurred in the early 1960's after urbanization increased impervious surfaces, changed the hydrology of the lake, and remobilized contaminated sediments that then flowed into the lake. (Figure is redrawn and modified from Spliethoff and Hemond (1996))

engines contributed significant amounts of PAHs to the lake water. The findings of Honkonen and Rantalainen (2013) illustrate that lakes may have multiple sources of the same compound, and differentiation of the sources based on hydrology and input source is critical in understanding the history of contaminants in lakes.

In addition to simple riverine inputs from point source pollution from industrial complexes, the hydrology of the watershed can also change as an area changes from an industrial area to an urban environment. In Mystic Lake, north of Boston, Massachusetts, USA, industrial runoff to the lake peaked in the early 1900's but subsequently declined as industry left the area (Fig. 5). Following urbanization of the area in the 1960's, increases in metal contamination in the lakebed sediment were not caused directly by urban runoff but rather by remobilization of the legacy industrial waste remaining in soils. Increased runoff, caused by the greater area of impervious surfaces, led to entrainment of contaminated soils entering the lake that likely were disturbed during construction (Spliethoff and Hemond 1996). Therefore, although the source of the contaminants is mainly from the former industrial complexes in the area, the later delivery of these contaminants after closure of these facilities was caused by changes in the hydrology of the catchment surrounding the lake.

On a regional scale in New England, USA, Chalmers et al. (2007) studied 21 river and lake sites that included re-coring Mystic Lake. They constructed a regional atmospheric-fallout gradient from lakes in remote undeveloped watersheds to a lake in an undeveloped watershed in the Boston urban area. The main assumption of this sampling strategy is that lakes in remote locations will only have contaminant contributions from atmospheric fallout and not from local riverine sources. Contaminant fallout was as much as an order of magnitude greater in the undeveloped urban lake than those from remote reference watersheds, indicating that atmospherically derived contaminants are sourced from the urban areas. However, contaminant accumulation rates in lake cores with urbanization in their watersheds were 1–3 orders of magnitude greater than those of reference lakes, which indicated the dominance of local sources and fluvial transport of local runoff over atmospheric inputs. They concluded that even though regulations relating to controlling atmospheric pollution in urban areas are useful, contaminant input from runoff caused by increasing urbanization around these lakes has continued to cause detrimental effects to lake water quality.

Groundwater Inputs

The role that groundwater input plays in delivering contaminants to lake sediments has been largely understudied. Reasons for this are: (1) the perception that hydrophobic or particle-associated contaminants cannot travel through the groundwater, (2) the difficulty in quantifying groundwater input to lakes, and (3) the perception that groundwater inputs (either volume or concentration) are small compared to surface water inputs to the lake. While some or all of these factors may be true for some lakes, they are not true for all lakes, and groundwater inputs may be the dominant contaminant source in some lakes. In fact, many lakes located at the surface of highly permeable aquifers such as karst, fractured-rock, and coarse sands, are dominated or completely controlled by groundwater flow (Hutchinson 1937; Winter 1976; Herczeg et al. 2003; Soler et al. 2007). However, studies of how contaminants enter groundwater-dominated lakes and how they are deposited in lake sediments are few.

The contribution of contaminants from groundwater inflow to lake water quality has been investigated frequently, but the impact on lake sediments has rarely been assessed in these studies. Vanek (1991) showed that groundwater entering Lake Bysjön, a small (0.12 km^2), shallow (mean depth of 3.6 m), kettle lake in Sweden, had higher specific conductance than lake water and contained high concentrations of phosphorus. The phosphorus was hypothesized to have been derived from transport from fertilizer application from farming and release from septic systems upgradient from the lake over time and stored in the riparian zone organic matter. Decomposition of organic matter in the riparian zone was thought to be the mechanism for release of the phosphorus into the groundwater that is discharging to the lake. A similar study by Hagerthey and Kerfoot (1998) showed that groundwater flow influenced the epibenthic algal biomass and nitrogen to phosphorus ratios at Sparkling

Lake, a seepage lake in Wisconsin, USA. Biomass and seepage flux were positively associated and pore-water phosphorus concentrations, phosphorus fluxes, and algal biomass were significantly higher at high groundwater discharge sites than at low flow sites. In both studies it was suggested that groundwater-related patchiness of the quality of near-shore lake water and pore water is widespread. This may be the case for many lakes where contaminants are transported by groundwater and should be considered when investigating the spatial distribution of contaminants in lake sediments.

One study that shows the significance of groundwater-derived contaminants to lake sediment concentrations was conducted by Vartiainen et al. (1995) at Lake Valkjärvi in southern Finland. Studies of fish from the lake and urine from residents of the town of Kärkölä had already shown contamination of the lake and groundwater supply in 1987. This contamination was caused by releases in the 1970s of a commercial fungicide used by the local sawmill. The Vartiainen et al. (1995) study followed up a previous study by Lampi et al. (1992) that analyzed four sediment cores that found highly elevated 2,3,4,6-tetrachlorophenol and pentachlorophenol concentrations in all four cores. The distribution of the chlorophenols was uneven in the cores, with much higher concentrations being detected in the estuary, near the source of the contamination. Conversely, low levels of PCB compounds were more evenly distributed throughout all the cores. Vartiainen et al. (1995) examined two new cores, one from the estuary close to the source and one from the basin center to see if polychlorinated dibenzo-*p*-dioxin (abbreviated as "dioxin" here) and polychlorinated dibenzofuran (PCDD/F) concentrations (also used at the sawmill) followed the same pattern as the chlorophenol compounds measured by Lampi et al. (1992). They found that, while dioxin and PCDD/F concentrations increased in both cores since the 1930s and 1940s, the concentrations were similar to atmospherically-derived concentrations in lakes sampled around the world, and were much lower than chlorophenol concentrations in the same cores. In addition, the concentrations were similar in the basin center cores as well as the nearshore core, further suggesting an atmospheric source for these compounds. Dioxins, PCBs, and PCDD/F compounds are in general more hydrophobic (K_{ow} of around 5.5) than chlorophenol compounds, and have higher K_{ow}s than Chlorophenol compounds (K_{ow} of around 2.5). The low concentrations of dioxins, PCBs, and PCDD/F compounds in all the lake cores indicates that these less water soluble compounds are not being transported through the aquifer to the lake because they are trapped by the aquifer materials. However, the more water soluble chlorophenols are transported through the aquifer. If all the compounds were being transported through the river system (as either water soluble or particle-associated contaminants) all the compounds would be higher in the estuary cores, but this is not the case. The selective contamination of sediment cores by more water-soluble compounds near where groundwater discharges to the lake indicates that groundwater is the source of the chlorophenols detected, not the river water. Furthermore, fish sampled in the lake have high concentrations of chlorophenols but low concentrations of dioxin and PCDD/F indicating that contamination of the lake water by dioxin and PCDD/F is unlikely (Vartiainen et al. 1995).

Hydrologic Modifications After Deposition

Contaminant distributions within lake sediments can change after deposition when the hydrology changes due to seasonal high flows, droughts or human modifications of river flows in or out of the lake. Changes in lake levels caused by seasonal snowmelt and rainfall, or human modification of the lake hydrology for hydropower or flood control, can modify the distribution pattern or temporal trend of contaminants in lakebed sediments. For example, Miller et al. (1995) found that during drought and/or summer water level drops in Lake Lahontan, Nevada, (a reservoir on the Carson River completed in 1915, for storing water for summer irrigation) the bottom floodplain materials were subaerially exposed, creating a closely spaced network of deep mud cracks. Windblown sands and mud, eroded from the lake bed, accumulated within the fractures as well as on the fractured surfaces. Renewed inundation of these areas by snowmelt runoff from the Sierra Nevada Mountains to the west in the winter and spring caused the sediment to expand, allowing the younger surface materials to mix with older buried sediment disrupting vertical trends in mercury concentrations in these units. Although historical trends are still present in some parts of the basin, trends in mercury concentrations in areas with significant subaerial exposure and deep mud crack development have been obscured. Therefore knowledge of lake level variations may be important in interpreting contaminant histories.

Chemical profiles in lake sediments may also be altered by changes in redox conditions caused by either changes in stratification to the lake or by subaerial exposure of the lake bottom sediments (Chen and Keeney 1974; Trolle et al. 2010; Pearson 2012). For example, a change in the redox state of selenium contaminated sediment in Lake Macquarie, Australia, caused by bioturbating organisms, resulted in a release of selenium under oxidising conditions (Peters et al. 1999). Callender (2000) showed that, when faster sedimentation prevails, there is less time for benthic organisms and bacteria to perform metabolic reactions (generally oxidation-reduction reactions) because organisms do not occupy a sediment layer for any length of time. Also, the quantity and quality of the organic matter input to the sediment layer may decline because terrestrial organic matter is generally more refractory than autochthonous aquatic organic matter. Changes in sedimentation rates are likely to be caused by changes in surface water or groundwater input to the lake.

Sediment Focusing

Sediment focusing, originally defined by Likens and Davis (1975), is a process by which water turbulence moves previously deposited sediment from shallower to deeper zones of a lake where it is redeposited (Blais and Kalff 1995). Sediment focusing occurs in lakes where sediment is eroded (coarse-grained sediments) and transported. Where sediment is transported, fine-grained sediment is discontinuously deposited and then moved (resuspension) toward the basin center and deposited.

Blais and Kalff (1995) showed that the morphology of a lake (particularly the slope of the basin) may directly influence sediment focusing and is more important than the depth of the lake for determining how much sediment focusing will occur. The extent of sediment focusing is important in determining sediment contaminant distributions. Sediment resuspension will affect the cycling and distribution of pollutants. Sediment focusing results in an enhanced accumulation of fine-grained particles in the accumulation zone (deep basins) of lakes, and these particles provide a large surface area for the sorption of heavy metals, organic pollutants, and nutrients such as nitrogen and phosphorus. Sediment focusing may enhance uptake of contaminants by benthic biota and internal loading of phosphorus and heavy metals from the sediments during periods of bottom-water anoxia.

Sediment focusing is not constant on annual to geologic timescales. Variations in sediment focusing over time have been related to the degree to which the lakes watershed has been forested after glaciation (Davis and Ford 1982). Where forests became well-established around a lake, less sediment was able to erode from the land surface leading to less sediment focusing. But as discussed above, changes in vegetation, whether natural or human induced, cause changes in surface water and groundwater input (i.e. changes to the hydrology) to the lake. The amounts of these inputs then control the water level of the lake. Therefore, while the slope of the basin and overall complexity of the slope and shoreline affect sediment focusing, if there is variability in the steepness of the slope with depth in the lake, the steepness of the slope may change for periods of years at a time in a lake's history during prolonged drought or wet periods. More subtle changes such as seasonal mixing or permanent stratification may also cause changes in sediment focusing over time (Fukuda and Lick 1980). All of this is related to how the hydrology of the basin is changing over time.

Hydrologic Controls on Lead-210 Dating

The hydrology of a lake not only affects the distribution and temporal accumulation of stable contaminants, but also the usefulness of radioactive contaminants used for dating lake sediments. Lead-210 is one of the most frequently used methods for dating lake sediments younger than ~100 years (Appleby 2001). The method relies on the relatively constant input of ^{210}Pb (flux, supply or initial concentration) from atmospheric fallout of natural ^{222}Rn as it exponentially decays rapidly through short-lived isotopes to ^{210}Pb. This process produces excess ^{210}Pb in the atmosphere and subsequently the hydrosphere. The ^{210}Pb is rapidly adsorbed onto or incorporated in particulate material within lake sediments and this produces excess ^{210}Pb over that in equilibrium with ambient ^{226}Ra from allochthonous material already within the sediments. In general, as long as the rate of atmospheric lead is relatively constant, the method works well. However, in some cases, where the hydrology of the lake system is more variable, where mixing occurs, or through human modifications to the hydrology of lakes (see below), ^{210}Pb measurements may be more difficult to interpret or may not be useful. Binford et al. (1993) measured ^{210}Pb profiles in sediment cores from 32 natural lakes from Florida to New England and showed that only seven of the cores, all from either the Adirondacks or the northern Great Lakes area, exhibit typical exponential decay curves. Deviations from the expected exponential profile included flattening of the profile in the top few centimeters or excursions of one or a few measurements away from an exponential curve. Several hypotheses, including sediment mixing, hydrologic regime, sediment focusing, and acidification, were proposed to explain these variation of the ^{210}Pb distribution among the lakes and regions. Hydrologic factors appeared to exert control on unsupported ^{210}Pb inventories in these lakes, and there appears to be a strong focusing effect in drainage lakes, but a weak focusing effect in seepage lakes. Therefore, although the ^{210}Pb profiles provided adequate age models for the lakes, the profiles also provided additional information on the hydrology of the watersheds, and also made interpretation of the profiles more difficult.

In a study of four relatively remote lakes in the Rocky Mountains, USA, Norton et al. (1985) showed that in three of the four lakes studied, groundwater was the source of the high ^{222}Rn in the water column. This groundwater-derived ^{222}Rn was, in turn, capable of supporting an unusually high ^{210}Pb flux to the sediment surface. Groundwater with high ^{222}Rn may control the ^{210}Pb budget of lakes where sediment cores have high unsupported ^{210}Pb activities. While the additional groundwater-derived ^{222}Rn did not appear to affect the age models for these lakes, it was assumed that the groundwater input of ^{222}Rn was constant. Given that the hydrology of most lakes is not constant over years or even seasons; this assumption may be suspect in lakes with short residence times.

These examples again point to the role that hydrology plays in interpreting age dating models. Relying on simple atmospheric input of both natural and human-derived contaminants should only be considered after accounting for all hydrologic sources.

Human Modifications to the Hydrology of Lakes

Many lakes have had their hydrology modified either directly or indirectly by human development. Indirect modifications are land use changes such as urbanization, irrigation of farmland surrounding a lake, deforestation that increases runoff or groundwater flow to the lake, or groundwater pumping that may decrease baseflow in streams or lower the water table around a lake. Direct modifications include raising the lake level with dams, redirecting flow to or from a lake, or directly piping stormwater or wastewater into a lake. Mining minerals from a lake either by directly extracting minerals or evaporating brines from a lake are also direct modifications to the hydrology and geochemistry of the lake. Many of the human-caused changes to natural lakes can have indirect consequences such as changing the duration or timing of lake stratification (Hutchinson 1937; Wetzel 2001), but other changes may have more direct effects on the hydrology of a lake. Of course, creating reservoirs is the greatest human modification that can occur in a watershed.

Human modifications to lake systems can lead to drastic changes to the hydrology of a lake and to the watershed surrounding the lake. Perhaps the most recognized example of human modifications to a natural lake is the use of the two major rivers (Amu Darya and Syr Darya) entering the Aral Sea for irrigation of cotton and other crops. Human-caused hydrological changes to the Aral Sea Basin has caused the Aral Sea to shrink to less than one tenth its volume from the 1960s to 2007 causing the lake to divide into smaller basins and increase the salinity from 10 g/L to more than 100 g/L in some of the sub-basins (Micklin 2007). The shrinking of the Aral Sea has led to widespread exposure of the fine-grained lake sediments to erosion and increased dust-borne particles that may affect human health in the region (Wiggs et al. 2003). In addition, pesticides used for cotton and other agriculture in the area have been transported down the rivers or atmospherically and deposited in the lake sediment over time. Some of these contaminants are now being exposed and are subject to erosion (O'Hara et al. 2000; Whish-Wilson 2002). Within the Aral Sea Basin, over irrigation of croplands in the Amu Darya watershed and development of canal systems to disburse water has led to the creation of numerous small shallow lakes in Khorezm, Uzbekistan. These small lakes also receive nutrients and legacy pesticides from the agricultural fields around them, and may not be sustainable without agricultural irrigation (Shanafield et al. 2010; Scott et al. 2011).

Human modifications to a lake's hydrology can also change ^{210}Pb concentrations and dating profile. In 21 Florida lakes, ^{210}Pb, ^{226}Ra, and ^{137}Cs activities were measured in sediment cores from lakes scattered throughout central Florida (Brenner et al. 2004). Nine lakes had relatively constant supply of ^{226}Ra, and 12 lakes had high and variable rates of ^{226}Ra input. In the group with variable rates of ^{226}Ra input, most displayed increases in activity towards the top of the core. The upper sediments from two lakes had very high ^{226}Ra activities that exceed total ^{210}Pb activities, illustrating disequlibrium between ^{226}Ra and supported ^{210}Pb. Supported ^{210}Pb activity is generally thought to be in secular equilibrium with ^{226}Ra activity, but since 1966, one of the lakes is known to have been augmented with ^{226}Ra-rich groundwater pumped from the local deep aquifer. Adsorption of dissolved ^{226}Ra to recent lake sediments was believed to account for the high measured ^{226}Ra activities and the disequilibrium between ^{226}Ra and supported ^{210}Pb in topmost deposits. Due to large amounts of groundwater pumping for agriculture, industrial, and residential uses in Florida, Brenner et al. (2004) suggested that the other lakes they measured with high ^{226}Ra activities in the upper parts of the cores were also affected by groundwater pumping and that many other lakes in Florida may also be affected by ^{226}Ra-rich runoff and seepage from groundwater. They showed that the ^{210}Pb profiles in these types of lakes are likely to be in error and should not be used for dating sediments (Fig. 6).

Herczeg et al. (2003) examined changes in the hydrology and nutrient input to Blue Lake, a groundwater-fed maar lake in South Australia, caused by groundwater pumping in the surrounding agricultural farmland. The maar is surrounded by a karstic carbonate aquifer that supplies much of the water to the lake. Pumping of the aquifer began in the early 1900s and increased markedly between 1950 and 1970 and has stabilized since. The lake level fell about 4 m between 1940 and 2000 mostly due to the pumping. In addition, nitrate concentrations in the aquifer are very

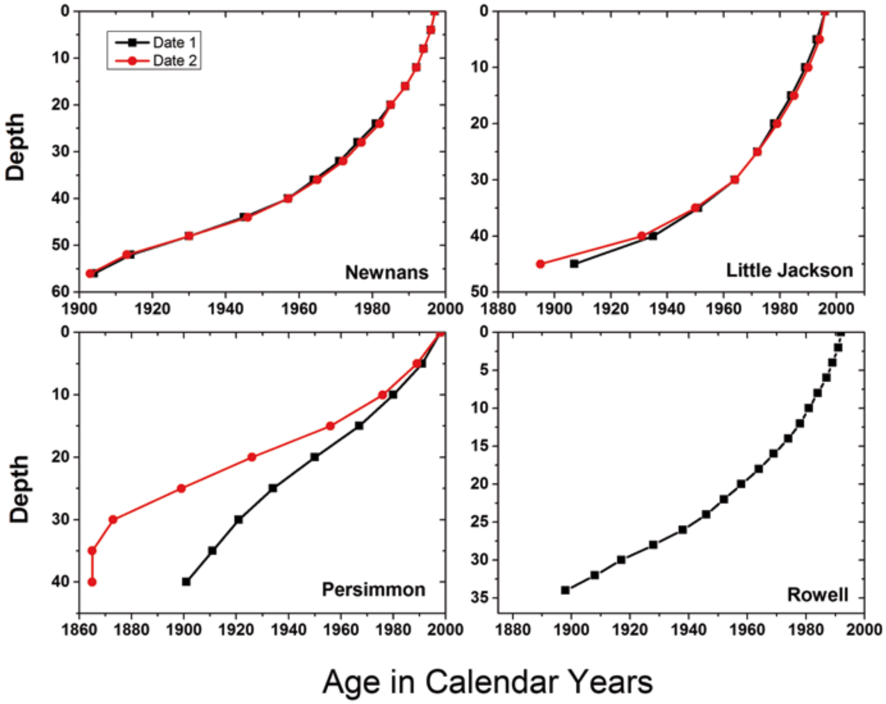
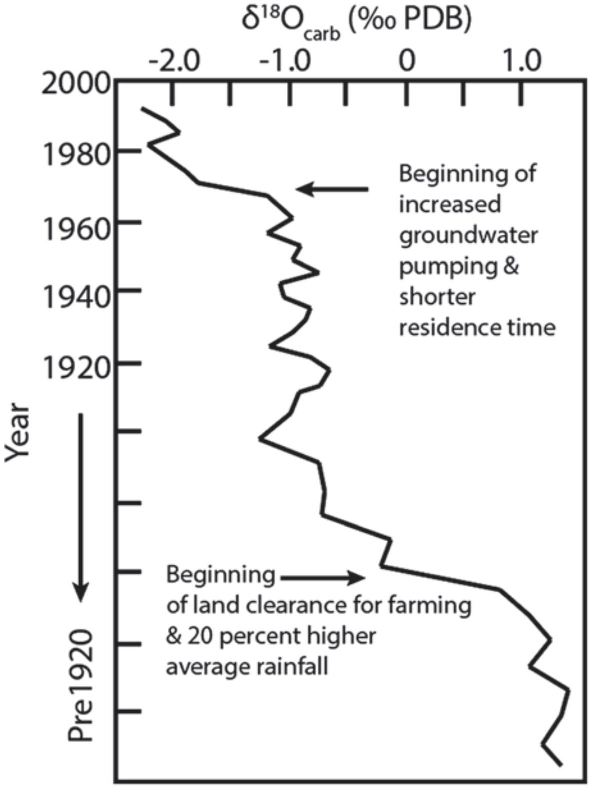


Fig. 6 The effect of adding ^{226}Ra from groundwater sources on modeled ^{210}Pb ages can be seen in these date versus depth plots for four Florida lakes: **a** Newnans. **b** Little Jackson. **c** Persimmon. **d** Rowell. Dates were calculated by Brenner et al. (2004) using the constant rate of supply (*CRS*) model. *Black lines* and *symbols* represent results of model runs in which unsupported ^{210}Pb activity was calculated as total ^{210}Pb activity minus supported ^{210}Pb activity (^{226}Ra activity) measured at each depth. *Red lines* and *symbols* represent results of model runs in which the mean down-core, asymptotic total ^{210}Pb activity was subtracted from each total ^{210}Pb value to obtain the unsupported activity for each depth, as if total ^{210}Pb activity was measured by alpha counting. For the Newnans core, with little groundwater addition and relatively low and constant ^{226}Ra activity, the two approaches are nearly identical. Little Jackson shows a slight up-core -increase in ^{226}Ra activity. Results of the two approaches differ only below about 1900, reflecting only minimal groundwater input. Persimmon shows a large up-core ^{226}Ra increase and the two dating approaches yield different ages in sediments older than 20 years, indicating a major source of additional ^{226}Ra from groundwater. For such cores, Brenner et al. (2004) argue that neither approach is correct. For the Rowell core, if total ^{210}Pb activity had been measured by alpha counting, a reasonable date-depth plot could have been generated, but would have likely been in error given the high and fluctuating ^{226}Ra in this core. In this case, ^{210}Pb dating is also untenable due to the large ^{226}Ra groundwater input. (Figure is modified from Brenner et al. (2004))

high due to direct disposal of farm waste into the aquifer over the past 100 years and the lake nitrate concentrations are also high. However, the lake is still oligotrophic due to low phosphorus concentrations in the lake and surrounding aquifer. Herczeg et al. (2003) measured oxygen and carbon isotopes of dissolved inorganic carbon (DIC) and total organic carbon (TOC) in lake water, sediment traps and lake cores to develop a carbon budget for the lake and explain changes in lake water

Fig. 7 Changes in the oxygen isotope composition of autochthonously precipitated calcite in the sediment from Blue Lake, South Australia, as the hydrology of the lake was modified by human development. Initially, the isotopic composition of the lake decreased due to land clearance for farming combined with a naturally wetter period at the beginning of the twentieth century. After increased pumping of the groundwater occurred in the 1940's residence time of water in the lake shortened from more than 20 years to less than 10, allowing the isotopic composition of the water to more closely resemble the groundwater as more groundwater flowed into the lake due to changes in the head between the water table and the lake. (Figure is redrawn and modified from Herczeg et al. (2003))



and sediment isotope compositions since the 1880s. Although the explanations are complicated by varying rainfall and some assumptions, overall the work showed somewhat counter-intuitively that decreased water levels in the lake led to shorter hydraulic residence times in the lake (from about 23 years before 1880 to less than 10 years by the late twentieth century) due to increased groundwater discharge. This in turn led to increased inorganic carbon (carbonate) precipitation (three times the rate in the 1880s) in the lake since the 1940s. The isotopic composition of the carbonate precipitated has become more negative over time (Fig. 7) due to shorter residence time. The isotopic composition of the carbonate precipitated now more closely resembles the isotopic composition of the groundwater than the lake water.

An almost exact opposite situation occurred in a maar lake in Nevada, USA. Big Soda Lake is a deep saline maar lake that was studied by I.C. Russell in 1885, and was shown to be relatively well mixed at least down to 30 m (Russell 1885; Kharaka et al. 1984). In this case, irrigation of farmland and leaking canal conveyances around the maar raised the groundwater table surrounding the lake. The lake level rose 18 m from 1905 to 1935 (Rush 1972) due to groundwater inflow of relatively fresh less dense water. The rise in lake level led to permanent stratification of the water column and has significantly changed the chemistry and biogeochemistry of the lake (Oremland et al. 1988). Addition of

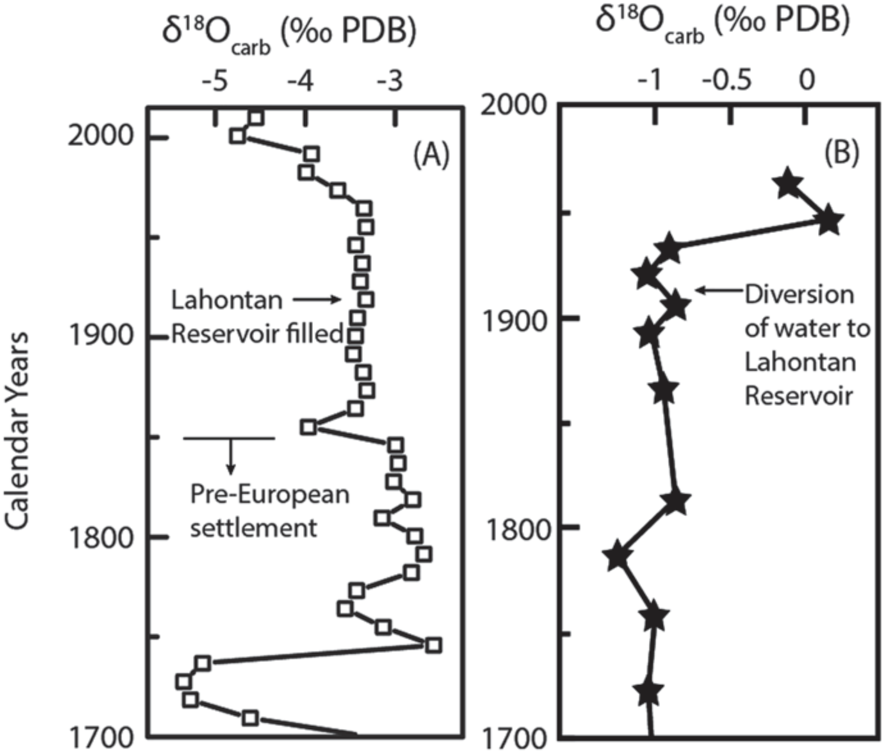


Fig. 8 Comparison of the $\delta^{18}O$ isotopic changes in (**a**) Big Soda Lake, and (**b**) Pyramid Lake over the last ~ 300 years. After the filling of Lahontan Reservoir between 1905 and 1930, Pyramid Lake level fell and Big Soda Lake level rose. The isotopic composition of precipitated calcite in Pyramid Lake became more positive due to the influences of greater evaporation and the termination of overflow to the neighboring lake. The isotopic composition of precipitated calcite in Big Soda Lake became more negative due to more groundwater inflow (with an isotopically more negative composition). The isotopic composition of Big Soda Lake is also 2–4 % more negative than Pyramid Lake due to the differences in water input. Big Soda Lake is dominated by groundwater flow (more negative) and Pyramid Lake is dominated by surface water flow (more positive). Note that the Y-axis dates are not exactly the same due to the difference of when the coring took place. (Data for Fig. 8a comes from Reidy (2013) and data for Fig. 8b comes from Meyers et al. (1998))

new fresh groundwater caused the formation of large (up to 4 m tall) tufa mounds (calcium and/or magnesium carbonate mounds precipitated near the shoreline of lakes, generally from the mixing of groundwater and lake water) that could not have formed at this elevation before the rise in lake level (Rosen et al. 2004) and caused the precipitation of a 0.5–1 cm thick carbonate layer in the lake core sediments (Reidy 2013). Stratification and fresh groundwater input also decreased the oxygen isotopic composition of the upper 7 cm of sediment in the lake above the carbonate layer (Fig. 8a). However, the decrease was delayed in time due to the time it took for this new groundwater to dominate the isotopic composition of the lake (Reidy 2013).

At the same time that Big Soda Lake was gaining water, Pyramid Lake to the north was losing water because some of the water from the Truckee River that would normally flow to Pyramid Lake was diverted for irrigation in the area around Big Soda Lake. This depletion in Truckee River inflow to Pyramid Lake caused a significant drop in lake level over much of the twentieth century and has caused changes to the inflow of organic matter and isotopic composition of lake sediments (Meyers et al. 1998; Benson et al. 2002; Yang et al. 2003). Pyramid Lake is currently a large terminal lake that is mainly refilled by water from the Truckee River, which is the outlet of Lake Tahoe. Prior to 1905, Pyramid Lake overflowed to Lake Winnemucca to the east over a low divide (Benson et al. 2002). After diversion of Truckee River water for irrigation, the lake stopped overflowing, preventing drainage via the outflow. The agricultural diversion of Truckee River water diminished the volume of the lake by 25 % between 1905 and 1990.

The input of ions and organic carbon to Pyramid Lake changed over the period of reduced flow, increasing both metal concentrations in the sediment over this period and changing the isotopic composition of organic carbon and carbonate minerals (Meyers et al. 1998; Yang et al. 2003). Meyers et al. (1998) examined sediment cores from the center and delta areas of the lake and found that the organic C:N ratio, organic $\delta^{13}C$ values, and terrigenous to aquatic n-alkane ratios all indicated that the proportion of land-derived organic matter in sediments decreased as river flow decreased. Algal productivity also appeared to have decreased in the lake from 1930 to 1998. The $\delta^{18}O$ signatures of the carbonate during this time period became more positive, indicative of a smaller volume of water in the lake and greater evaporation (Fig. 8b). Yang et al. (2003) showed that the concentrations of K, Al, Na, Zn, and Mn in sediment cores all began to increase in Pyramid Lake after 1860, a time when the landscape in the watershed was being deforested for processing silver and gold from mining in the area. The increase in these metals was interpreted to indicate that deforestation increased soil erosion in the watershed. These studies point out that multiple human modifications to the hydrology of a lake can lead to different hydrologic responses in a lake over time and can even lead to conflicting responses if they occur simultaneously. Furthermore, these studies and the studies at Big Soda Lake, indicate that the same human modification can lead to different or opposite responses in nearby lakes located in adjacent watersheds.

Climate change can lead to changes in the hydrology of the arctic and lake systems within the cold regions of the Earth (MacDonald et al. 2005) as well as affect precipitation patterns globally (Trenberth 2011). Climate change over the past 150 years has led to melting of ice and thawing of permafrost in Polar Regions that can change the biology and chemistry of a lake and add contaminants to the water column and sediment (Overpeck et al. 1997; Macdonald et al. 2005; Smol and Douglas 2007). In addition, the release of contaminants, such as methane, can be caused by thawing permafrost (Walter et al. 2006). Additional melt water adds ions and nutrients to lakes, creates a longer growing season and warmer temperatures, and can release contaminants stored in the ice and soil, such as mercury and other metals. The sources of these contaminants come from the atmosphere over long time periods, from the soil or bedrock, or from globally circulated pollution (Rydberg et al.

2010; Schuster et al. 2011). Although factors affecting contaminant transport to lake archives caused by climate change is covered in more detail by Kirk and Gleason (this volume), it is important to point out that these changes are manifested by the change in the hydrological regime of these lakes. Greater runoff caused by melting snow and ice, warmer temperatures and the possible addition of groundwater to these lakes, at least on a seasonal basis, for the first time will have dramatic effects on contaminant transport to these lakes (Jepsen et al. 2013).

Summary and Future Work

The flow of water to, and currents within lakes, are important for determining the spatial and temporal distribution of particle-associated contaminants in lake sediments, and should not be underestimated in determining the contaminant history of a lake. Knowledge of the timing, source, and volume of flow, along with contaminant sources, may lead to more efficient placement of coring locations and provide a more cohesive history of contaminant inputs to a lake. Lakes with complex morphologies and shorelines require more careful consideration for coring locations than lakes with more uniform morphology because movement of contaminants may be hindered by bottom surface variations and promontories that restrict contaminant movement. Although dissolved contaminants may not be directly detected in lake cores, changes in the biotic community or organic matter accumulation rates that are affected by the chemicals may be recorded in sediment cores, and changes in the isotopic composition of minerals precipitated from the water column may also be detected in lake cores.

Both natural and human-induced changes to the hydrology of lakes are important to consider in determining contaminant histories of lake systems. Groundwater pumping and inputs in particular are often unaccounted for or unknown when determining the hydrologic balance for a lake. Changes in redox state and lake stratification may also accompany changes to the timing or amount of inputs to a lake and these changes may cause post-depositional movement of contaminants (diagenesis) in the sediment.

The influence that changing hydrology can play in geochemical reactions and stability of contaminants within lake sediments that undergo seasonal stratification is beginning to be understood, but further research (coupled with the models suggested below) on how redox sensitive contaminants may be released to, or kept from, the water column is needed.

Future work on quantitatively measuring contaminant flux from all water inputs to lakes would allow models to be developed on how contaminants are distributed spatially and vertically and could allow a mass-balance approach to remediation efforts. Determining quantitative fluxes would require year-round measurements of water volumes (flows) and concentrations of contaminants entering lakes. New technologies using continuous monitoring sondes for carbon, turbidity (suspended solids as well as a surrogate for mercury and other trace elements), nitrogen, and phosphorus could be used to better constrain the yearly concentrations of these contaminants. Multiple deployments of passive samplers could be used for organic contaminants and metals. Well-characterized spatial and vertical distributions of contaminants could then be used to construct three-dimensional models of lake circulation, which currently exist for only very few lakes. These flow models would need to be coupled with reactive transport models to determine how contaminants would accumulate in the sediment. Studies that incorporate multiple coring points that define gradients would be beneficial to further develop process-based models. For example, redox conditions at the sediment-water interface would also need to be modelled, and gradient based coring would be able to identify changes that may occur above and below redox boundaries at the transition. Further quantifying diagenetic changes, particularly for organic compounds, that may be occurring in the lake sediment with depth is also needed to ensure contaminant profiles reflect contaminant inputs and not post-depositional changes.

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The Stability of Metal Profiles in Freshwater and Marine Sediments

Peter M. Outridge and Feiyue Wang

Abstract The stability of sedimentary metal profiles (defined as the absence of significant changes in profile shapes or concentrations as the accumulated metals are progressively buried), or the ability to reconstruct the original profiles following dispersion by diagenetic processes, is a key requirement for the robust interpretation of metal deposition histories from these natural archives. Diagenesis is a common problem in the study of metals in freshwater and marine sediments, but its effects are difficult to generalize because they are metal- and site-specific. There are two types of diagenetic processes, both of which may be strongly influenced by benthic biological activity: (1) physical processes, involving the mixing of surface and deeper sediments by bioturbation or wind and wave action, which may affect all metals in upper sediment layers; and (2) geochemical processes which involve chemical reactions between certain metals in solid-phases and in porewater, the vertical redistribution of dissolved metals, and their precipitation/adsorption elsewhere in the sediment column. A minority of the metals of environmental interest, such as Hg and to a lesser extent Pb, are thought to be geochemically stable in most settings. Others, such as As, Cd, Cu, Mo, Ni, Re, U and Zn, are relatively sensitive to changes in oxic-anoxic (oxidation-reduction) conditions down-core and are often redistributed during burial. This review has several aims: (1) to describe the patterns and mechanisms of physical and geochemical diagenesis; (2) to describe three tests of metal profile stability; (3) to review environmental and geochemical factors that influence the occurrence and severity of diagenesis; (4) to present case stud-

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ies that illustrate working approaches for correcting diagenetically-altered profiles so that part or all of the original history of accumulation can be reconstructed; and (5) to present practical recommendations concerning study site selection, and approaches to detecting diagenesis, which may assist in minimizing or at least identifying the severity of metal redistribution.

Keywords Sediments · Geochemistry · Diagenesis · Metals · Bioturbation · Redox reactions

Introduction

Freshwater, estuarine and marine sediments preserve a potentially useful archive of the chronological accumulation of particle-associated elements, contaminants, and other limnological and oceanographic properties in aquatic environments. As this present volume attests, the historical records contained in sediments are used in numerous ways. With respect to metals (including metalloids), these uses include: reconstructing recent rates and trends of deposition of atmospheric pollution, inferring the physico-chemical properties of ancient oceans and lakes, and recording climate histories, among others.

An essential prerequisite for all such sediment-based studies is that the record of particulate metal accumulation in sediment must be stable over the time frame of interest so that the archived chronology accurately reflects history. The time frames involved typically range from decades to a few centuries in the case of atmospheric pollution studies, to millennia or millions of years for paleooceanographic or paleolimnological studies. Here, "stable" refers to an absence of significant rates of metal remobilization and vertical redistribution compared to the rate of burial in deeper sediments. When the redistribution rate is comparatively negligible, metal concentrations deposited at the sediment surface will propagate downwards with little dispersion as the sediment layers are buried, until their subsequent permanent accumulation in deep sediments. Therefore, stable profiles can be readily interpreted as a reliable record of metal accumulation at the sediment surface. By corollary, significant redistribution of the original profiles of metals through post-depositional processes (i.e., "diagenesis"), or an inability to correct for the effects of diagenesis, may render the observed profiles unreliable in terms of reconstructing metal deposition histories.

The stability and diagenesis of metal profiles are thus inextricably linked, and so the effects of diagenesis on metal profiles form a major theme of this review. Diagenesis can occur through the physical redistribution of metal-carrying particles, or through various geochemical processes described below. Both types of diagenetic processes may be highly influenced by biological activities (e.g., bioturbation and bioirrigation). Although models typically treat diagenesis as a one-dimensional phenomenon (i.e., processes occurring perpendicular to the sediment-water interface), spatially variable biological activities in sediments often result in diagenetic "hot-spots" which may be better considered as three-dimensional geochemical "microniches" (Sochaczewski et al. 2008).

It should be noted that usage of the term "diagenesis" by other branches of geoscience concerned with sediments only partly overlaps with the environmental geochemistry definition employed here, and no universally accepted definition appears to exist (Chilignar and Larsen 1983). A perhaps generally accepted broad definition is that diagenesis (sometime referred to as "early diagenesis") is any physical and geochemical change in sediments after deposition and before lithification (sedimentary rock formation) (Berner 1980). More specific usages can be found in every branch of geoscience. For example, the science of organic matter geochemistry defines diagenesis in terms of changes in organic matter and its major constituent elements, particularly the kinetics, end-products and geochemical consequences of processes such as aerobic decomposition, and anaerobic humification (Emerson and Hedges 2004).

The overall goal in this review is to provide the reader with information that enables them to recognize when significant diagenetic alteration of a sedimentary metal profile has occurred, understand the key environmental and geochemical features of a study setting that promote stable metal profiles, and outline approaches to correcting (either partly or wholly) and properly interpreting diagenetically-altered profiles. Our first aim is to describe the patterns and mechanisms of the two main processes of diagenesis (physical and geochemical). As will be seen below, diagenetic processes produce distinctive down-core profiles of element concentrations and multi-element correlations which may be useful as a diagnostic aid. Second, the literature concerning tests of metal profile stability based on comparisons with known external input histories, time-series resampling of profiles, and modeling of the impact of geochemical diagenesis is summarized. Third, we review the environmental and geochemical factors that influence the occurrence and severity of diagenesis. Some of these factors differ significantly between the two types of diagenesis. We also consider the speciation characteristics that make a metal mobile in sediments, for the most commonly employed metals in atmospheric pollution or paleoceanographic and paleolimnological studies. Fourth, even in settings where significant redistribution of metal profiles has occurred, all is not necessarily lost (although sometimes it is!). Case studies are presented that illustrate working approaches for correcting diagenetically-altered profiles so that part or all of the original history of accumulation can be reconstructed. Finally, practical recommendations are presented concerning study site selection, ancillary parameters to be measured, and approaches to detecting diagenesis, which may assist in minimizing or at least identifying the severity of metal redistribution in any sediment case study.

Patterns and Mechanisms of Diagenesis in Metal Profiles

Metal deposition to a water body could occur via the atmosphere (Fig. 1, panel A), surface runoff, and groundwater inflow (see Rosen, this volume), and may include both natural and anthropogenic sources. For sediments to serve as a useful atmospheric deposition archive, the metal or its dominant species have to be particle-reactive (i.e., primarily bound to particles via sorption and/or precipitation) (Fig. 1, panels W1 and W2), so that it will sink to the sediment-water interface and subsequently be buried as new particles continue to accumulate. Should diagenesis

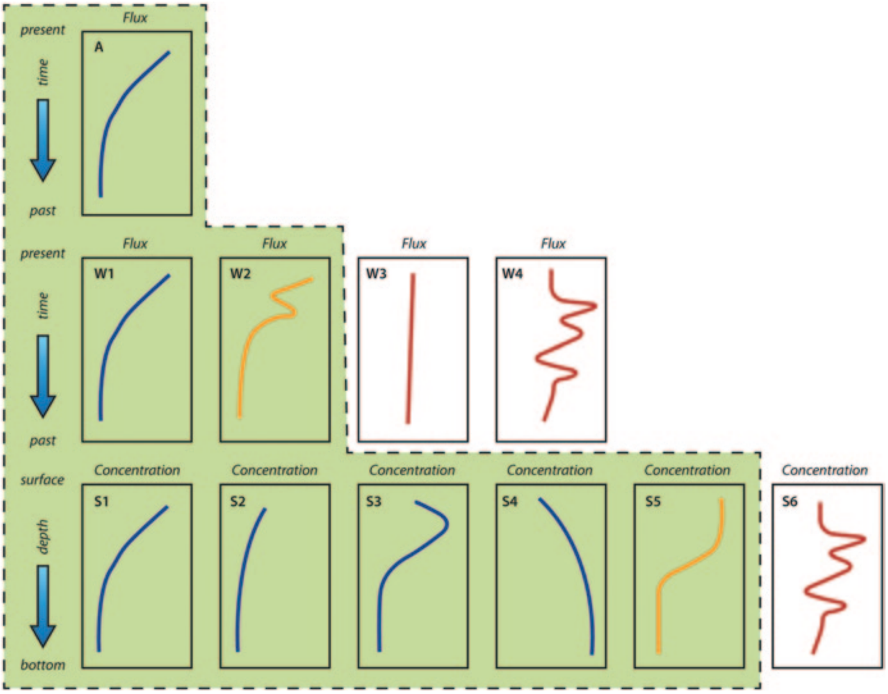

Fig. 1 Schematic diagrams of various types of post-diagenesis patterns of metals in sediments (*bottom panels*), compared to the atmospheric deposition history (*upper panel*) and incident flux to sediment surface (*middle panels*). (The *dashed line* and shaded area denote those examples in which the original atmospheric deposition record can be reconstructed from the sediment record, either directly (*W1, S1*) or after modeling and subtraction of the diagenetic overprint (other panels). Panels outside the dashed line are examples in which the atmospheric record cannot be reconstructed. *A*: hypothetical atmospheric flux to a water body. *W*: Flux to the sediment. *W1*: when the metal is bound primarily to aquatic particles and atmospheric deposition is the dominant supply; *W2*: when the metal is bound primarily to aquatic particles but there are also other known supplies (e.g., riverine, erosion); *W3*: when the metal remains primarily dissolved; *W4*: multiple sources and significant diagenesis. *S*: Concentration profiles in sediments. *S1*: negligible diagenesis with constant sedimentation rate; *S2*: negligible diagenesis with recently increasing sedimentation rate; S3: significant geochemically-based diagenesis (types 2 and 3); *S4*: significant geochemically-based diagenesis (type 1) involving water to porewater diffusion and precipitation at the oxic/anoxic redox boundary; *S5*: physical mixing resulting in a surface mixing layer; *S6*: multiple sources and significant diagenesis

be absent following sedimentation (Fig. 1, panel S1), then the sediment metal concentration at a specific depth would reflect the metal input from the overlying water at the time when the corresponding sediment layer formed. In other words, the depositional history of the metal (Fig. 1, panels A and W1) can be readily reconstructed from the metal concentration profile (Fig. 1, panel S1), provided that the sediment chronology is known (e.g., by radioisotopic dating). Even in the absence of diagenesis, changing sedimentation rates over time in a water body can affect sediment metal concentration profiles through varying dilution of trace metals by major elements (e.g., Carignan et al. 2003; Fig. 1, panel S2). These variations will be corrected when metal fluxes (concentration × sedimentation rate) are calculated. However, a scenario with no diagenesis is only hypothetical, as a variety of physical, chemical and/or biological processes in the sediments or across the sediment-water interface will often result in post-depositional changes in the sediment metal concentration profiles (Fig. 1, panels S3–S6).

More detailed discussions on early diagenesis and its theoretic treatment in aquatic sediments can be found elsewhere (Berner 1980; Boudreau 1997, 1999). For our purposes, two general categories of diagenetic processes are recognized: (1) physical processes, which are site specific; and (2) geochemical processes which are both metal- and site-specific. Each category gives rise to characteristic post-redistribution patterns of elements and other chemical entities. Both are strongly influenced by the level of biological activity in sediments.

Physical Processes of Diagenesis

The physical mixing of sediment particles and their associated metals, which is typically confined to the upper layers of sediments, results in a surface mixing layer (SML). While this can be caused by water currents, gas bubbling up from deeper sediment layers, wave action, and episodic events such as storms and flooding, the most common process resulting in sediment mixing is bioturbation, a general term referring to physical mixing of sediments by the burrowing and feeding activities of benthic organisms (Boudreau 1997; Burdige 2006). In addition to mixing sediment particles, these activities also mix porewaters and alter sediment porosity, texture and other physical properties (Burdige 2006). Physical mixing tends to homogenize metal pulses within the SML and shift metal distributions to deeper sediment layers (Carignan et al. 2003), resulting in the reduction or elimination of any variations in the original metal accumulation history (Fig. 1, panel S5; see also Kuzyk et al., this volume).

The thickness of the SML is highly variable among different water bodies, ranging from negligible in lake sediment overlaid by a seasonally anoxic hypolimnion (e.g., Alfaro-de la Torre and Tessier 2002) to more than 20 cm in sub-oxic marine sediments inhabited by numerous benthic macrofauna (e.g., the Strait of Georgia, British Columbia; Johannessen et al. 2005). The presence and thickness of SML can also be highly variable at different sites of the same water body, and can usually be diagnosed with a steady state radioisotope tracer (such as ^{210}Pb) where the radioactivity shows a distinct flattening or plateau in the upper profile (see Fig. 1, panel S5) rather than the expected exponential decay pattern associated with no mixing and a constant sedimentation rate (Appleby et al. 1979). A ^{210}Pb plateau is not, however, an unequivocal indicator of an SML. Uncommonly, the same pattern may also be produced by increasing sedimentation rates in recent years such that the increasing sediment load dilutes the ^{210}Pb concentration to an approximately constant level at the core top.

Geochemical Processes of Diagenesis

Geochemical diagenetic processes involve chemical reactions between metals in sediment and in porewater, and the associated dispersion of metal species through porewater transport. Diffusion of solutes into or out of sediments, although itself a physical process, is included here under geochemical processes, because diffusion from the water column into sediment porewater without subsequent partitioning to the solid phase (a geochemical process) will not alter the sediment metal profile (Fig. 1, panel W3). Similarly, diffusion of a metal from sediment to overlying water will not occur unless dissolution of a solid phase entity (another geochemical process) has preceded it. Unlike physical processes, geochemical diagenesis is not confined to the SML, and occurs as a result of geochemical changes or reactions possibly occurring throughout the upper sediment column. Figure 2 presents a general schematic of geochemical diagenetic processes in coastal marine sediments which is also applicable to freshwater sediments. In general, sediment-bound (solid

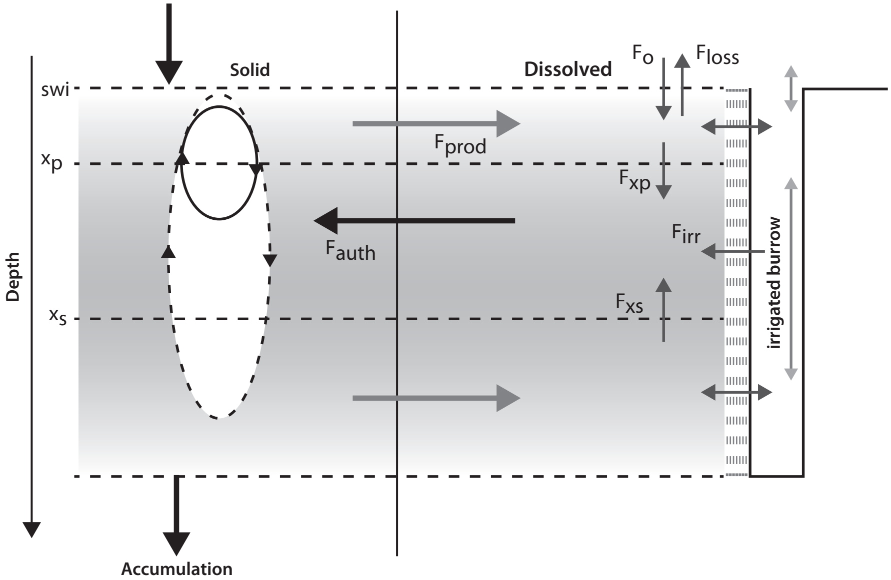

Fig. 2 Schematic diagram of the cycling of redox-sensitive metals (Re, Mo and U) in coastal marine sediments. (Source: adapted from Morford et al. 2009). On *left* of diagram, the mixing effect of bioturbation and geochemical diagenetic processes on the original metal profile (*solid line ellipse*) is shown by the *dotted line* ellipse. Additions of solid phase metal by particulate sedimentation to the surface of the sediment column, and by consumption of dissolved metal within the sediment column, are shown as black arrows. On *right* of diagram, exchange of dissolved metals between macrofaunal burrows and sediment porewater, water column and porewater, and within the sediment column, are shown by *grey arrows*. Exchange between solid and dissolved phase metals is shown as horizontal arrows indicating net production (*grey*) and consumption (*black*) of dissolved metals in different sediment zones. The "zone of net production" indicates where a net production of authigenic solid phase metal (and net removal of dissolved metal) occurs by redox-related geochemical processes

phase) metals can be made mobile through their reversible, dynamic exchange with dissolved species in porewater via reactions such as sorption-desorption and precipitation-dissolution (see black and grey arrows in Fig. 2). Once in porewater, a dissolved metal species may be readily transported vertically and horizontally via diffusion (e.g., molecular diffusion, bioturbation) and/or advection (e.g., bioirrigation). The dissolved species may then either undergo reactions to form authigenic (i.e., diagenetically created *in situ*) solid phase metals at a different depth (see zone of net authigenic production in Fig. 2), or exchange with the overlying water.

Three basic geochemical processes of diagenesis include:

- *Type 1*, diffusion of dissolved metals from the water column into sediment porewater (see panel S4 in Fig. 1; and Fig. 2) where they may be precipitated or sorbed at a subsurface geochemical nexus, typically an oxic/anoxic redox boundary (e.g., Carignan and Nriagu 1985; Alfaro-de la Torre and Tessier 2002; Morford et al. 2009);
- *Type 2*, the desorption and dissolution of significant quantities of metals from sediment particles, diffusion through pore-waters and subsequent re-precipitation or re-sorption at a new location within the sediment column (see panels W4 and S6 in Fig. 1), or their loss to overlying waters (S3 in Fig. 1) (e.g., Gobeil et al. 1987; Widerlund et al. 2002); and
- *Type 3*, the redistribution of metals because of reduction-oxidation (redox)-related decomposition of their carriers such as Fe- or Mn-oxyhydroxides or particulate organic matter (Fig. 1, panels W4, S3 and S6) (e.g., Benoit and Hemond 1991; Toevs et al. 2006).

Bioirrigation, the process by which benthic dwellers flush their burrows or tubes with overlying water, can enhance the exchange of metals between porewater and overlying water, as well as increase or maintain redox gradients within sediments (see Fig. 2; e.g., Aller and Yingst (1978), Gobeil et al. (1987), Wang et al. 2001). A common result of geochemical diagenesis is the creation of new subsurface peaks in metal concentrations, or the reduction of peaks in concentration as originally deposited at the sediment surface (Berner 1980; Carignan and Nriagu 1985). If not corrected (see below), this process may lead to an erroneous interpretation of the history of metal deposition and accumulation.

A characteristic feature of the occurrence of Types 2 and 3 geochemical diagenesis is similar down-core profiles of multiple elements including well-known redox-sensitive metals such as Fe, Mn, Mo, Cd and U. For example, the solid phase As and Fe profiles were strikingly similar in the upper few centimeters of sediment in a perennially oxygenated basin (Basin A) of a Canadian Shield lake, but not in another seasonally anoxic basin (Basin B) of the same lake (Fig. 3; see more details in Sect. 4.1). This correspondence with Fe in one basin but not in the other strongly hinted at diagenesis influencing the As profile in basin A but not in basin B, which had a seasonally-anoxic hypolimnion. Subsequent porewater modeling confirmed this suggestion (see insets in Fig. 3) and also provided a means of correcting the As profile in basin A (see Sect. 5.2). Numerous other examples of co-occurring element profiles indicative of diagenesis can be found in the literature (e.g. Gobeil et al. 1999; Outridge et al. 2005; Toevs et al. 2006; Macdonald et al. 2008; Couture et al. 2010).

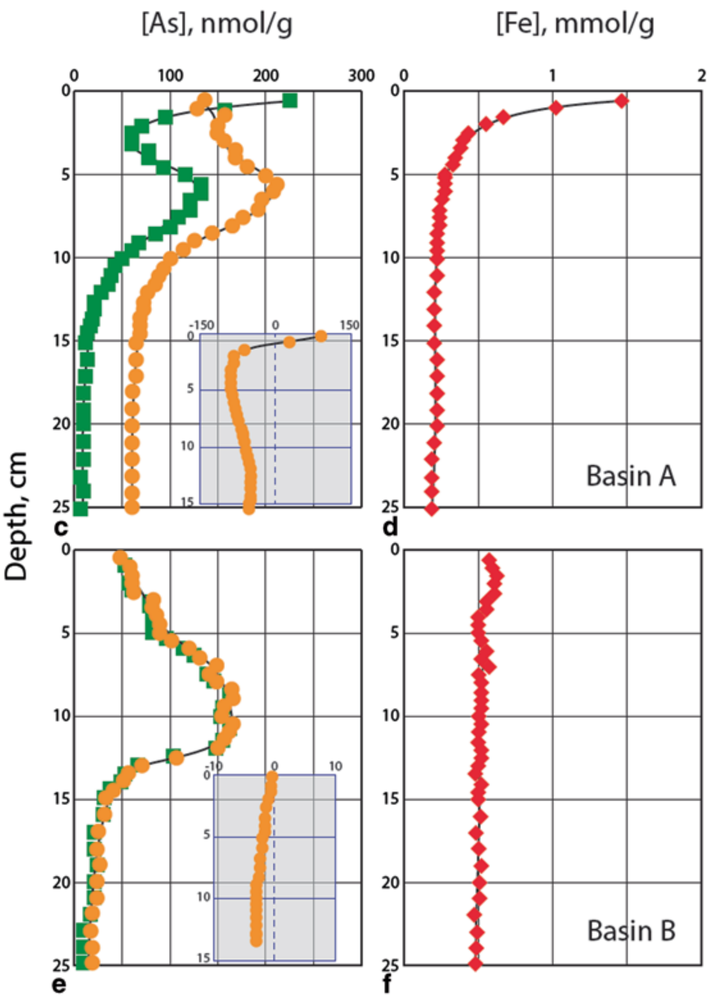

Fig. 3 Depth profiles of solid phase As and Fe concentrations in oxygenated *Basin A* (panels *a* and *b*) and seasonally anoxic *Basin B* (panels *c* and *d*) in Lac Tantaré, Canada. (Source: adapted from Couture et al. 2008). Legend: uncorrected measured As—*green* squares; reconstructed As concentrations accounting for diagenesis—*orange* circles; diagenetic As contribution—*grey* inset panels; measured Fe concentrations—*red* diamonds)

Environmental and Geochemical Factors Influencing Metal Profile Stability

For physical diagenetic processes, the amount of particle mixing near the sediment-water interface, which is often related to macrofaunal activity, can be indirectly affected by local hydrological and limnological conditions. In particular, low oxygen content of the hypolimnion may constrain the amount of biological activity. For geochemical diagenetic processes, the most influential geochemical factors include the sedimentary redox status, which is a function of oxygen status and pH. Redox status may be affected in turn by water depth, rates of sedimentation, oxygen supply and organic matter inputs. Another, non-sediment, factor is the characteristics of different metals that make them variably sensitive to geochemical processes.

Reactivity of the Metal

The long-term stability of metal profiles varies between elements in part because of innate characteristics which confer different solubilities and mobilities under the same sediment conditions. For example, most alkali (e.g., Li, Na, K, Cs) metals are less particle-reactive than transition metals, and tend to remain dissolved in the water column or porewater; thus their sediment profiles are often not indicative of their depositional history (Fig. 1, panel W3). Peak activities of ^{137}Cs in a sediment profile may be useful to mark the ages of sediment deposited from the mid-1950s to early 1960s (^{137}Cs source was fallout from nuclear bomb testing) or in 1986 (fallout from the Cheronobyl accident). However, in many cases its profile is not stable enough over time to reliably reconstruct a detailed ^{137}Cs depositional history or to determine a sedimentation rate (e.g., Klaminder et al. 2012), although contrary examples exist (e.g. Outridge et al. 2005; Rosen and Van Metre 2010). A more particle-reactive radioisotope, such as ^{210}Pb or ^{241}Am, is often more suited for the purpose. The most reliable dating approach involves measurement of multiple radioisotopes (commonly, ^{210}Pb and ^{137}Cs) as a means of mutual corroboration (Smith 2001).

Most metals of environmental and ecological concern (e.g., Cd, Cu, Hg, Pb, Mo, Ni, Tl, U, Zn) are particle-reactive in the aquatic environment, thus sorbing onto aquatic particles or “carrier phases” such as organic matter, Fe- and Mn-oxyhydrides. They may also precipitate or coprecipitate as relatively insoluble mineral phases, for example as metal sulfides, depending on the metal and the redox condition of the environment (Stumm and Morgan 1996). Comparison of the relative importance of binding by Fe oxyhydroxides and organic matter (humic material) in oxic sediments found that anionic metals such as As, Mo and Sb as well as the cationic metal Pb were preferentially bound to oxyhydroxides, whereas Hg, methyl-Hg, and to a lesser extent Ag, Cd, Cu, Zn were predominantly attached to organic matter (Feyte et al. 2010). While a few of these metals appear to be quite immobile and exhibit stable profiles once deposited in some sediments (e.g., Hg: Lockhart et al. 2000; Rydberg et al. 2008; Feyte et al. 2012; Percival and Outridge 2013), others could be subject to significant remobilization and redistribution depending on biogeochemical conditions, as discussed below. Even the profiles of relatively immobile elements such as Hg have been shown to be significantly altered over long periods of time in some marine settings, such as the extremely low sedimentation rate environment of the Central Basin of the Arctic Ocean (Gobeil et al. 1999).

Another factor in the reactivity and stability of deposited metals is their speciation in the original geological host rock, which is often overprinted by speciation changes during anthropogenic processing prior to release into the environment.

While the speciation of metal emissions is likely source-dependent and can occur as a wide variety of mineral phases, particulate-bound metals such as Zn, Cd, Pb, Ni and Cu released from high-temperature sources such as base metal smelters and coal-fired power plants are often found as metallic alloys, sulfides, silicates, oxides or sulfates (e.g., Choël et al. 2006; Sivry et al. 2010; Skeaff et al. 2011). Mercury, on the other hand, has a very different speciation in the atmosphere (primarily as gaseous elemental Hg, with varying fractions of gaseous oxidized and particulate Hg) and in industrial emissions and atmospheric deposition (primarily as gaseous oxidized and particulate Hg; Fitzgerald and Lamborg 2007). Weathering of deposited metal particles in soils can further alter their speciation prior to entry into aquatic systems (Manceau et al. 2000; Lanteigne et al. 2012). The connection between the speciation of metals emitted from different sources, their weathering and subsequent stability in sediments, is an under-investigated area of research.

A general association has been found between increasing distance from point sources, declining average particle size in air and the chemical reactivity, solubility or "exchangeability" of metals contained in those particles (Spokes and Jickells 2007). Smaller particles of nanometer-scale diameter are generally more reactive than larger particles of micrometer size, probably because of their larger surface area to mass or volume ratios. This pattern suggests that sediments closer to point sources may receive a higher proportion of less chemically reactive particles than more distant lakes, although whether this has any implications for metal profile stability in those sediments has not been investigated to our knowledge.

Environmental Factors

pH

The stability of the sedimentary profiles of many metals can be highly dependent on the pH of the overlying water and sediment porewater due to the pH-dependence of complexation, sorption, precipitation and redox reactions that govern metal partitioning between solid and aqueous phases. Desorption of cationic metals typically follows a negative asymptotic relationship with pH, with modeling indicating Cu, Pb, Zn and Cd desorption from natural sediments goes from nearly 0 % to almost 100 % within one pH unit beginning at a pH of 6.0–7.5 depending on the metal and sediment conditions (Wang et al. 1997). For instance, in an acidic, oligotrophic lake (Lac Tantaré) on the Canadian Shield, a pH increase from about 5.5 in the overlying water to 6.5 in the sediment porewater is at least partially responsible for a significant increasing gradient of dissolved Cd concentration from the overlying water to sediment porewater. As a result, there is a considerable amount of dissolved Cd being transported from the overlying water to the surface sediment, complicating the determination of the deposition history of Cd from its sedimentary record (Alfaro-de la Torre and Tessier 2002). High contributions of diffusing dissolved metals to sedimentary solid phase metal profiles in acidic lakes have also been reported for Zn, Cu and Ni (Carignan and Nriagu 1985; Carignan and Tessier 1985).

The reverse process could also occur in which lower pH in sediment porewater results in dissolved metals diffusing upwards to the overlying water (Widerlund et al. 2002; Lesven et al. 2008). There are a number of reports in the literature of Pb being released to overlying waters by lake acidification, which suggests post-depositional alteration of Pb profiles (e.g., White and Driscoll 1985; Widerlund et al. 2002). However, the commonly reported findings of agreement between sedimentary and atmospheric Pb histories (Lockhart et al. 2000; Gallon et al. 2004), or between ^{210}Pb-derived age dates and sediment varve counts (Appleby et al. 1979; Crusius and Anderson 1995; Gajewski et al. 1997) suggests that Pb profiles are stable in many freshwater sediments.

Although significant pH changes do not often occur in marine environments, they may in estuarine environments owing to the tidal exchange of freshwater and seawater which affect pH, salinity, organic matter concentrations and other geochemical parameters. Here, pH changes from near-neutral (freshwater) to alkaline (seawater) can reduce the release of dissolved Cd, Zn, Fe and Mn from porewaters into overlying waters (Hong et al. 2011). However, in the controlled microcosm study performed by Hong et al. (2011), total metal release was significantly higher for Cd in seawater because of anion complexation just above the sediment-water interface, suggesting a possible impact on Cd profile stability. Total Zn release from these sediments was comparatively unaffected by changes between freshwater and seawater.

Redox Condition

The stability of sedimentary profiles of many particle-reactive metals is sensitive to the redox condition of sediment and hypolimnetic waters as indicated by redox potentials (Eh). Redox condition in sediments is strongly influenced by factors including the extent of oxygen penetration, flux of labile organic matter, rate of inorganic sedimentation, and benthic macrofaunal activity. Anoxia occurs naturally within the first few centimeters of the sediment profile when the oxygen flux into sediments is exceeded by the rate of labile organic matter input (Stumm and Morgan 1996; Gobeil et al. 2001). Even in organic matter-poor systems, such as the Arctic Ocean Central Basin, redox gradients can develop if sedimentation and surface mixing rates are sufficiently low to allow anoxia to develop in the upper sediment layers. This then results in significant diagenetic remobilization of Hg associated with Fe cycling in these sediments (Gobeil et al. 1999). Slowly accreting sediments also provide more time for dissolved metals in porewaters in the upper core to interact with the water column.

The significance of the redox condition of sediments is that it directly controls metal speciation in sediments, which in turn affects the stability of metal profiles. In strongly reducing sediments below the depth of oxygen penetration, metals and metalloids often precipitate as insoluble sulfides or co-precipitate with Fe pyrites (e.g. Huerta-Diaz et al. 1998; Sundby et al. 2004; Canavan et al. 2007) provided sufficient sulfide is present. Sulfide production is driven by microbial sulfate reduction during organic matter decomposition (Stumm and Morgan 1996). In marine sediments and salt marsh soils, abundant sulfate and microbial communities produce generally high concentrations of sulfide, with pyrite being the most common end-product (Huerta-Diaz and Morse 1990; Soto-Jiménez and Páez-Osuna 2008). But even in many anoxic freshwater sediments, which generally exhibit lower sufate levels than marine sediments, sulfide mineral phases may also immobilize trace metals (Huerta-Diaz et al. 1998; Canavan et al. 2007). In surface sediment layers exhibiting oxic and sub-oxic conditions, metal adsorbed onto Fe and Mn oxyhydroxides typically dominates metal speciation (Canavan et al. 2007; Soto-Jiménez and Páez-Osuna 2008). Given on-going sediment accumulation, metals are ultimately buried in permanently anoxic deep sediment layers, unless oxidative dissolution of the sulfide mineral phases occurs upon sediment mixing by physical or biological sediment disturbances.

Scholz et al. (2011) demonstrated the dominant role of redox status in an elegant study of redox-sensitive metal cycling on the Peruvian continental shelf. Transient fluctuations in the spatial extent of oxygenated bottom waters across the shelf and slope, brought about by variations in ocean upwelling, primary productivity and oxygen depletion related to the El Niño Southern Oscillation (ENSO), resulted in dramatic changes in the cycling of Fe, Mn, V, and Mo between water and sediments and within sediment profiles. During positive-ENSO years (El Niño events) when bottom waters are well oxygenated, terrestrial Fe and Mn oxides and oxyhydroxides which precipitated at the edge of the retreating oxycline transferred particulate V and Mo to shelf sediment surfaces. During anoxic conditions prevailing in negative-ENSO years (La Niña), the Fe and Mn carriers in surface sediments were reductively dissolved and the adsorbed V and Mo released into porewater where they were precipitated by sulfides. This alternation between deposition from the water during oxic periods and authigenic V and Mo attachment to pyrites during anoxic periods led to the preferential accumulation of V and Mo in shelf sediments. During subsequent oxic years, authigenic V was readily reoxidized and remobilized while authigenic Mo remained sequestered. Scholz et al. (2011) suggested that these processes could lead to enriched bands of Mo that may be interpretable as long-term histories of ENSO-related oxygenation of bottom waters. From a Swiss lake, Schaller et al. (1997) similarly reported that bands of high Mo concentrations and Cr/V ratios in a sediment cores were strongly correlated with the occurrence of long periods of eutrophication and hypolimnetic anoxia during part of the twentieth century. High Mo concentrations were formed by scavenging of dissolved Mo by precipitating Mn oxides at the oxic/anoxic boundary and Fe sulfides in the hypolimnion. High Cr/V ratios were caused by high particle reactivity of chromate and low reactivity of vanadate which were reduced in the anoxic water column. The transition from oxic to anoxic conditions was marked by peaks in Fe, Mn and As concentrations.

Metals differ in their redox reactions and solubilities under oxic and anoxic conditions. Some metals (e.g., As, Cr, Fe, Mn, Mo, Re, U) exhibit different solubilities among their various oxidation states. For instance, sedimentary Fe and Mn are typically enriched under oxic conditions as Fe(III)- and Mn(IV)-oxides and oxyhydrides, depleted under reduced conditions as soluble Fe(II) and Mn(II) species in porewater, and can be enriched again under sulfidic conditions as Fe(II)- and Mn(II)-sulfides.

On the contrary, metals such as As, Cd, U, Mo, and Re tend to be soluble under oxic conditions and precipitate or co-precipitate with pyrites under reducing conditions (Sundby et al. 2004; Morford et al. 2009). Therefore, the sedimentary profiles for these elements can be used in paleoceanographic studies to infer past changes in bottom water oxygenation (e.g. Burdige 2006; Morford et al 2009; Scholz et al. 2011), but do not represent the atmospheric depositional histories of these metals.

Even if a particle-reactive metal is not subject to direct redox reactions in sediments, the shape and magnitude of its concentration distribution can still be affected by redox conditions due to remobilization of the metal's carrier phases. Reductive dissolution of Fe- and Mn-oxyhydroxides, for instance, is known to result in diagenetic remobilization of Pb (e.g. Benoit and Hemond 1991; Balistrieri et al. 1994; Gallon et al. 2004) and As (Couture et al 2008) in some freshwater settings. In the open ocean, sinking organic matter represents the dominant source of most metals to the sediments (Morel and Hudson 1985). Upon oxidative degradation of organic matter (remineralization) in the sediments, the metals carried by this organic matrix can be released, followed by subsequent re-adsorption by Fe- and Mn- oxyhydroxides that are subject to remobilization upon reduction (Burdige 2006).

Other Factors

In addition to the site-specific environmental conditions described above that affect geochemical diagenesis of metals, physical diagenesis is influenced by other factors such as the water depth (shallow water tends to see more mixing because of wind and water current action), sediment bathymetry (more mixing in estuaries and continental shelves with shelving bottoms than in deep basins), and especially by benthic faunal activity (bioturbation). Bioturbation is a particularly common problem in coastal and shelf marine sediments (Johannessen and Macdonald 2012). Its importance in perturbing the profiles of metals (and other sediment properties) can be gauged using a diffusion model developed by Guinasso and Schink (1975) which involves a biodiffusion coefficient (D, cm^2 $ky{-}^1$), the thickness of the mixing zone (L; cm) and the sedimentation rate (v; cm ky^{-1}). The model predicts that the importance of biological mixing in shaping the peak of a contaminant depends on the mixing parameter ($G = D/(L \cdot v)$). According to Guinasso and Schink (1975), for $G > 10$ the contaminant profile in the SML becomes homogeneous before the sediments are permanently buried below the SML, whereas for $G < 0.1$, negligible mixing takes place. Between these values, varying amounts of homogenization of the contaminant peak can be expected.

Tests of Metal Profile Stability

Three general approaches have been explored to test metal profile stability: measurement of porewater metal concentrations in association with modeling of the impact of their diffusion on solid phase (total) metal profiles; comparison of sediment metal profiles against well-documented input histories; and resampling of sediments over decades to judge whether marked changes in profile peak shape and height have occurred.

Porewater Metal Modeling

The first approach has been elegantly demonstrated with different metals in a series of papers by the Tessier–Gobeil research group in Quebec, Canada. The main study lake, Lac Tantaré, Quebec, is a small (1.1 km^2), acidic, and oligotrophic (chlorophyll-a: 0.2–0.9 nM; total P: < 5 nM; planktonic primary production: 50 mg C m^{-2} d^{-1}) lake (Alfaro-de la Torre and Tessier 2002), which is typical of many Canadian Shield lakes. The lake has several distinct basins, with Basin A (pH 5.5–5.8, maximum depth = 15 m) having a perennially oxygenated hypolimnion, and Basin B (pH 6.6–7.0, maximum depth = 22 m) exhibiting a seasonally anoxic hypolimnion (Feyte et al. 2010). Through analysis of porewater and solid phase sediment profiles of the metals of interest and other variables, along with diagenetic modeling, it was found that the contribution of diagenetic processes to the profiles of total metal concentrations in the sediment of the seasonally anoxic basin (Basin B) was negligible to low for Hg (Feyte et al. 2012) and As (Fig. 6; Couture et al. 2008). As a result, the sediment profiles of those metals from this basin can be used directly for reconstructing depositional histories with no or minor correction for diagenesis.

The stability of sedimentary metal profiles in the perennially oxic basin (A), however, is metal-specific. While the diagenetic addition to total metal concentrations was low (≤3 %) for sedimentary Hg (Feyte et al. 2012), Pb (Gallon et al. 2004), and U (Chappaz et al. 2010), diagenetic processes contributed about one-third of the total sediment concentrations of Cd (Alfaro-de la Torre and Tessier 2002), Tl (Laforte et al. 2005), Re (Chappaz et al. 2008b), and Mo (Chappaz et al. 2008a), and up to 60 % of As (see Fig. 6; Couture et al. 2008) in upper sediment layers. Therefore, correction for the impacts of diagenesis on the accumulation profiles of these elements in oxic sediments is essential to arrive at an accurate history of the original fluxes of particle-bound elements at the sediment surface (see Sect. 5.2). The explanation for the stability of As and Mo profiles and their accurate representation of atmospheric deposition histories in basin B, but not in basin A, lies in the seasonally fluctuating anoxia in the hypolimnion of basin B (Couture et al. 2008). This fluctuation prevented the formation of the authigenic Fe oxyhydroxides in the surface sediments of basin B to which Mo and As became associated in oxic basin A. Subsequent burial and reductive dissolution at depth of the Fe oxyhydroxides in basin A released the associated As and Mo into porewater, to ultimately either partly enter the water column (Mo) or become bound again with Fe oxyhydroxides near the sediment surface (As and Mo).

This series of studies has not only established porewater measurement and modeling as a powerful tool to evaluate the stability of sedimentary metal profiles in lakes, but also reinforced the dominant importance of sediment oxygen status in redox-sensitive metal geochemistry. It should be noted, however, that the events in this freshwater lake sediment is different from that in coastal or marine sediment (e.g., the Peruvian Shelf discussed above) where sulfide concentrations are much higher.

Concurrence with Known Inputs

There is a voluminous literature concerning the second approach to testing metal profile stability, from which it is possible to select only a few examples. Lockhart et al. (2000) compared Hg profiles in three Canadian Shield lakes. Two had received particulate Hg in tailings discharge from a gold mine or a cinnabar mine, whereas the third lake received liquid elemental Hg discharges from a chlor-alkali plant during the 1960s. In all three cases, the radiometrically-dated depths of the Hg peaks in sediment cores were in good agreement with the periods of operation of the pollution sources, suggesting negligible Hg mobility after deposition. In a contrary example, Widerlund et al. (2002) reported Pb remobilization from deeper sediment layers in a lake in Sweden that received liquid effluents from an adjacent Pb-Zn mine. The result was higher Pb concentrations in recent sediments deposited after the mine closed than were predicted based on the reduction in emissions.

Comparison of metal profiles with an independent marker of an anthropogenic source is also a powerful check on metal profile veracity. Poly-aromatic hydrocarbons (PAHs), for example, are a marker of coal-combustion related emissions. In Lac Tantaré, Quebec, the uncorrected flux profile of As (of which coal is a major airborne source) in basin B agreed with that of PAHs, supporting the view that the sediment As profile in that basin faithfully represented atmospheric As deposition trends without any modeling correction required (see Fig. 6).

Resampling

The third approach, namely resampling of sediments, although visually compelling is uncommon because it requires the availability of cores from lakes which were previously sampled decades ago. To date only three such studies have appeared. Lockhart et al. (2000) used multiple samplings of Clay Lake (Ontario, Canada) over 24 years to show that total Hg profiles were stable in terms of their maximum peak height and shape over this time span. Rydberg et al. (2008) reported stable total Hg profiles in multiple cores taken over 28 years from a remote Swedish lake receiving atmospheric Hg deposition (Fig. 4a). Methyl Hg (MeHg) profiles, on the other hand, were highly unstable, exhibiting marked declines in specific sediment layers within a few years of their original sampling, and up to 60 % loss over 20 years (Fig. 4b). Net demethylation as the layers became more deeply buried was the most likely explanation, as was reported in other sediments showing elevated surface

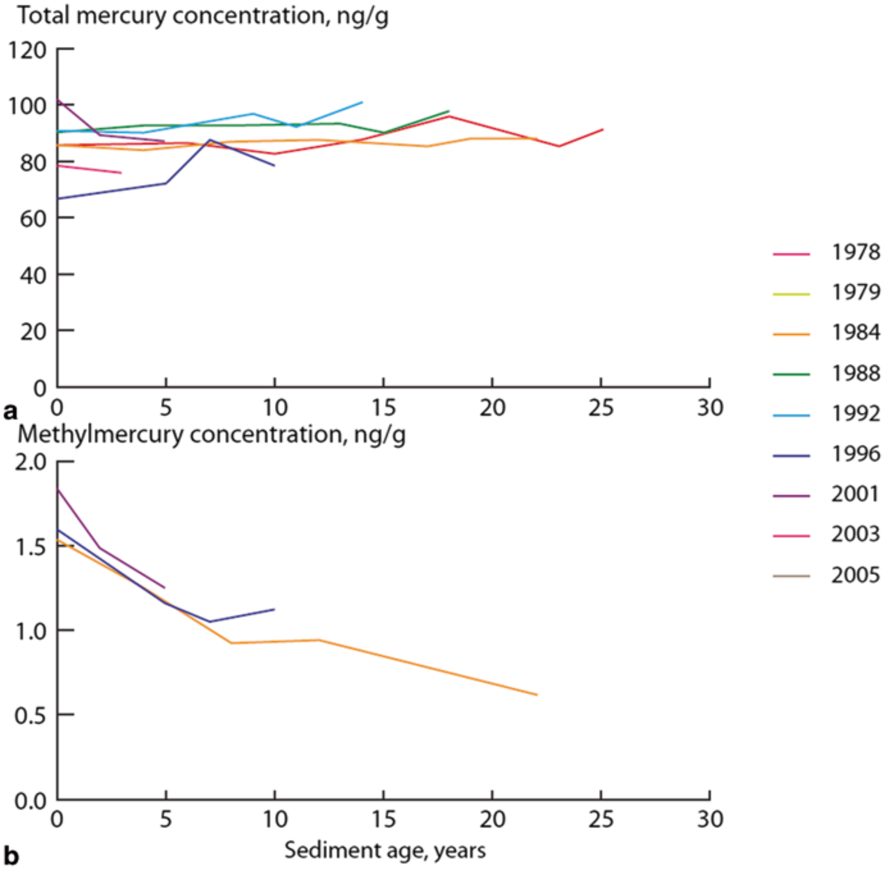

Fig. 4 Concentration changes in sediment layers repeatedly sampled **a**) over 25 years in total mercury, and **b**) over 22 years in methylmercury concentrations, between 1978 and 2003 in a lake in northern Sweden. (Source: adapted from Rydberg et al. 2008). Different symbols indicate cores taken in different years; sediment age of 0 is when the sediment was newly deposited

MeHg (Hines et al. 2004; Feyte et al. 2012). In this context, therefore, demethylation can be regarded as a type of diagenesis.

Multiple elements (Cd, Cu, Hg, Pb and Zn) were compared in sediment cores taken in 1985 and 2004 from four lakes near a base metal smelter (Percival and Outridge 2013). Increases in metal concentrations commenced significantly deeper in the sediment profiles than the documented start of smelting in 1930, which could be attributable either to ^{210}Pb dating inaccuracies, or smearing of the smelter input signal by surface sediment mixing, or to the transport and deposition of metals from long-range industrial sources prior to 1930. In most study lakes the metal profiles between 1930 and 2004 were consistent between repeated samplings in 1985 and 2004, indicating that even if physical mixing had occurred at historical sediment surfaces, diagenesis below the depth of the surface mixed layer in 2004 was insignificant.

In the most polluted lake, however, there was evidence of some degree of remobilization of Cd, Cu and Pb, which exhibited higher concentrations in the upper few centimetres of the 1985 cores when the lake was resampled in 2004 (Fig. 5a, b, c). Those sediment layers were found at a depth of 7–10 cm in 2004 (Fig. 5f). Mercury and Zn profiles on the other hand did not show this remobilization (Figs. 5c, e), as the concentrations of these metals in the sediment layers in 2004 overlapped those in the same sediments sampled in 1985. The agreement between most profiles concerning the timing of the initial onset of metal increases in the early 1930s is also particularly suggestive of a long-term stability. Because these increases occurred in sediments deposited during the early decades of the twentieth century, the agreement between profiles determined in the 1985 and 2004 sampling campaigns suggests a stability of that portion of the trace metal profiles over at least seven decades (Percival and Outridge 2013).

Correcting and Interpreting Diagenetically-Altered Metal Profiles

The impact on metal profiles of the two types of diagenetic processes (physical and geochemical) may be correctable in different ways. The consequences for interpreting diagenetically-altered metal profiles are also different in each case.

Correction for Mixing

Significant mixing of upper cores interferes with ^{210}Pb dating such that dates can no longer be attached to specific sediment depths (Johannessen and Macdonald 2012). Being unable to attach a reliable chronology to down-core sediments obviously limits the scope of the interpretation and conclusions that can be drawn from metal profiles. In extremely slowly accreting sediments such as in deep-ocean basins, SMLs may also introduce errors into radiocarbon age-depth models, if the SML represents a significant fraction of the depths that have been dated. Particle-bound carbon is no more immune to mixing than lead.

However, as discussed in detail by Johannessen and Macdonald (2012), some information can be gleaned from mixed metal profiles, such as the total historical inventory of contaminants deposited at a site, and the maximum possible sedimentation rate. Increasing and decreasing trends may be qualitatively discernable, although rates of change and fluxes cannot be estimated without additional modeling of ^{210}Pb profiles and transient signals such as ^{137}Cs. Insights can also be gained into plausible hypotheses of metal input histories which could explain the observed metal profile; the modeling thus constrains the interpretive possibilities.

Hare et al. (2010) provide an example of the treatment and interpretation of metal profiles in sediments with significant SMLs. Twelve sediment cores were taken

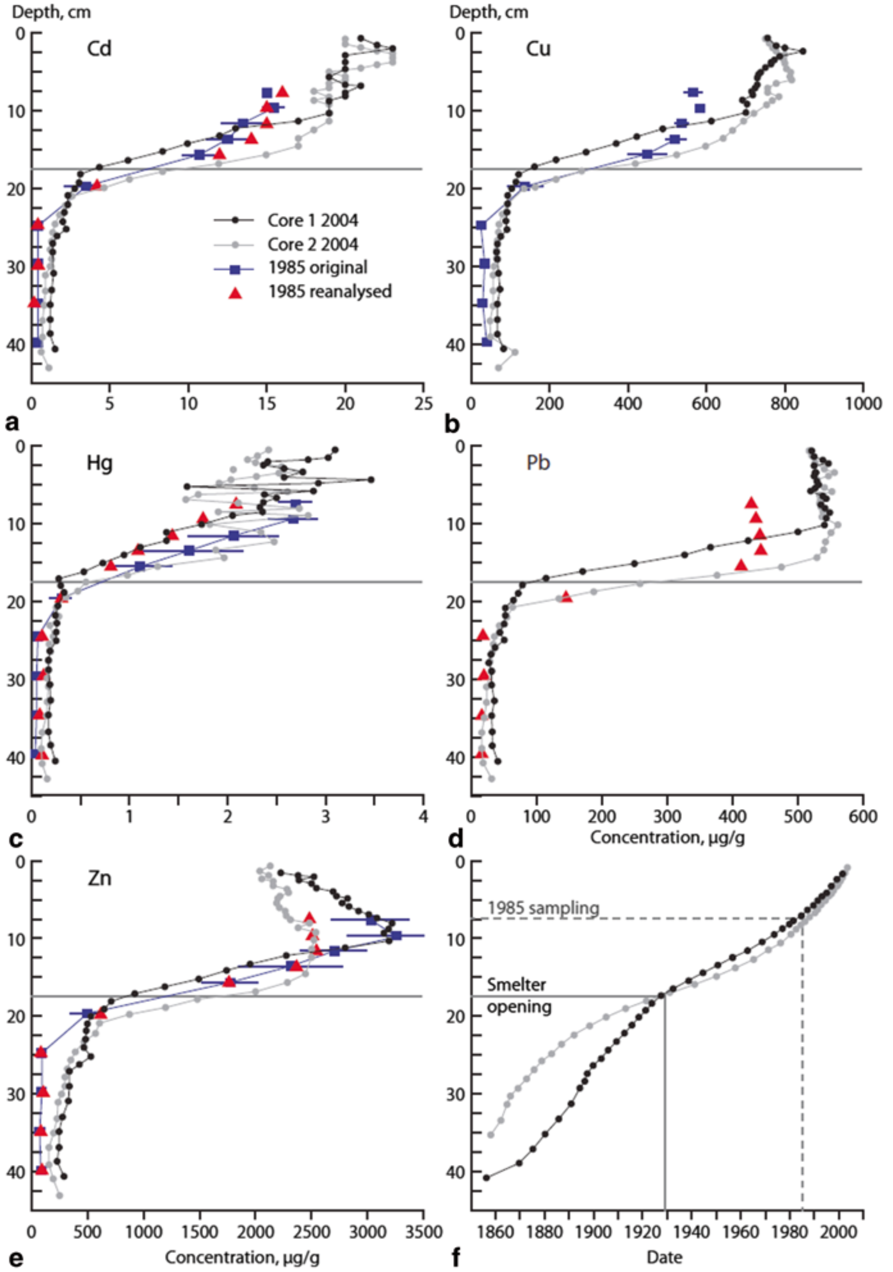

Fig. 5 Down-core concentration profiles of **a**) Cd, **b**) Cu, **c**) Hg, **d**) Pb, and **e**) Zn in 1985 cores, and duplicate cores in 2004, taken from Meridian Lake (South Basin), Manitoba, and **f**) the depth-date chronology (based on ^{210}Pb activity) for the 2004 cores. (Source: adapted from Percival and Outridge 2013). 1985 data originally presented by Harrison et al. (1989). The undated 1985 core data were aligned with 2004 core data using the 2004 depth-date chronology (panel f) to identify the depth of 1985. Cores 1 and 2 in 2004 were taken within a few metres of each other in the

from Hudson Bay, which varied in the depth of the SML (from 1 to 10 cm) and exhibited very different Hg profiles. To correct for the mixing, mercury flux histories in the cores were modeled with a two-layer sediment mixing model previously applied to understand transient Hg inputs to coastal marine sediments (Johannessen et al. 2005). Mercury profiles were reproduced with a combination of input functions representing time periods with steady Hg concentrations, and time periods with linearly increasing or decreasing Hg concentrations in the incident particles. A second input function for each core, corresponding to a second change in Hg concentration, was included when necessary to reproduce the observed profile. Such changes in Hg flux were adjusted to match the observed vertical profiles by manipulating the Hg concentration, the date of onset, and the time over which an input signal lasted. The resulting Hg flux histories represented the simplest input functions that reproduced the observed sediment Hg profiles. Using this approach, Hare et al. (2010) were able to correct for the effect of mixing, with the resulting flux reflecting the known history of atmospheric Hg deposition in North America. This successful reconstruction allowed them to show that the Hg record contained in Hudson Bay sediments was largely controlled by natural changes in organic matter composition, dynamics and particle flux in the system, which were at least as influential as changes in atmospheric Hg emissions.

Modeling Corrections for Geochemical Diagenetic Processes

For correcting the effects of geochemical processes, the work of Tessier and Gobeil and their students provides clear direction about modeling approaches to be employed. This typically involves the application of one-dimensional (1-D; i.e., perpendicular to the sediment-water interface) diagenesis models to porewater metals data to estimate the amount of a metal added to or removed from the solid phase during diagenesis (e.g., Gallon et al. 2004; Laforte et al. 2005; Couture et al. 2008; Chappaz et al. 2008a, b; Feyte et al. 2012). Since most metals are bound to the solid phase, even small concentration changes in the solid phase can produce large changes in porewater concentrations, making porewater a sensitive indicator of ongoing diagenetic reactions. If diagenesis has significantly altered the sediment profiles, subtraction of these estimates from the measured total concentrations in sediment can lead to a robust reconstruction of atmospheric deposition histories. Application of this approach to As profiles in Lac Tantare, Quebec, resulted in good

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deepest point of the lake; the sampling point in the lake in 1985 was not identified. Sediment depth in 2004 cores associated with the 1930 opening of the Flin Flon smelter is indicated by a solid *grey* line in all panels. “1985 original” metals data (mean ± 1 standard deviation (SD) of 4 cores) as reported by Harrison et al. (1989); “1985 reanalysed” data are from one remaining 1985 core that was reanalysed with the 2004 sediments. “1985 original” Pb data were not reported by Harrison et al. (1989). Evidence of remobilization of Cd and Cu is inferred because metal concentrations in the upper 2004 cores (8 to ~12 cm) differed by more than one SD from the mean values in the same sediments sampled in 1985; remobilization of Pb is inferred because the Pb data from one “1985 reanalysed” core were ~20 % lower than the same sediments resampled in 2004

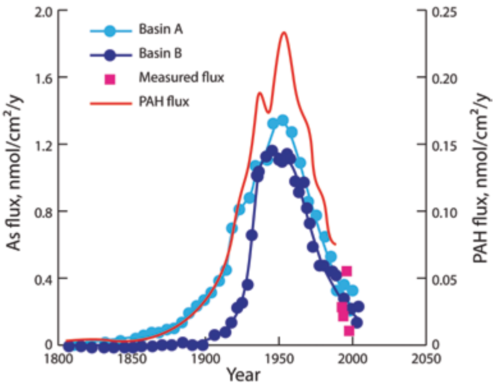

Fig. 6 Reconstruction of atmospheric anthropogenic As deposition in sediments of *Basins A* and *B* of Lac Tantaré, compared with flux of polycyclic aromatic hydrocarbons (*PAHs*) in Basin A and measured atmospheric As fluxes in rural North America. (Source: adapted from Couture et al. 2008). Contrast profiles of uncorrected As concentrations (*green squares* in Figs. 3a, c) and this figure's corrected fluxes. Anoxic Basin B originally gave a correct history whereas oxic Basin A data required significant modeling correction

agreement between the As fluxes determined in the oxic (A) and anoxic (B) basins of the lake, and with measured atmospheric As and PAH fluxes (Fig. 6). Similarly good agreement was reported with correction of profiles of Tl (Laforte et al. 2005) and Mo (Chappaz et al. 2008a), both of which, like As, derived mainly from atmospheric emissions of coal combustion in North America.

Readers who are interested in a detailed mathematical treatment of diagenesis are advised to consult Berner (1980), Boudreau (1997, 1999) and Burdige (2006). Briefly, assuming that: (i) the concentration C of a metal at a specific depth x is at steady state; (ii) molecular diffusion and bioturbation are the only important diffusive processes in porewater; and (iii) bioirrigation is the only important advective process in porewater, then the standard 1-D conservation (i.e., balance) equation for porewater concentration can be simplified to (Boudreau, 1997; Chappaz et al. 2008a):

$$\frac{\partial \varphi C_{PW}}{\partial t} = \frac{\partial}{\partial x}\left(\varphi(\underbrace{D_S}_{\substack{molecular\\ diffusion}} + \underbrace{D_B}_{bioturbation})\frac{\partial C_{PW}}{\partial x} \right) + \underbrace{\varphi\alpha(C_{burrow} - C_{PW})}_{bioirrigation} + \underbrace{R_{Net}}_{reaction} = 0 \quad (1)$$

where C_{PW} is the metal concentration in porewater (mol cm^{-3} of porewater), C_{burrow} is the metal concentration in the burrows of benthic animals (mol cm^{-3} of porewater), φ is the porosity (volume ratio of porewater to bulk sediment), D_s is the effective molecular diffusion coefficient in the sediment pores ($D_s = D_w/\theta^2$ where D_w is the molecular diffusion coefficient (cm^2 s^{-1}) in free solution, and θ is tortuosity which can be empirically estimated from φ), D_B is the biodiffusion coefficient (cm^2 s^{-1}), α is the bioirrigation coefficient (s^{-1}), and R_{net} is the net rate of production of dissolved metal in porewater (mol cm^{-3} of whole sediment s^{-1}).

Equation (1) can be solved numerically for R_{Net} using the computer code PROFILE (Berg et al. 1998) or by the Rate Estimation from Concentration (REC) model (Lettmann et al. 2012). The metal concentration due to diagenetic reactions that add to or remove from the solid phase during sediment burial can then be calculated as:

$$C_{s,diagenetic} = -\int_{x=0}^{x=x_i} \frac{R_{net}}{mv_s} dx = -\sum_{x=0}^{x=x_i} \frac{R_{net}}{mv_s} \Delta x \tag{2}$$

where x_i is the depth of a sediment layer, m is the dry bulk density of whole sediment (g cm^{-3} of whole sediment) and v_s is the sedimentation rate (cm yr^{-1}). Therefore, the metal concentration in the settling particles deposited at the sediment surface ($C_{s,deposited}$) can be calculated from the difference between what we measured ($C_{s,\ measured}$) and $C_{s,diagenetic}$:

$$C_{s,deposited} = C_{s,measured} - C_{s,diagenetic} \tag{3}$$

The corrected $C_{s,deposited}$ can then be plotted against sediment depth (and age) to established the depositional history.

To make the solution to Eq. (1) simpler, the choice of sampling site is important. For instance, when a sediment core is taken from a lake with a seasonally or permanently anoxic hypolimnion, the biodiffusion and bioirrigation terms in Eq (1) can be neglected due to the absence (or small population) of benthic animals. Otherwise, the D_B and α parameters must be estimated which requires at least an evaluation of the benthic community.

An important consideration for this approach is that porewater profiles of the metals need to be measured reliably to avoid cross-contamination and alterations in metal speciation. In situ sampling techniques such as dialysis samplers (“peepers”) (e.g., Carignan et al. 1985) and thin-film probes (e.g., the diffusive gradient in thin film technique—DGT; Davison and Zhang 1994) are the preferred techniques wherever feasible.

Practical Recommendations

Numerous practical criteria guide decisions such as which lakes or basins are to be sampled, how many sediment cores are taken, and subsequently which analytical parameters are determined. In order to minimize problems associated with metal instability and diagenesis, and to aid in interpreting problematic metal profiles, the following considerations should be added to those criteria. While other factors may ultimately constrain the selection of study sites to less than ideal locations (from a diagenesis perspective), and one may have only limited prior limnological or sedimentological information (especially in remote areas), being aware of the features that promote metal stability may help to make positive choices. These then will increase the confidence one has in the interpretation of metal profiles in the chosen lakes. Above all, the possibility of diagenetic alteration of metal profiles must always be considered, and its occurrence should be evaluated with appropriate ancillary chemical data.

Site Selection The series of studies in Lac Tantaré, Quebec, reviewed above, clearly points to stratified lakes or lake basins with anoxic hypolimnia as advantageous study sites for metal deposition research because of the minimal diagenetic alteration of most metal profiles. The advantage stems from the fact that surface sediment oxyhydroxide formation, the diffusive influx of metals which are dissolved in oxygenated waters, and the amount of bioturbation are all limited by the low-oxygen conditions that develop during extended periods of stratification. Thus, monomictic, dimictic and meromictic lakes are recommended over polymictic lakes. Low-oxygen marine basins would be similarly preferred. Deeper lakes are preferred over shallow lakes, as wind-driven disturbance of water column stratification will be lessened.

Minimizing the period of time during which recently deposited sediments may be perturbed by benthic biota, and porewaters can exchange dissolved metals with the water column, is also desirable as this reduces the opportunity for surface mixing layers to develop and for certain types of geochemical diagenesis to operate on solid-phase metal profiles. Therefore, metal profiles from lakes or marine basins with higher sedimentation rates should have on average fewer diagenesis issues than sites with lower sedimentation rates. Finally, because of site-specific hydrology, oxygen status, and biological activities, sediment cores taken from different sites within the same water body could exhibit quite different metal profiles (see Rosen, this volume). Therefore, reproducibility (or lack thereof) of metal profiles from the same water body is not necessarily indicative of stable and reliable (or unstable and unreliable) depositional histories. Assessment of the stability and reliability of target metal profiles is preferred in the light of ancillary geochemical data on known redox status indicators such as Fe, Mn and S (see below).

Profile Interpretation Evaluating whether metal profiles are stable and so accurately represent a depositional history, or have been significantly altered by diagenesis, requires ancillary parameters to be measured in addition to the primary metals of interest. The radioisotopic tracers needed for establishing a sediment chronology and sedimentation rates—primarily ^{210}Pb and secondarily ^{137}Cs or an alternate such as ^{241}Am—can serve as a check on the degree of physical mixing of the profiles. However, recent increases in sedimentation rate in some instances can result in flattened, homogeneous isotope profiles at the tops of sediment cores, which mimic the effects of bioturbation and sediment mixing. Analysis of single metals in isolation is to be avoided, because the similarities and differences between the profiles of different metals and other elements, especially those such as Fe, Mn, Mo, Re, S or U that are known to be redox-sensitive, can provide important information about the degree of geochemical diagenesis that may have occurred. Analysis of other surrogate measures of pollution inputs, such as PAHs, relevant to the metals of interest can also serve as an independent check on the interpretation of their profiles.

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Calculating Rates and Dates and Interpreting Contaminant Profiles in Biomixed Sediments

Zou Zou A. Kuzyk, Robie W. Macdonald and Sophia C. Johannessen

Abstract Contaminant profiles in well-dated sediment cores represent extremely valuable natural archives of environmental contamination, by which contaminant sources, history and cycling may be determined and contaminant concentrations in surface sediments projected into the future. However, most marine and estuarine sediments are mixed by benthic organisms to a depth of at least 2–20 cm, which introduces significant risks of misinterpreting and misapplying these archives if biomixing is not explicitly taken into account. This chapter offers a step-by-step guide to avoiding common pitfalls and appropriately applying biomixed sediment archives to reconstructing contaminant inputs to the environment. By the use of simple models, radioisotope tracers (^{210}Pb, ^{137}Cs) may still be applied to establish geochronologies in biomixed cores and to validate the sedimentation rates and dates derived. Having obtained (and validated) sedimentation and mixing rates for biomixed cores, contaminant profiles may then be interpreted through the further use of models in a way that explicitly accounts for mixing. As with any sediment core, the main caution when one attempts to infer contaminant releases from deposition histories reconstructed from biomixed sediment cores are the unknown possible impacts of environmental variation and change.

Keywords Contaminants · Sediment cores · Marine and estuarine sediments · Bioturbation · Biomixing · ^{210}Pb · ^{137}Cs · Geochronology · Sedimentation rates

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Introduction

Sediments are widely used as natural archives of environmental contamination. Fine-grained sediments represent major sinks for particle-reactive contaminants that are resistant to degradation, including polychlorinated biphenyls (PCBs) (cf. Kuzyk et al. 2010), dioxins and furans (Macdonald et al. 1992), polybrominated diphenyl ethers (PBDEs) (Johannessen et al. 2008), polycyclic aromatic hydrocarbons (PAHs) (Yamashita et al. 2000), and trace metals like Cu, Pb, Cr, Zn (Bopp et al. 1993) and Hg (Hare et al. 2010; Johannessen et al. 2005). These contaminants may be supplied by local sources (Valette-Silver et al. 1993) or may be transported by rivers, long-range atmospheric transport or, in the marine environment, by ocean currents (Gustafsson et al. 2001; Kuzyk et al. 2010; Macdonald and Thomas 1991).

Contaminant archives in sediments have been applied to several important questions. In some instances, the contaminant burden in sediments is used to assess the exposure and possible risks to wildlife from contaminated sediments. For this application, it may be appropriate to collect only surface sediment grab samples (cf., Brown et al. 2013; Kuzyk et al. 2005; Power and Chapman 1992). However, to determine the contaminant sources, history and cycling, or to project future contaminant concentrations in surface sediments, contaminant profiles in well-dated sediment cores are required. In areas where long-term monitoring has been limited (or nonexistent) and/or sources of contaminants are unknown, the proxy records in the sediments may represent the *only* means of reconstructing the sources and long-term trends in contaminant release to the environment. Contaminant profiles in dated cores can also provide two of the most important components of contaminant budgets—the rate at which a contaminant is being buried and its inventory in regional sediments (cf., Hare et al. 2008; Outridge et al. 2008).

Despite the tremendous potential of sediments as tools for reconstructing contaminant sources and inputs, there are significant risks of misinterpreting and misapplying these archives. The major risk arises from the assumption that sediments are inert, passive repositories that conveniently store layer upon layer of local or regional contamination history. In lake sediments, mixing is generally insignificant because of a less active benthic community or anoxic bottom waters (Appleby 2001; Robbins 1978). In contrast, most marine and estuarine sediments are mixed by benthic organisms to a depth of 2–20 cm (or occasionally $\leq$40 cm) (Lavelle et al. 1985; Robbins and Edgington 1975). These organisms affect the physical and chemical properties of sediments and profoundly alter the depth distributions of both geochronological tracers (e.g., ^{210}Pb, ^{137}Cs) and contaminants (Boudreau 1998; Crusius and Kenna 2007). To determine sedimentation rates accurately and to reconstruct contaminant inputs in most marine and estuarine sediments, biomixing must be taken into account explicitly.

Some previous studies have discussed various aspects of interpreting mixed cores (e.g. Appleby 2008; Crusius and Kenna 2007; Guinasso and Schink 1975; Johannessen and Macdonald 2012). The goal of this chapter is to provide a practical, step-by-step approach by which common pitfalls can be avoided and biomixed sediment archives applied appropriately to reconstructing contaminant inputs to the environment. Although the approach applies to any biomixed sediment archive, we focus on marine and estuarine sediments because these archives are very commonly affected by biomixing. We will discuss: (1) The range of tasks that can be accomplished with contaminant profiles in marine and estuarine sediment cores; (2) What sediments record and what they do not; (3) How sediments operate on signals, or produce their own signals; and (4) How to use simple models to obtain the most information possible from the records at hand.

After outlining the problem of mixing (how it complicates the interpretation of sediment archives (Sect. 2)), the chapter discusses the sequence of critical steps required to develop accurate contaminant histories from biomixed cores (Fig. 1). After collecting and subsampling a core (Sect. 3), the next step is to establish a robust sediment geochronology (Sect. 4), which accounts for mixing. Geochronology provides the foundation from which contaminant profiles can be interpreted (Sect. 5). Following the step-by-step guide, we present some caveats on the interpretation of biomixed cores (Sect. 6), including the risk of false correlations and post-depositional mobility, and offer a cautionary note about inferring contaminant releases from deposition histories reconstructed from sediment cores because of the impacts of environmental variation and change (Sect. 7).

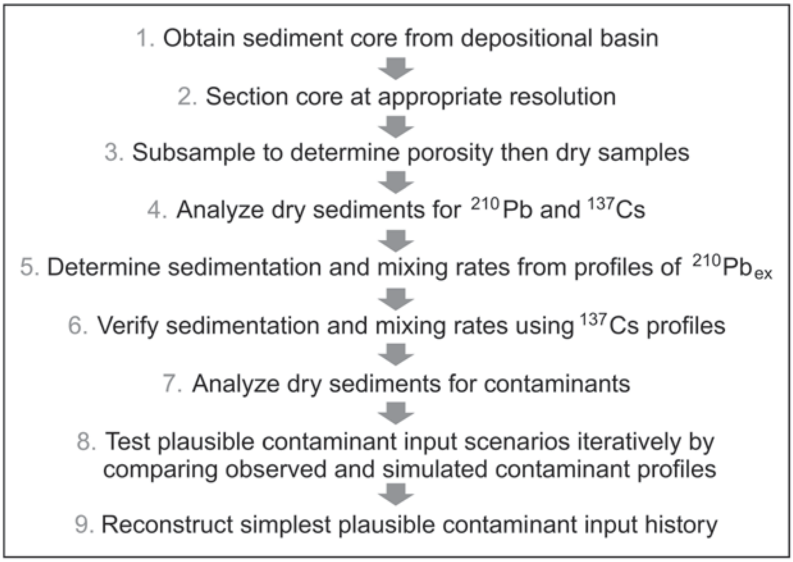

Fig. 1 Flowchart outlining the key steps required to develop a sediment contaminant profile that can be fully interpreted in the context of deposition and post-depositional processes

The Effects of Biomixing on Contaminant Profiles

Figure 2 illustrates the effect of biomixing (i.e., bioturbation) on a discrete contamination event. It compares the theoretical development over time of a 3-year addition of 3 μg g^{-1} of a contaminant to the surface of an accumulating sediment with no biomixing (left-hand sequence) to sediments having the same sedimentation velocity (0.35 cm yr^{-1}) and biomixing at a rate typical for sediments in productive coastal areas (50 cm^2 yr^{-1} in the SML, 0.01 cm^2 yr^{-1} below). A numerical advective-diffusive model that explicitly accounts for both sedimentation and mixing (see Sect. 5) has been used to simulate the profiles in the two cores.

The background concentration of the contaminant is 0.1 μg g^{-1} in both cores. After 3 years, the concentration of the contaminant in accumulating sediment declines to 0.3 μg g^{-1}. This set of circumstances might well apply to Hg or Pb, for example, where the contamination adds on to a natural background, and some of the contaminant continues to cycle in the system after the event. Without mixing, the pulse (square wave) maintains its concentration and, over time, is simply buried deeper into the sediment column at the sedimentation velocity of 0.35 cm yr^{-1} (left-hand sequence).

In the right-hand panel, the only change that has been made in the model is to include biomixing at a rate of 50 cm^2 $year^{-1}$ within the SML (top 2 cm of the core). In the mixed sediment simulation, a contaminated layer added to the surface is mixed downward within the surface layer in < 1 year, resulting in a concentration gradient (decreasing downward) that extends throughout the SML. Concentrations are initially higher near the surface because mixing is not instantaneous; however, mixing within the SML nearly keeps pace with the addition of contaminated material to the surface. As time progresses (by year 2), the contaminant concentration is nearly constant throughout the SML. Meanwhile, a partially mixed contaminant profile is being shed off the bottom of the mixed layer. That is, the contaminant record preserved in the sediment below the mixed layer reflects the time evolution of the concentration of contaminant at the bottom of the mixed layer. During the next few years, the concentrations at the top of the SML decrease as additional uncontaminated sediment is added to the surface. The process of rapidly contaminating the SML, and then diluting this slowly with clean material results in a nose-like feature that has a sharper gradient during the rising phase (bottom of the nose) than during the declining phase (see, for example, the profile at 5 years, Fig. 2b (right panel) and Fig. 1 in (Guinasso and Schink 1975)). As clean material is added to the top of the sediments, the continued mixing maintains moderately elevated concentration at the top of the SML by mixing some of the contaminant back up toward the surface. A gradient in contaminant concentrations (increase with depth) is often maintained for many years because the mixing is too slow to keep up with the rate of addition of uncontaminated material. Under these circumstances, the loss of contaminant by burial below the SML scales with the average concentration in the mixed layer, which implies that decline in SML contaminant concentration with time can be described as a first-order kinetic (exponential decay, essentially). Sediments shed off the bottom of the mixed layer with time reflect the concentration in the SML at the

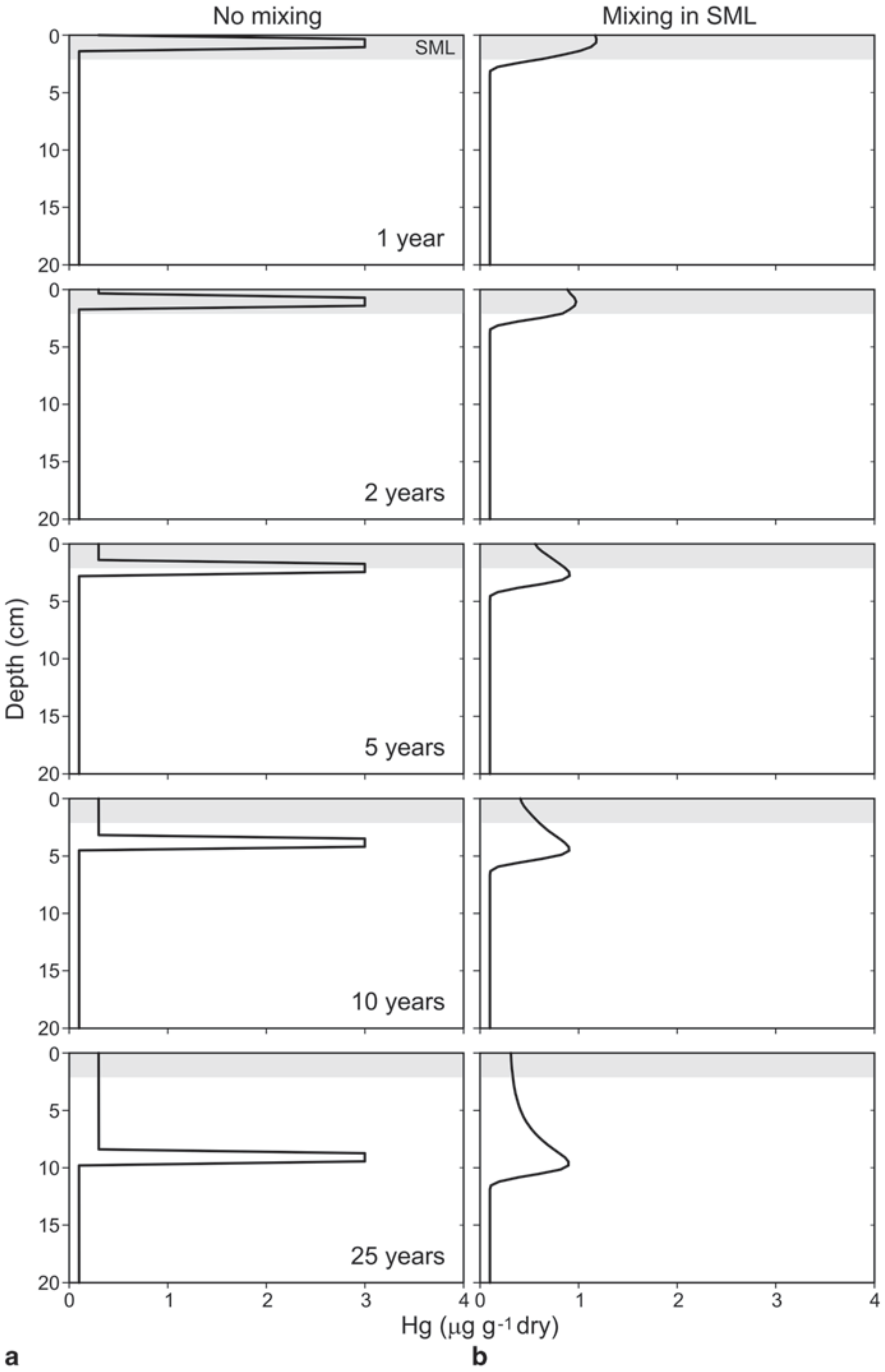

Fig. 2 The effects of mixing on a contaminant pulse introduced to sediments with sedimentation velocity of 0.35 cm yr^{-1}. In the left set of panels, **(a)** a contaminant pulse (3 µg g^{-1} beginning in year 0 and extending over a 3-year period) is preserved and buried at a rate of 0.35 cm yr^{-1}. In the

time of shedding, so the concentrations present deep in the core reflect the changing concentration in the SML, not that of the original pulse. Varying the relative rates of mixing and sedimentation velocity and the depth of the mixed layer produces a family of curves (cf., Guinasso and Schink 1975; Johannessen and Macdonald 2012; Johannessen et al. 2005; Silverberg et al. 1986). In particular, Fig. 1 in Guinasso and Schink (1975) presents a very clear illustration of the variation in contaminant profiles that can come about from identical source inputs subjected to different mixing conditions. The net effects of surface mixing are to spread the contaminant pulse over a range of depths; to push the pulse deeper in the core than the sedimentation velocity by itself would do (compare right and left panels in Fig. 2); and to reduce the peak concentration of a contaminant from that of the original pulse. The profiles of other substances (e.g., dating tracers) introduced to sediments will also be affected by biomixing. Consequently, biomixing needs to be taken into account even for relatively simple efforts to establish sedimentation rate (e.g., using the first entry of ^{137}Cs to identify 1954). A feature used for dating such as a peak in tracer loading (e.g., 1963 for ^{137}Cs) may be preserved in a mixed core but moved to deeper in the core and changed in shape.

Another implication of the profound effects of biomixing on contaminant concentrations in the upper portion of the sediment column is that spatial gradients delineated using the contaminant concentrations in surface sediments (especially grab samples representing a composite of the top ~2–10 cm of sediment) are extremely challenging to interpret. These effects are illustrated in Fig. 3, where the advective-diffusive model was used to simulate the effect of varying the thickness of the SML from 1 to 8 cm for the sediments modeled in Fig. 2 (sedimentation velocity 0.35 cm yr-^{1}, surface mixing rate (K_{b1}) of 50 cm^{2} year^{-1}). For an identical pulse of contaminant (3 μg g^{-1} for 3 years and 0.3 μg g^{-1} thereafter) a 10–40 % difference in the contaminant concentration that would be measured in a typical 'grab' sample (comprising the top 5 cm of the sediment column) would be observed based solely on depth of mixing at that site. The implication is that spatial variation in sediment geochemical properties (mixing, sedimentation rate) may be just as important as proximity to a source in determining the surface concentration associated with a point-source contaminant. This effect is strongest when the contaminant flux is changing, because sediment gradients are strongly affected by the residence time of contaminant in the mixed layer. The effect of mixing, therefore, casts doubt on the common practice of interpreting surface contaminant distribution patterns to pinpoint proximity to a source (cf., Cai et al. 2012; Cesar et al. 2009; Choueri et al. 2009; Ramdine et al. 2012).

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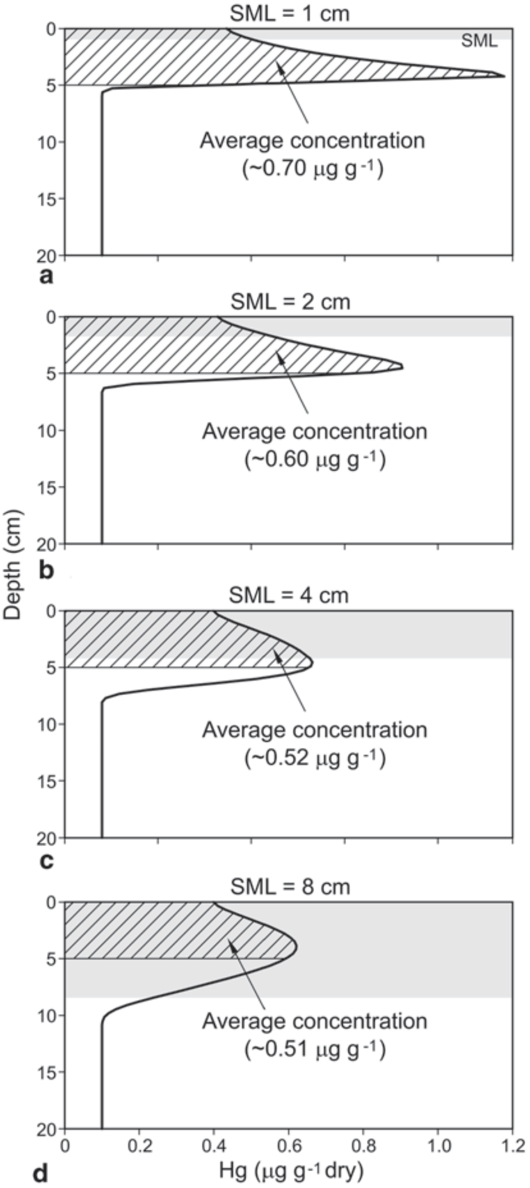
right-hand panel, **(b)** a surface mixed layer of 2 cm (and mixing rate 5 cm^{2} yr^{-1}) alters the simple square wave seen in the *left*-hand sequence of panels to a more diffuse shape, which penetrates more deeply into the sediments. Surface sediments also remain contaminated for a longer period of time, and the contaminant peak in sediments is seen to be deeper in the core and of lower concentration. In this simulation, the background concentration has been assumed to be 0.1 μg/g before the contamination event and 0.3 μg/g afterward. (See text for further details)

Fig. 3 The effects of variable biomixing (surface mixed layer (*SML*) = 1 cm (**a**), 2 cm (**b**), 4 cm (**c**), and 8 cm (**d**)) on contaminant concentrations in the upper portions of a mixed sediment ($\omega = 0.35$ cm yr^{-1}, $K_{b1} = 50$ cm^2 yr^{-1}). Simulated contaminant profiles are shown 10 years after a pulse (thus Fig. 3b is the same as Fig. 2b—2 years) except for scale). Average contaminant concentrations for a 'grab sample' comprising the upper 5 cm of the sediment are given



Clearly, mixing produces dramatic differences in contaminant signals introduced to the top of sediment. Even if a core is correctly dated, if not accounted for, the effect of biomixing on contaminant profiles will produce a misleading contaminant history (overestimating the magnitude of early inputs, estimating an earlier date of deposition than actually occurred, and implying a slower response to mitigation than actually occurred at the sediment surface). In the following sections, we describe the step-by-step process that we have found to be successful in interpreting contaminant archives in biomixed cores.

Sediment Core Collection and Processing

Sediment sampling requires special care because errors made here cannot later be fixed in the lab. The coring location needs to be chosen with program objectives in mind; quiescent basins are convenient, because sediments accumulate at reasonable rates, but one needs to keep in mind that coring only in such locations will likely provide a biased representation of the region. Clear-vented, slow entry coring devices provide the best results and large box cores yield more material than do small gravity cores. During coring, it is important to capture the sediment surface. The preservation of the surface can be identified by the presence of clear overlying water and by benthic organisms and structures that appear to be undisturbed. The core should be sectioned immediately to avoid dewatering and cut into layers at intervals that ensure adequate resolution of the features of interest (usually ~20 intervals down a 50 cm core collected in coastal waters, with the finest resolution in the uppermost 10 cm). The outermost layer (~1 cm) near the wall of the corer should be discarded if possible, as it will contain some material 'smeared' downward from the top of the core along the core tube wall (Harvey et al. 1987). The extent of smearing depends on sediment type and obviously the smaller the sample mass, the greater the risk of concentration profiles being significantly affected (Chant and Cornett 1991). In the case of industrial contaminants, and considering the half-life of ^{210}Pb, one is usually attempting to gather detail for sediments that have accumulated over the past ~100–150 years. The depth of such sediments will vary depending on sedimentation rate, but usually we are interested in the top 20–100 cm of the sediments. Further discussion of coring technique has been published by other authors (Anderson et al. 1987; Chant and Cornett 1991; Crusius and Kenna 2007; Lebel et al. 1982).

Establishing Geochronologies in Biomixed Cores

Two radionuclide chronometers are commonly used to date sediment cores for contaminant studies, the naturally-occurring radionuclide ^{210}Pb and the artificial fallout radionuclide ^{137}Cs. ^{210}Pb, which has a half-life of 22.26 years, is the primary basis of most sediment dating. ^{210}Pb is introduced to marine sediments from three sources (Cochran 1992; Cochran et al. 1986; Robbins 1978). 'Supported' ^{210}Pb, is produced *in situ* (within the sediments) by decay of ^{226}Ra contained within the inorganic sediment matrix (Fig. 4). Supported ^{210}Pb varies from site to site, and may even vary within a given core, although it is usually assumed to be constant within the sediment column at any particular site. A second source is ^{210}Pb produced in the

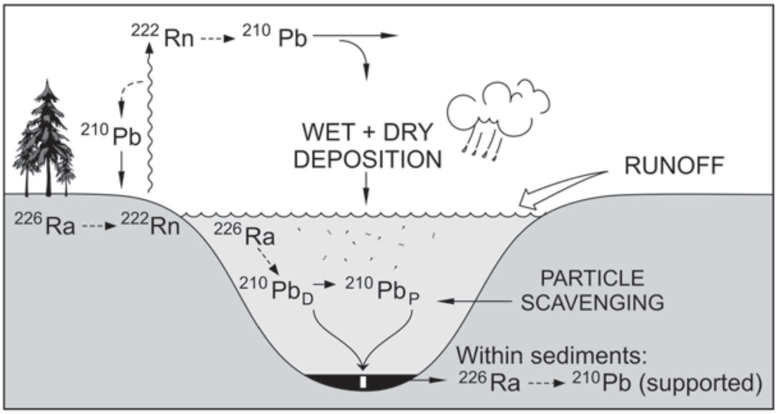


Fig. 4 A schematic diagram illustrating the cycling of ^{210}Pb in the environment

atmosphere by decay of gaseous ^{222}Rn, which itself is produced at the Earth's surface by decay of ^{226}Ra. The ^{210}Pb produced in the atmosphere by ^{222}Rn decay (half life ~3.8 d) is quickly scavenged and brought back to the Earth's surface in rain and dry fallout. A third (frequently neglected) source of ^{210}Pb in marine systems is produced within the water column by decay of dissolved ^{226}Ra, which is essentially a conservative element in seawater (i.e., it correlates with salinity). ^{210}Pb is strongly scavenged from surface waters by particulate matter and thence delivered to the seafloor with the particle flux. ^{210}Pb introduced to sediments by particle scavenging in the water column is called the 'unsupported' or 'excess' ^{210}Pb (^{210}Pb$_{ex}$), and it is this component that provides the means to date sediments. Excess ^{210}Pb activity is calculated from total ^{210}Pb activity by subtracting supported ^{210}Pb, which is estimated either from the measured activity of ^{226}Ra or from the total ^{210}Pb profile itself if a constant activity has been reached in the deeper part of the core.

Excess ^{210}Pb (^{210}Pb$_{ex}$) is assumed to be a *steady-state* tracer, meaning that it is supplied at the top of the core at a constant rate reflecting various regional processes, and then decays away within the sediments as they age. If the sediments have sufficient time to come to steady state with respect to ^{210}Pb$_{ex}$ (~150 years) then the rate of supply at the top of the sediments will balance the radioactive decay loss of ^{210}Pb$_{ex}$ from the inventory within the sediments. This balance has a useful implication; if the inventory of ^{210}Pb$_{ex}$ can be established in a core, the flux of ^{210}Pb$_{ex}$ to the surface can be inferred, even without knowing anything about the internal workings of that core (e.g., mixing, sedimentation rate). In a case where there is no mixing- for example in a lake or an anoxic basin—and the sediment accumulation rate is constant, ^{210}Pb$_{ex}$ activities will exhibit an exponential decrease with depth in sediment from the surface and reach negligible ("background") values at a depth approximating sediments accumulated 150 years previously (Fig. 5a). Sedimentation velocity (ω, cm yr^{-1}) may be calculated simply as $-\lambda/m$, where λ is the decay constant (0.03114 year^{-1}) and m is the slope of the line of the natural logarithm of ^{210}Pb$_{ex}$ activity in units of Bq cm^{-3} vs. depth (cm) (Fig. 5) (Robbins 1978).

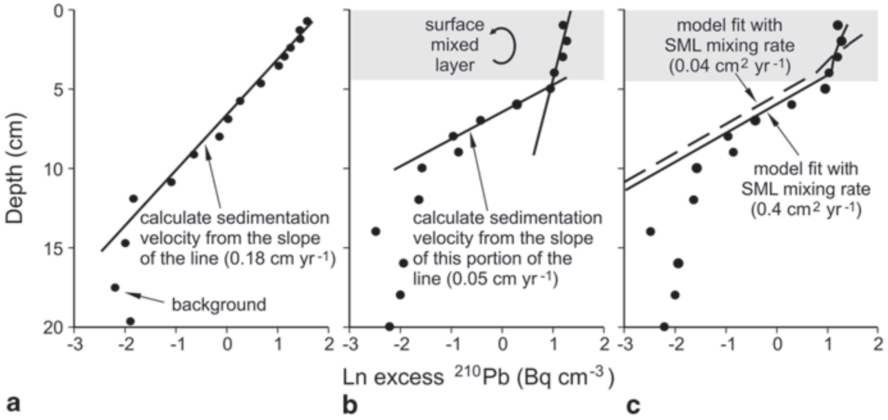


Fig. 5 Log-linear $^{210}Pb_{ex}$ decay profiles in (**a**) an unmixed core; (**b**) a core with a surface mixed layer (*SML*) overlying relatively unmixed sediments in which biomixing has been neglected in producing decay slopes and (**c**) the same core as (**b**) modeled with diffusive mixing rates of 0.04 and 0.4 cm^2 yr^{-1}

$$\omega = -\lambda / \mathrm{m} \tag{1}$$

In mixed marine sediments, the surface mixed layer (SML) can be identified as the uppermost section of a core, where ^{210}Pb activity decreases only slowly, if at all, with depth (Fig. 5b). Where surface mixing occurs, the assignment of a unique date to a sediment layer is no longer possible. However, it is often still possible to obtain a valid estimate of the sedimentation rate from the $^{210}Pb_{ex}$ distribution (Fuller et al. 1999; Guinasso and Schink 1975; Johannessen and Macdonald 2012; Lavelle et al. 1986; Robbins 1978). The depth of the SML is estimated by eye, and the sedimentation velocity is calculated as above from the exponential decay of $^{210}Pb_{ex}$ with depth, but starting below the SML.

Most sediments tend to compact with time, which means that depth interval is not conserved. The sedimentation velocity can be converted to a mass accumulation rate, r (g cm^{-2} year^{-1}), using the average porosity (ϕ) measured below the mixed layer.

$$r = \omega(1-\phi)\rho_s \tag{2}$$

where ρ_s is the density of the dry sediment, usually taken to be 2.65 g cm^{-3}, the density of quartz. Organic matter can have a density as low as 1.8 g cm^{-3}, but since most marine sediments contain a low proportion of organic matter (< 10 %) and have high porosities (0.6–0.9), the calculated sediment accumulation rate is not very sensitive to the exact choice of sediment density. In addition, if the wet volume (cm^3) and dry mass (g) have been measured, the porosity can be left out of the calculation.

$$r = \omega(\text{dry mass/wet volume}) \tag{3}$$

As newly deposited material (not yet impacted by radio-decay), is transported to depth by biomixing, the $^{210}Pb_{ex}$ activities will be increased slightly in the deeper portion of the SML and decreased in the upper portion of the mixed zone. Thus, the greater the intensity of mixing in the SML, the more the $^{210}Pb_{ex}$ distribution will reflect complete homogenization within this zone (cf., Fig. 9.10 in Robbins 1978). It should be noted also that biomixing can extend to depths of ~30 cm or more in continental shelf sediments (cf., Kuzyk et al. 2013), which means that even $^{210}Pb_{ex}$ profiles that do not exhibit a well-defined SML may have been influenced by mixing (see Silverberg et al. 1986).

If a contaminant is in steady state (constant supply over many years), then its flux into the sediments can be estimated by multiplying the mass accumulation rate (Eq. 2 or 3) by the surface concentration of the contaminant. Indeed this approach sometimes provides the only option for estimating contaminant inventories, if the concentration of a particular contaminant has been measured only at the surface. However, if the supply of the contaminant is changing, then this method will give only an upper or lower bound on the contaminant flux, depending on whether its concentration in the newly-accumulated material is higher or lower than that in the older sediment.

Where the flux of a contaminant is changing, contaminant profiles as well as an estimate of the sediment mixing rate are required to interpret the nature of the changes in the flux. Mixing rate can be calculated from ^{210}Pb profiles using an advective-diffusive model (cf., Robbins 1978):

$$\omega \delta C/\delta z - \delta/\delta z\ (\mathrm{K}_b \delta C/\delta z) = \lambda C \tag{4}$$

where C is $^{210}Pb_{ex}$ (Bq cm^{-3}), z the vertical coordinate (cm, positive downward), ω, a constant sedimentation velocity (cm yr^{-1}), K_b the mixing coefficient due to bioturbation (cm^2 year^{-1}) and λ (=0.03114 year^{-1}) the decay constant. This equation may be solved numerically using a sediment mixing model (Crusius and Anderson 1995; Crusius et al. 2004) but analytical (exact) solutions to the differential equations have also been published (Lavelle et al. 1985, 1986), which make it relatively straightforward to model the entire $^{210}Pb_{ex}$ profile simply using a spreadsheet.

In the Lavelle approach, $^{210}Pb_{ex}$ profiles are evaluated with a steady-state, two-layer advection-diffusion model in which the diffusion coefficient, K_b, is taken to be discontinuous having a constant value (K_{b1}) in an upper bioturbated layer (thickness h) and a negligible value below ($K_{b2}=0$, or e.g., 0.01 cm^2 year^{-1}). Although the transition from the upper layer mixing rate (K_{b1}) to a negligible rate ($K_{b2} \sim 0$) must actually occur over a finite interval, in general, sediment core data cannot resolve the apparent rapid transition from one region to another (Lavelle et al. 1985, 1986). By adopting these constant values K_{b1} and K_{b2} in the upper and lower layers, respectively, and imposing two boundary conditions: (1) the activity flux of the surface equals ω A_o and (2) activity at depth is zero, the following equations may be used to simulate observed $^{210}Pb_{ex}$ profiles:

$$A_1 = a_1\, e^{(\beta 1+\gamma 1)\mathrm{z}} + a_2 e^{(\beta 1-\gamma 1)\mathrm{z}} \quad 0 < \mathrm{z} < \mathrm{h}\ \text{(i.e., in the mixed zone)}$$

$$A_2 = a_3 e^{(\beta 2-\gamma 2)\mathrm{z}} \quad \mathrm{z} > \mathrm{h}\ \text{(i.e., below the mixed zone)}$$

where:

$$a_1 = \{-2\beta_1 A_0 (\gamma_2 \beta_1 - \gamma_1 \beta_2)\ e^{-\gamma 1\mathrm{h}}\}/D$$

$$a_2 = \{2\beta_1 A_0 (\gamma_2 \beta_1 + \gamma_1 \beta_2)\ e^{+\gamma 1\mathrm{h}}\}/D$$

$$a_3 = \{4\beta_1 \beta_2 \gamma_1 \mathrm{A}_0 \mathrm{e}^{-(\beta 2-\beta 1-\gamma 2)h}\}/D$$

$$D = [(\beta_1 + \gamma_1)(\gamma_2 \beta_1 + \gamma_1 \beta_2)]\ e^{\gamma 1\mathrm{h}} [(\beta_1 - \gamma_1)(\gamma_2 \beta_1 - \gamma_1 \beta_2)]\ e^{-\gamma 1 h}$$

Here, $\beta_i = (\omega/2\mathrm{K}_{bi})$, $\gamma_i = (\beta_i^{\,2} + \lambda/\mathrm{K}_{bi})^{1/2}$, and the flux to the sediment surface is $\omega\ \mathrm{A}_0$. Values for K_{b1}, C_0 (surface activity), and ω are determined by least-squares fitting the two-layer solution to the profile data. The accuracy of ^{210}Pb-derived sedimentation rates obtained from the two-layer model depends on how well the various assumptions are met. Specifically, the major assumptions are (1) constant sedimentation and mixing rates over time, (2) no loss or movement of ^{210}Pb by diffusion in porewater; (3) sampling intervals small relative to the total amount of sediment accumulated during the period of interest (Carpenter et al. 1985; Lu and Matsumoto 2005), and (4) negligible mixing below the SML. With respect to K_{b2}, the equations result in a deeper layer with log-linear $^{210}\mathrm{Pb}_{ex}$ profiles but the exponential decay length scale (i.e., $(\beta 2-\gamma 2)^{-1}$) depends on both ω and K_{b2}. Neither parameter can be uniquely determined by a single tracer profile in the deeper layer; the only limits on the ranges of values for these parameters are that both must be positive numbers. Fortunately, small non-zero K_{b2} values tend to have little effect on ω provided that the exponential decay length scale is relatively small (as in the cases of interest here). For instance, in a sediment profile with $\omega = 0.35$ cm yr^{-1} and decay length = 10 cm, ω will be overestimated by 10 % if one assumes $\mathrm{K}_{b2} = 0$ when it is, in fact, 0.01 cm^2 year^{-1} (and see, Silverberg et al. 1986). Various workers have applied K_{b2} values of 0.01–0.1 cm^2 year^{-1} and occasionally values up to 1 cm^2 year^{-1} (Guinasso and Schink 1975; Johannessen et al. 2005; Kuzyk et al. 2009, 2013; Macdonald et al. 1992).

A simple check on the sedimentation rates obtained from the two-layer model may be made by comparing the flux of $^{210}\mathrm{Pb}_{ex}$ to the surface (Bq cm^{-2} year^{-1}) calculated as $\omega\mathrm{A}_o$ (where the units of A_o are Bq cm^{-3} wet sediment), with the loss flux derived from the inventory of $^{210}\mathrm{Pb}_{ex}$ in the sediment column (Bq cm^{-2}) multiplied by the decay constant (0.03114 year^{-1}). The inventory of $^{210}\mathrm{Pb}_{ex}$ is calculated simply as the activity of $^{210}Pb_{ex}$ (Bq g^{-1}) multiplied by the mass-depth (g cm^{-2}) of each sediment section, summed over the length of the core. The two estimates should agree closely (within propagated error limits).

Because various combinations of sedimentation and mixing can conspire to generate $^{210}Pb_{ex}$ distributions that resemble pure exponential decay, developing a robust geochronology in mixed sediments is rendered considerably more reliable by using two independent tracers. The combination of ^{137}Cs and ^{210}Pb is ideal (Appleby 2008; Smith 2001), because these radioisotopes differ not only in their input signals and expected profiles (transient tracer vs. steady-state) but also their sensitivity to mixing, with transient signals being the more sensitive of the two (Johannessen and Macdonald 2012). Furthermore, because ^{210}Pb (range ~ 5 half-lives = 110 years) and ^{137}Cs (1954—present) tend presently to overlap in the age range they apply to, one expects them to record processes on the same time scale and hence yield similar sedimentation rates. (This agreement might not occur if one compared results using $^{210}Pb_{ex}$ with results using a short-lived radioisotope such as ^{228}Th (($t_{1/2} < 2$ yrs), Crusius and Kenna 2007; Smith et al. 1993) or a long-lived radioisotope such as ^{14}C ($t_{1/2} \sim 5700$ yrs).) The complementarity of the tracers is clear if one imagines a problem during sampling where the top of an unmixed sediment core has been lost. In this situation, the sedimentation rate inferred from the $^{210}Pb_{ex}$ profile in the core would be correct because it is derived from the slope of ln activity vs. depth; however, recent dates assigned to the surface or any other layer in sediments would be incorrect, and the estimated flux of $^{210}Pb_{ex}$ to the sediment surface would be biased low. On the other hand, the sedimentation rate inferred from the ^{137}Cs profile would be incorrect (being based on the depth in sediments of the 1963/1986 peaks in the ^{137}Cs profile, or the 1954 date of first detection) but dates assigned to those specific locations would be correct.

In contrast to ^{210}Pb, ^{137}Cs is a transient tracer. By that, we mean that it has been introduced into sediments in a pulse extending for only a few decades, similar to many other contaminants, and it is therefore used as a temporal marker rather than as a radio-clock. ^{137}Cs was first released in substantial quantities into the environment in 1954 as a result of atmospheric weapons testing, peaked in 1963, and decreased thereafter due to a ban on atmospheric testing ((Monetti 1996) and see also Fig. 6). Some regions (e.g., northern Europe) were strongly influenced by ^{137}Cs fallout from the 1986 Chernobyl reactor fire (Appleby 2008). Thus, ^{137}Cs profiles in unmixed sediments have one or two distinct peaks, which date back to 1963 and possibly 1986. The depth of ^{137}Cs penetration in sediments is also often used to identify 1954, the year when significant atmospheric fallout began (Hülse and Bentley 2012). This method works in unmixed sediments but gives incorrect sedimentation rates when applied to most biomixed marine sediments.

To use ^{137}Cs profiles to verify $^{210}Pb_{ex}$-derived sedimentation and mixing rates (Johannessen and Macdonald 2012; Koide et al. 1972; Smith 2001), requires a bit more work because, unlike $^{210}Pb_{ex}$, analytical solutions to model a transient added to a mixed core are not generally available. Instead, a reasonable estimate of the history of ^{137}Cs deposition (cf., Monetti 1996) may be used together with a numerical advective-diffusive model to simulate the ^{137}Cs profile (Fig. 6). The numerical

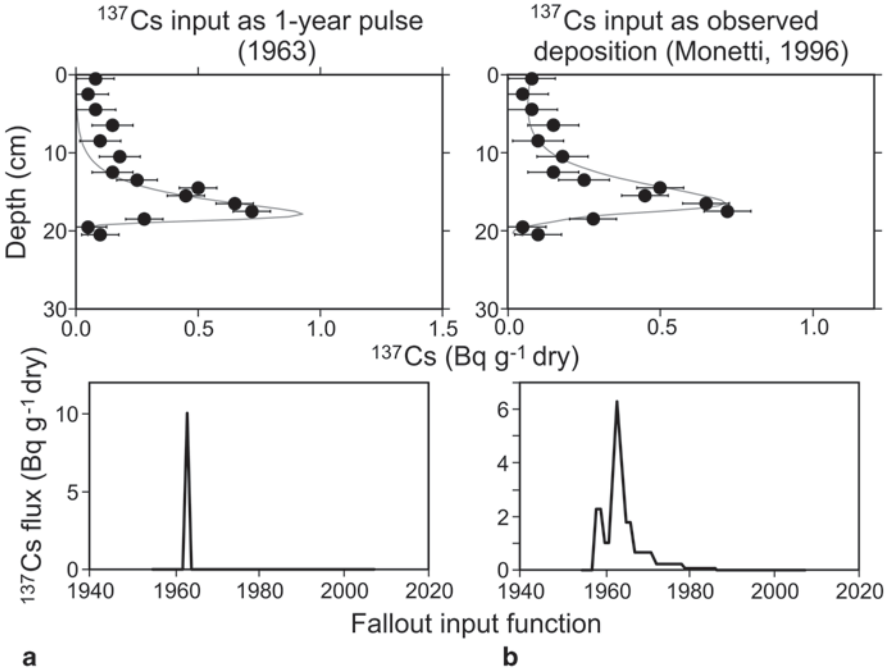


Fig. 6 Measured (*dots*) and modeled (*lines*) profiles of ^{137}Cs in a sediment core. The models were constrained by the ^{210}Pb$_{ex}$-derived sediment accumulation and mixing rates ($\omega = 0.35$ cm yr^{-1}, SML = 2 cm, and $K_{b1} = 50$ cm^2 yr^{-1}) and ^{137}Cs deposition, represented by a simple 1-year pulse in 1963 (**a**) and as the more complex measured deposition time series (Monetti 1996) (**b**)

advective-diffusive model, which uses the parameters (ω, K_b, h) derived from the ^{210}Pb$_{ex}$ profile and considers the loss of ^{137}Cs through radio-decay, can be run in a Matlab^{TM} program. The simulated ^{137}Cs sediment profile may be compared with measured values in terms of depth of penetration of ^{137}Cs, location of the peak, and goodness of fit (cf., Bailey et al. 2013; Johannessen and Macdonald 2012; Kuzyk et al. 2009, 2013). The parameters may be tuned to give the best fit for both ^{210}Pb$_{ex}$ and ^{137}Cs. Where both chronological parameters cannot be accommodated, the core dates must be considered as suspect. Sometimes a contradiction between the two can be explained by post-depositional mobility of ^{137}Cs, particularly if the ^{137}Cs penetrates more deeply into the core than is predicted from the ^{210}Pb-derived sedimentation rate.

Other transient tracers may also be applied to verify ^{210}Pb$_{ex}$-derived sedimentation and mixing rates (e.g., see Kuzyk et al. 2009). In principle, any contaminant that attaches strongly to particles, does not move in sediments subsequent to burial, is reasonably well preserved, and has a known input history could be used to validate ^{210}Pb$_{ex}$ dating.

Developing any geochronology requires a number of assumptions, some explicit and some implicit (Table 1). The accuracy of the derived sedimentation rates

Table 1 Common assumptions made when developing geochronologies

Constant sedimentation rate
Constant flux of ^{210}Pb
No mixing deep within sediments
Supported ^{210}Pb can be estimated from ^{210}Pb deep within core or ^{226}Ra in a few measured sections
Immobility of tracers within the sediments

depends on how well these assumptions are met. Some of these assumptions pertain to how ^{210}Pb cycles in the environment (see generalized scheme in Fig. 4). We often assume that both sedimentation rate and ^{210}Pb deposition are constant. In mixed cores, this may be a relatively safe assumption, because mixing tends to smooth out interannual variation in sedimentation rate and $^{210}Pb_{ex}$ flux. A useful parameter, the intrinsic time resolution ($t^* = h/\omega$ (Eisenreich et al. 1989)) gives a reasonable idea of how much averaging is occurring in any given core. Furthermore, it is often implicitly assumed that atmospheric deposition is the only significant source of $^{210}Pb_{ex}$ to a water body (as commonly assumed for lakes) without quantifying the production of $^{210}Pb_{ex}$ from the decay of ^{226}Ra dissolved in the water body. Although water-column profiles of ^{226}Ra are rarely available, the conservative behaviour of ^{226}Ra in the ocean permits a reasonable estimate from the salinity profile alone (cf., Kuzyk et al. 2013). With respect to the environmental cycling of ^{137}Cs, it is commonly assumed that fallout signals have been transferred to sediments with negligible delay. However, there is good evidence that coastal marine and estuarine sediments can receive delayed inputs of ^{137}Cs from temporary storage in the drainage basin (Smith et al. 1987), from resuspension and lateral transport of ^{137}Cs-containing coastal sediments (Robbins et al. 2000), or in polar locations from delivery by sea-ice rafted debris (Kuzyk et al. 2013). These processes have been observed to delay peak fluxes by 1–2 years (Robbins et al. 2000; Smith et al. 1987), which is well within the error of most geochronologies. However, sediment profile shapes may be altered, affecting, for instance, the depth of a contaminant peak. Fortunately, the onset of ^{137}Cs deposition, 1954, seems little affected by subsequent delayed inputs, meaning that the maximum penetration of ^{137}Cs in the sediments may still be used as a time-stratigraphic marker. (Remember that ^{137}Cs is only at the correct depth in unmixed cores. In mixed cores the maximum penetration depth of ^{137}Cs must be used in conjunction with numerical modeling that accounts for mixing.)

Another assumption, likely valid for $^{210}Pb_{ex}$, is that radionuclide tracers are immobile in the sediments. Post-depositional remobilization of ^{137}Cs within the sediments may be detectable (Kuzyk et al. 2009, 2013; Oughton et al. 1997) or even significant (cf., Sholkovitz et al. 1983; Sholkovitz and Mann 1984; Sugai et al. 1994) under some sediment regimes. One must also be careful about assuming that ^{226}Ra, which supplies the supported ^{210}Pb, is immobile in sediments. Commonly, we estimate supported ^{210}Pb from measurements of ^{210}Pb activity in a few sediment sections deep in the core where $^{210}Pb_{ex}$ has decayed away. However, dissolved ^{226}Ra diffuses within sediments, particularly when strong concentration gradients result from rapid adsorption to highly-concentrated Mn and Fe oxides in a surface oxic layer (Berner 1976; Kadko et al. 1987). Under these conditions, assuming supported ^{210}Pb activities measured deep in sediments apply equally to shallow sediments may be inaccurate. The significance of the error will depend on the extent of ^{226}Ra redistribution and the relative size of the contribution from $^{210}Pb_{ex}$: smaller errors result when supported $^{210}Pb_{ex}$ activities are relatively high. Variations in ^{226}Ra (supported ^{210}Pb) within sediments may also come about as a result of processes that concentrate or dilute the solid phase, such as textural changes. To avoid assumptions associated with supported ^{210}Pb, it is best to measure ^{226}Ra activities in each sediment section within a core and use these depth-specific values.

Despite the many assumptions on which geochronologies rest, there have been many instances where the rates derived from radioisotope data have been validated externally (using, for example, varved sediments (Ojala et al. 2012) or the presence of microfossils). The calculated sedimentation and mixing rates can be tested for sensitivity to the various assumptions (e.g., supported ^{210}Pb, depth of mixed layer, mixing rate, sedimentation rate). For example, within the numerical model one can readily vary the assumed thickness of the mixed layer or the assumed supported ^{210}Pb activity to determine how these parameters affect the modeled sedimentation rate. This process provides a more realistic evaluation of error in the dating process than does, for example, calculating a confidence interval around the slope of a log-linear line fitted to the $^{210}Pb_{ex}$ data.

Evaluating Plausible Contaminant Input Histories

Having obtained (and validated) sedimentation and mixing rates for biomixed cores, it is possible to interpret contaminant profiles in a way that explicitly accounts for mixing. This step is done in an iterative, semi-quantitative way to match the simulated profile to the observations. Since it is not practical to try every possible combination of parameters (date of onset, rate of increase, peak date, rate of decline), visual inspection of the simulated and observed profiles may be used as a guide.

Plausible input histories for the contaminant may be tested iteratively by using each proposed history as input to the model and comparing the results with the actual profiles in the sediments (cf., Hare et al. 2010; Johannessen et al. 2005, 2008; Kuzyk et al. 2010; Macdonald et al. 1992) to determine whether the record in a the sediment core could be the result of a particular contaminant history. To narrow the range of potentially infinite contaminant histories, one might start with measured deposition time series or known emission histories published in the literature (e.g., ^{137}Cs deposition records, PCB production statistics), or with very simple deposition curves based only on the knowledge of first use, peak use, present use. Even if absolutely no information is available for the input function, one can determine the simplest sort of deposition history that would reproduce the observed record in the sediment core, given the mixing and sedimentation regime (Johannessen and Macdonald 2012). A reasonable estimate of the initiation of contaminant deposition, or

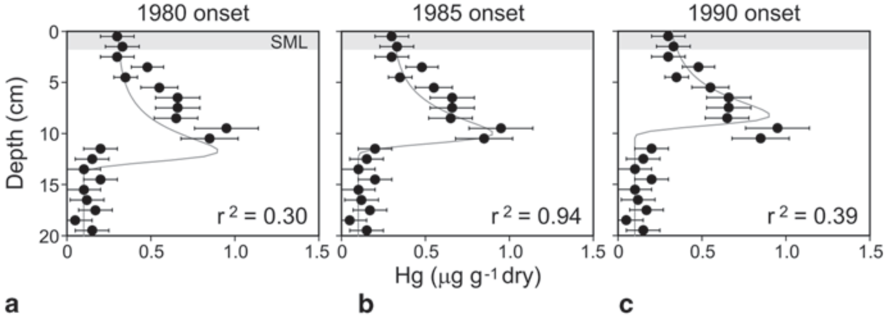


Fig. 7 Observed (*points*) and simulated (*lines*) Hg profiles in the sediment core described in Fig. 2 (i.e., $\omega = 0.35$ cm yr^{-1}, SML= 2 cm K_{b1}=50 cm^2 yr^{-1}). In each simulated profile, a pulse of Hg (3 μg/g) was introduced to the sediments over a 3-year period, following background inputs of 0.1 μg/g, and subsequently inputs decreased to 0.3 μg/g. Varying the simulated date of entry of the Hg pulse (1980, 1985, and 1990) shows that the best fit occurs with a 1985 onset (*middle panel*)

the timing of peak deposition of a contaminant to a sediment can always be determined using a well-constrained model.

An example of how modeling may be used to reconstruct a contaminant profile is given in Fig. 7, using the sediment core discussed earlier in Fig. 2 (i.e., $\omega = 0.35$ cm yr^{-1}, SML=2 cm K_{b1}=50 cm^2 year^{-1}). The contaminant profile measured in the sediments (in this case, Hg) is shown as dots and model results as lines. In each simulated profile, a pulse of Hg (3 μg/g) was introduced to the sediments over a 3-year period, following background inputs of 0.1 μg/g, and subsequently inputs decreased to 0.3 μg/g. The three panels illustrate the effects on the simulated profile of varying the timing of the onset of this pulse by ± 5 yrs. The best fit to the data is provided by a 1985 onset (B or middle panel, $r^2 = 0.94$). Varying the onset date by ±1 year around 1985 ($r^2 = 0.92$ and 0.88, respectively; not shown) shows that this date does indeed give the 'best fit'. Thus, we may infer from the constrained model for this core that the pulse of Hg deposition began in 1985. We can also tell by inspection and through the model, the Hg contamination occurred as a fairly strong pulse as indicated by the rapid rise in Hg concentration at the bottom of the nose. For this core, we could also reasonably propose the rate of decline in Hg concentration of surface sediments in the future, a decline that is set by the residence time of Hg in the SML rather than by the removal of the contaminating source.

This sort of advective-diffusive modeling has been applied to sediments collected from locations spanning remote regions receiving contaminants only by long-range transport to coastal regions affected by a wide variety of local sources. For example, in Hudson Bay, modeling of PCB profiles yielded a scenario with an onset of PCB deposition in 1930, an exponential increase until 1965–1985, and a decrease thereafter, which is a timeline consistent with those inferred from mid-latitude to subarctic records, implying little delay in the onset of PCB deposition, despite the remoteness of Hudson Bay from the industrial regions of the Northern Hemisphere (Kuzyk et al. 2010). Historical Hg deposition to sediments in Hudson

Bay reflects the known history of atmospheric Hg deposition in North America, with an onset of anthropogenic Hg emissions in the late 1800s and early 1900s and a reduction of Hg deposition in the mid- to late-1900s (Hare et al. 2010). In a locally contaminated region, the Strait of Georgia, located between Vancouver Island and mainland British Columbia, Canada, sediment cores revealed a history of mercury deposition dating back to the first local gold mining activities of the 1860s followed by episodic contamination during World War II and in the late 1960s (Johannessen et al. 2005). In an earlier study of the Strait of Georgia (Macdonald et al. 1992), the advective-diffusive model developed using ^{210}Pb profiles explained the contaminant profiles for PCB, OCDD (octachlorodibenzo-p-dioxin) and 2,3,7,8-TCDF (tetrachlorodibenzofuran), each of which had differing emission histories. A more recent study showed that very different deposition histories for PCB and PBDEs (polybrominated diphenyl ethers) were operated on by identical mixing processes in sediments to produce the observed sedimentary profiles (Johannessen et al. 2008).

Not all cores are dateable but even where a plausible geochronology cannot be developed for a core, information can be extracted. From a contaminant profile in a sediment core one can determine the contaminant inventory (μg cm^{-2}) by summing the product of contaminant concentration (μg g^{-1}) and mass-depth (g cm^{-2}) over the length of the core. Inventories are, in some circumstances, more appropriate for comparing among sites than contaminant concentrations because they are not affected by variations in mixing rate. If contaminant inventories are being used to compare among sites, sediment (and contaminant) focusing into sedimentary basins (i.e., horizontal sediment transport) needs to be taken into account (for an introduction to this topic see Blais and Kalff (1995)). The most common approach to address focusing, particularly in lacustrine environments, is to use the inventory (or flux) of ^{210}Pb$_{ex}$ in the sediments, relative to the regional atmospheric ^{210}Pb$_{ex}$ flux (known or estimated), as a "normalizing" (or focus-correcting) factor that is applied to the contaminant inventory (or flux) at each site (cf. Couture et al. 2008; Muir et al. 2009; Stern et al. 2005). The premise of this approach is that the efficiency with which the contaminant is transferred from the atmosphere to the water column and subsequently to the sediments matches that of ^{210}Pb$_{ex}$. For some contaminants (e.g., PCBs), differences between the cycling of contaminants and ^{210}Pb may invalidate this approach, at least in some systems. For example, an attempt to focus-correct PCB burial fluxes in sediments in Hudson Bay using ^{210}Pb introduced wide variation into inferred rates of atmospheric PCB deposition (Kuzyk et al. 2010). Methods of correcting for sediment focusing in the marine environment are more complicated and still very much under discussion (Francois et al. 2007; Lyle et al. 2005, 2007). A complication with using ^{210}Pb$_{ex}$ to correct for sediment focusing in marine environments arises from the two sources in marine sediments: atmospheric deposition of ^{210}Pb and water-column production of ^{210}Pb from the decay of dissolved ^{226}Ra. The ^{226}Ra-derived ^{210}Pb$_{ex}$ input can dwarf that derived from atmospheric deposition; it can be extremely variable from site to site depending on water mass histories, depth of the water column and particle supply; and it may or may not have an analogue in contaminant dynamics, depending on the nature of the contaminant. Recent continental margin marine sediment data suggest that ^{210}Pb and ^{137}Cs can be used in tandem to distinguish scavenging and sediment focusing and thus, ultimately, to infer the relative strength of focusing among sites (Kuzyk et al. 2013). However, more work needs to be done to confirm the best approach to correct for sediment focusing when contaminant inventories in marine sediments are to be compared.

Caveats on the Interpretation of Biomixed Cores

Several mistakes may be made if the effects of mixing are not well understood (Table 2). For instance, one ramification of the extensive reworking of contaminant signals within mixed sediments is that statistical relationships, such as correlations, can develop among different signals (i.e., contaminants) that enter the sediments independently. The introduction of different contaminants from different sources and at different times, years or decades apart, is common in industrialized coastal areas (cf., Johannessen et al. 2008; Macdonald et al. 1992). However, once these different contaminants are brought together within sediments and subjected to common mixing and sedimentation processes, the net effect is to reduce the differences among original disparate signals. In some cases, the effect is sufficiently strong to produce high correlations among different contaminants, despite inputs that were independent and uncorrelated. In such a case, it would be incorrect to infer from these correlations in sediments a common source or history.

Potentially misleading correlations are most likely to develop where the sedimentation rate is low and the SML is thick (Fig. 8). Put simply, the longer the contaminants reside in the SML, the more likely it is that correlations will develop among them. The other factor is the gap between contaminant pulses. For instance, for a sedimentation rate of 0.25 cm/yr, two contaminants introduced 4 years apart will develop a correlation of greater than 90% ($R > 0.9$) if the SML is ≥ 3 cm thick (Fig. 8). With a 6-year gap between the inputs of the two contaminants, a correlation of greater than 90% will develop for SML thicknesses of 5 cm or more (Fig. 8). These correlations take time to develop within the core but then may persist for

Table 2 Summary of the ramifications of biomixing

Date of entry, peaks and valleys in deposition are deeper in the core
Surface fluxes estimated as the product of surface concentration and sedimentation rate are wrong
Response to contamination and mitigation is masked by the mixing/residence time within the mixed layer
No layer in the sediment corresponds logically to a given year; rather, each layer contains a mixture of sediment from a number of years approximately equivalent to the intrinsic time resolution (the contribution from each year within that time frame is not necessarily equal among years)
Mixing may create correlations that do not exist in the deposition histories

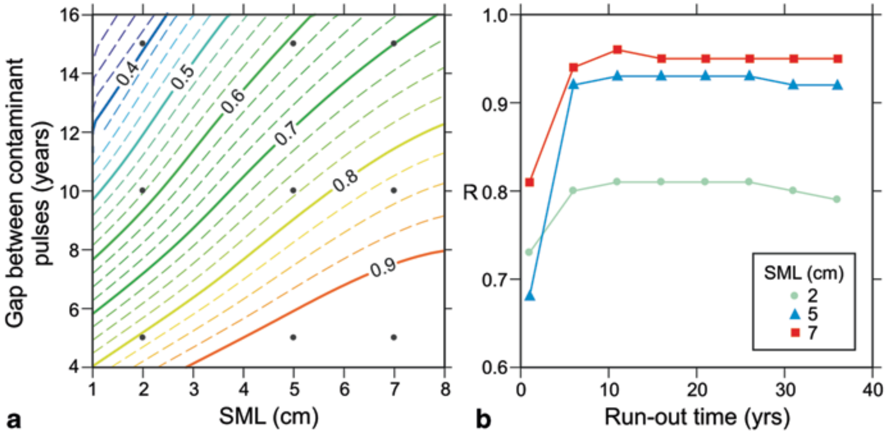


Fig. 8 (**a**) Correlation coefficients (R-values) between the modeled concentrations of two contaminants that have entered sediments at different times ($\omega = 0.25$ cm yr^{-1} and $K_{b1} = 50$ cm^2 yr^{-1}). The R values have been determined by varying the thickness of the SML (X-axis) and the time elapsed between the contaminant pulses (Y-axis). An 11-year run-out in time after the second pulse was allowed. (**b**) The effect of varying the run-out time, showing how the correlation between contaminant concentrations in mixed sediments takes time to develop but then persists in the sediments

many years (Fig. 8b). Clearly, caution is required in the interpretation of correlations within biomixed sediments, and one should always keep in mind that several processes other than source inputs contribute to shaping the contaminant profiles in marine sediments.

A discussion of interpreting sediment contaminant profiles would not be complete without some mention of chemical diagenesis. For details on this subject, we refer the reader to Outridge and Wang (this volume)) as well as earlier reviews (Boudreau 1997; Emerson and Hedges 2003). Most diagenetic chemical changes in marine sediments are driven by reduction-oxidation (redox) reactions, which involve the oxidation of the labile organic matter that reaches the seafloor and becomes mixed into sediments (Emerson and Hedges 2003; Froelich et al. 1979). The stronger the supply of labile organic matter, the faster the O_2 in sediment pore waters is consumed and the more likely it is that the rate at which O_2 can be resupplied by diffusion from the overlying water column will be less than the rate at which it is consumed, driving to anoxia the sediments below the depth of O_2 penetration. Under these conditions, other oxidants besides O_2 (such as NO_3^-, Mn(IV), or SO_4^{2-}) become important. In the coastal ocean, the rate of organic matter deposition is usually sufficient to produce an oxic-anoxic interface within 5–10 cm of the sediment surface. Because SO_4^{2-} is available in seawater, sulphate reduction and the production of hydrogen sulphide is a crucial sediment process in virtually all estuarine and coastal sediments (cf., Jørgensen 1977).

There are two primary mechanisms by which the redox conditions in marine sediments control the cycling of trace metals. One mechanism occurs in sediments with thick surface oxic layers, enriched in manganese and/or iron oxides.

As particles are buried, their depth below the sediment-water interface increases, whereas the position of the redox boundary remains constant (assuming constant fluxes and other conditions). Thus, during burial, particles are moved downward across a boundary between oxic and anoxic conditions. For manganese and iron, which are sequestered as oxides in surface sediments, reducing conditions cause dissolution and subsequent diffusion. Upward diffusion and redeposition frequently produces enrichments in Fe and Mn at the sediment surface (Froelich et al. 1979; Kadko et al. 1987). Surface enrichments of Mn and Fe can sequester other trace elements, such as Co, Mo, Cu, Ni, and Zn. These redox-sensitive metals and associated elements may be strongly rearranged in sediment profiles after deposition, casting doubt on any inferred history of deposition or estimated burial rate, even when accurate mixing and sedimentation rates have been derived.

The second important redox mechanism affecting contaminant profiles is precipitation and concentration with sulphide minerals—acid volatile sulphides (AVS; i.e., iron monosulphides) and pyrite (FeS_2) (Huerta-Diaz and Morse 1992; Morse and Luther III 1999). Indeed, this process may be more prevalent in marine coastal and estuarine sediments than sequestration with oxides because the labile organic carbon supply is high and sulphate readily available (e.g., see Burdige 2006). Elements at risk for concentration due to processes associated with the production of sulphides include Hg, As, U, Cd, Cr, Zn, Fe, Mo and Pb (Couture et al. 2008; Erickson and Helz 2000; Feyte et al. 2012; O'Day et al. 2004; Zheng et al. 2000). In some cases, reliable histories for these sorts of elements can, nevertheless, be produced in sediments where diagenesis is weak (cf., Feyte et al. 2012) or if the contaminant element has entered the sediments within an inorganic matrix and is, therefore, relatively immune to post-depositional remobilization.

Chemical diagenesis can also alter contaminant records in sediments when compounds are not well-preserved, either in quantity or quality. Changes in quantity may be obvious when one inspects a sediment core profile (e.g., resembling the exponential decrease in organic carbon content with depth in sediments (Goni and Hedges 1995)), but changes that affect the quality of a contaminant can be subtle. For example, the composition of a contaminant such as PCBs, which comprises a complex mixture of up to 209 congeners, may change significantly with depth in a sediment column because certain congeners are selectively degraded (cf., Gustafsson et al. 2001). This in-core shift can be misinterpreted as a change in the source function, leading to incorrect conclusions about the contaminant input history. Polycyclic aromatic hydrocarbons (PAHs), also popular compounds for contaminant studies, may be subject to diagenetic alteration, although these compounds are generally well preserved and reasonably immobilized in sediments (cf., Yunker et al. 2011). Compounds like perylene, for example, may actually be produced within sediments (Meyers and Ishiwatari 1993). A final diagenetic alteration that can impact contaminant archives is chemical diffusion in porewater, whether because of strong concentrations gradients (as described earlier for ^{226}Ra and Mn) or simply because of the solubility of the compounds. Vertical migration within sediments of the lighter, more water-soluble PCB congeners is a case in point (Gustafsson et al. 2001).

Cautionary Note About Environmental Change

There are various changes in the environment that may indirectly affect the nature or quantity of a contaminant delivered to the sediment. Thus, there is a need for caution when making a leap from the reconstructed deposition history of contaminants inferred from a sediment core record, to reconstruction of contaminant *release from a source*. Various physical and biogeochemical processes shape contaminant concentrations, distributions and fluxes in the environment between emission and deposition in sediments; many of these processes are changing with potential effect on the deposition strength (Macdonald et al. 2005). In particular, the primary productivity and the nature and quantity of other particle and organic matter sources determine in large part where a scavenged contaminant will end up (in the water column vs. shelf sediments vs. basin sediments) and what its chemical state will be (e.g., whether Hg is methylated or not). Thus, the timeline of release from sources is not the sole factor, and may not even be the most important factor, in depositional history at a given site. Both the rate and magnitude of contaminant deposition in marine sediments depend on the elemental or molecular nature of the contaminant as well as on the abundance and composition of the type of particle with which it is associated.

A special attribute of sediment cores is that they integrate or capture both the input signal (the contaminant discharge history) and the environmental signals, which reflect the contaminant pathway within the system prior to reaching the sediments. This recording of both the input signal and other geochemical properties can complicate, but also enrich, the interpretation of contaminant histories from sediment cores, e.g., when increases in contaminant concentrations in surface sediments result from climate change (cf., Outridge et al. 2007) or other types of environmental change (cf., Hare et al. 2010) rather than from changes in contaminant inputs.

The specific biogeochemical/environmental controls important for contaminant distribution and fluxes in marine and estuarine environments differ among contaminants, depending on their physical/chemical properties. In general, organic contaminants tend to be relatively insoluble in water (hydrophobic) and highly soluble in fats (lipophilic), which means that they bioconcentrate in and adsorb onto organic matter. Therefore, the abundance and composition of organic matter can influence the distribution of persistent organic pollutants (POPs) (Dachs et al. 2002).

A general strategy to address complications in the interpretation of a contaminant profile in a single core is to collect sediment cores along an ocean section, for example from estuary to shelf to basin. This approach provides a far better basis to distinguish between processes within the cores and processes occurring prior to deposition. Furthermore, examining a wider selection of cores helps to address the challenge of up-scaling, as required to generate regional contaminant budgets. Generalizing from the results of a single core to a large area is fraught with uncertainty because of the significant spatial variability typical of estuarine and coastal areas. It is not uncommon for estuaries to exhibit strong spatial gradients in salinity, temperature, primary production, fluxes of particulate matter and POC, sediment resuspension, deposition and focusing (Lauff 1967), which may all affect contaminant behavior.

Conclusions

Sediment cores provide useful archives of contamination, and in this chapter we have provided a practical, step-by-step approach by which common pitfalls can be avoided and biomixed marine and estuarine sediment archives applied appropriately to reconstructing contaminant inputs to the environment. Most marine sediments are mixed by the activities of benthic animals; this biomixing changes profiles and thus must be considered in the interpretation of tracer and contaminant profiles in cores. In particular, it is wrong to associate dates with specific layers in biomixed cores. Despite mixing, ^{210}Pb may still be used to determine sedimentation velocity, surface mixed layer depth and mixing rate. A second tracer such as ^{137}Cs helps to refine the estimates of sedimentation and mixing obtained from ^{210}Pb profiles and really is essential for establishing reliable geochronologies in biomixed cores. Knowing the sedimentation and mixing rates in biomixed cores, contaminant histories can be reconstructed by modeling the contaminant profiles. Even without dating, it is possible to estimate regional patterns of contaminant flux by determining sediment inventories. Besides biomixing, observed contaminant profiles can also be affected by redox processes, diffusion and environmental change. Taking advantage of the environmental signals captured in cores, together with the contaminant signals, and collecting cores along ocean sections which span environmental gradients can provide a better basis to distinguish between processes within cores and processes occurring prior to deposition and ultimately strengthen interpretations of contaminant histories from the archives in sediment cores.

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Contaminants in Marine Sedimentary Deposits from Coal Fly Ash During the Latest Permian Extinction

Hamed Sanei, Stephen E. Grasby and Benoit Beauchamp

Abstract The Latest Permian Extinction (LPE) event, the greatest mass extinction in Earth history, was marked by major explosive volcanic eruptions through thick layers of coal and carbonaceous deposits at the time. This resulted in significant dispersion of volcanic-derived ash and other particulate and gaseous hazardous substances, which may have caused extensive contamination of the global marine ecosystem.

A continuous geological sedimentary record from the Canadian High Arctic revealed evidence of unprecedented mercury loading that may have contributed to the extinction. Mercury loading is attributed to combined effects of volcanic emissions in association with volcanic combustion of surface and subsurface coal and carbonaceous deposits.

Mercury influx exceeded the scavenging capacity of organic matter (OM) in the Late Permian ocean, leading to major disruption of mercury drawdown processes mediated by organic carbon. This resulted in buildup of dissolved mercury to maximum levels at the LPE boundary. The transition of the Latest Permian ocean to euxinic conditions allowed sulphide scavenging of mercury from ocean water, beginning a self-mitigation process that led to gradual recovery from toxic marine conditions.

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Introduction

The Latest Permian Extinction Event

The Latest Permian Extinction (LPE) occurred just prior to the time boundary between the Permian and Triassic geologic periods (end of the Paleozoic and onset of the Mesozoic eras), which occurred approximately 252 Ma ago (Shen et al. 2011). It is regarded as the Earth's greatest known mass extinction event, which resulted in the dramatic disruption of global biogeochemical cycles and consequently loss of over 90 % of marine species and approximately 70 % of terrestrial vertebrate species (Erwin 2006; Sahney and Benton 2008).

Siberian Traps

While numerous extinction mechanisms have been proposed over time, recent research supports a close correspondence between the extinction and timing of massive volcanic eruptions of the Siberian Traps (Reichow et al. 2009; Saunders and Reichow 2009), as suggested by Campbell et al. (1992). The Siberian Traps is a large region of volcanic (igneous) rock in Siberia, Russia, covering about 2 million km^2, approximately equal in area to Western Europe. The Siberian Traps is believed to be a remnant of a massive volume of basaltic lava that covered a vast expanse of this region. This igneous province is related to the series of eruptive events that occurred during the latest Permian, and is believed to be the largest known volcanic event of the last 500 million years of Earth's geological history (over 1000 Gt of magma released) (Saunders and Reichow 2009). The Siberian Traps were located in north-eastern Pangaea during the Late Permian (Fig. 1a).

The Siberian Traps were a "megascale eruption" characterized by a highly explosive nature (Svensen et al. 2009). Major flood basalt eruptions initiate with an explosive phase that generated plumes over 20 km high, sufficient to inject ash into the stratosphere (Thordarson et al. 2009). Once in the stratosphere, dispersion of the volcanic ash (and coal fly ash) would be a function of the initial plume height, the particle density, and stratospheric wind velocity. It is unclear how effectively ash derived from a northern latitude could be dispersed, however some models suggest that a super eruption could form inter-hemispheric ash clouds (Baines et al. 2008), allowing global ash distribution. Models have suggested potential significant global impact of volcanism due to release of CO_2 and methane associated with combustion of extensive Siberian coal and other organic rich deposits (Reichow et al. 2009; Saunders and Reichow 2009; Korte et al. 2010; Retallack and Jahren 2008; Svensen et al. 2009).

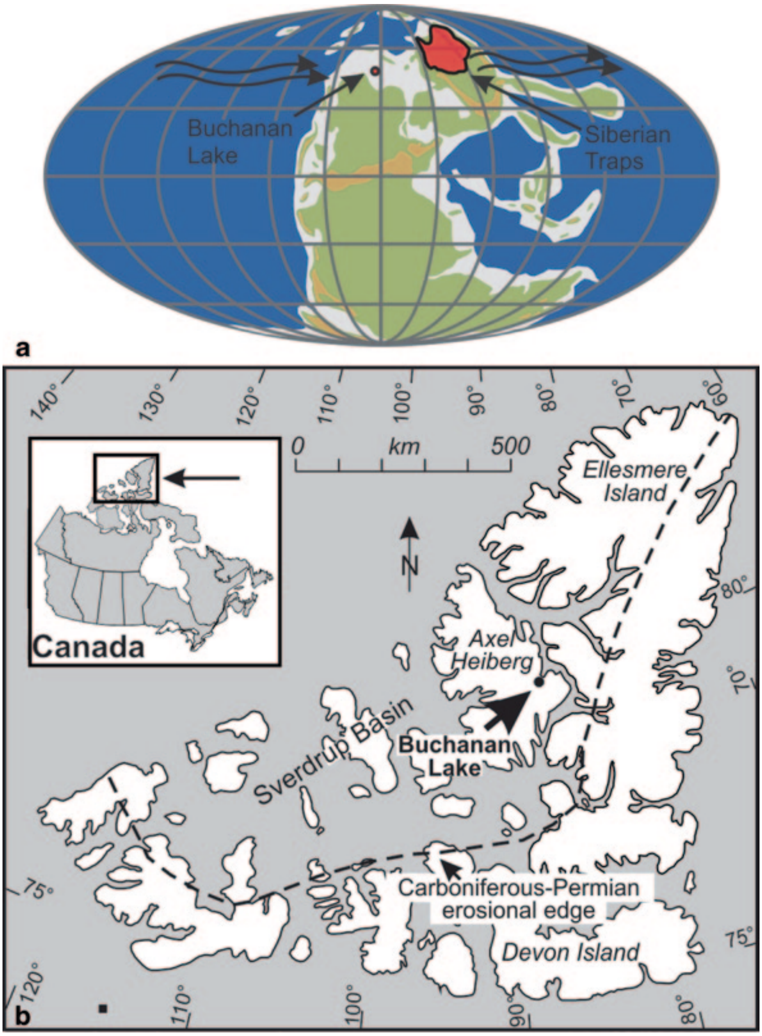

Fig. 1 Maps showing: **a** The paleogeography of the Late Permian, location of the Buchanan Lake section, and extent of the Siberian Traps (Figure reproduced from Grasby et al. 2011). **b** Location of the LPE sedimentary record in the Canadian Arctic Archipelago (Figure reproduced from Sanei et al. 2012)

Geological Evidence of the Link Between Great Extinction and Major Volcanism

Along with disappearance of marine and terrestrial taxa, the LPE boundary is marked globally by a significant negative shift in $\delta^{13}C$ values in both inorganic and organic sedimentary records (Korte and Kozur 2010). The Sverdrup Basin, in the Canadian High Arctic (Fig. 1a and b), holds an excellent record, from shallow to deep-water marine settings that record this carbon isotope shift across the LPE event on the NW margin of Pangaea (Beauchamp et al. 2009; Grasby and Beauchamp 2008; Grasby and Beauchamp 2009; Embry and Beauchamp 2008). The Sverdrup Basin was situated downwind of the Siberian Traps and was ideally located to preserve a record of the impacts of these eruptions. The unique geological archive of the Sverdrup Basin revealed evidence of coally-derived pyrolyctic chars particles deposited in the sediments of the latest Permian ocean that show remarkable similarity to fly-ash particles generated by modern coal-fired power plants (Grasby et al. 2011). Pyrolyctic chars, deposited just prior to the negative carbon isotope shift that marks the global extinction boundary, are believed to be formed and originated by rapid combustion of surface and/or subsurface carboniferous (or older) coal and carbonaceous deposits during the volcanic eruptions. The fine size of the particles and stratospheric injection by the Siberian Trap eruptions allowed for long-range atmospheric transport and deposition of this coal fly ash into the ocean. This provides a direct temporal linkage for volcanic-derived combustion of coal just prior to the LPE event boundary and a correspondence between the extinction boundary and onset of massive volcanism of the Siberian Traps (Reichow et al. 2009; Saunders and Reichow 2009).

Catastrophic Volcanic Mercury Emissions

Volcanic emissions and coal combustion are the two largest primary inputs to the modern global mercury (Hg) cycle (~90 Mg yr^{-1} and ~842 Mg yr^{-1}, respectively) (Pirrone et al. 2010). Perhaps the most devastating feature of the Siberian Traps eruptions was the association with combustion of extensive coal and carbonaceous deposits. It is estimated that up to 3 trillion t of carbon was released when the Siberian Traps erupted through thick carbonaceous deposits (Retallack and Jahren 2008; Svensen et al. 2009). Mercury, one of the most toxic elements on the planet, is the most important by-product of both processes, thus the volcanic eruption, which ignited thick coal deposits, combined two major emitters of mercury: volcanic eruptions and coal burning.

Emissions of mercury from volcanic eruptions can be estimated using known Hg/SO_2 ratios for different eruptive styles. The Siberian Traps are believed to be the product of violent and explosive eruptions (Campbell et al. 1992) associated with high velocity escape structures (Svensen et al. 2009). Therefore, the Hg/SO_2 ratio of 10^{-4} for explosive volcanics (Pirrone et al. 2010; Pyle and Mather 2003) can be used in combination with the estimate by Beerling et al. (2007) that a total SO_2 release of 3.8×10^{10} Mg was associated with the Siberian Traps eruptions (Beerling et al. 2007). These events result in an estimation of upwards to 3.8×10^{6} Mg Hg emission associated with the Siberian Traps.

Additionally, there was an estimated 3 trillion t of carbon released from coal combustion (Retallack and Jahren 2008; Svensen et al. 2009) during this volcanism. The mercury content of Carboniferous coal in the Kuznetsk Basin of Siberia ranges from 15 to 100 μg kg^{-1} (mean 38 μg kg^{-1} Hg, with low ash content of 11 %, Tewalt et al. 2010; average Siberian coal ranges between 20 and 50 μg kg^{-1}, Yudovich and Ketris 2005). Assuming that mercury content of coal in this region has remained unchanged since the Late Permian, we can estimate an additional 1.75×10^5 Mg Hg released from coal combustion. Collectively, combustion of these coal and carbonaceous rich deposits associated with the Siberian Traps eruptions would have resulted in upwards of 4×10^6 Mg of mercury emissions (Sanei et al. 2012). This mercury would have undergone long range atmospheric transport due to its long atmospheric residence time (~ 1.5 year) (Schroeder and Munthe 1998); as a result, the LPE event would have been associated with significant mercury atmospheric dispersion and aerial deposition into large aquatic sinks. At this stage it remains uncertain if the Sverdrup Basin, which was directly downwind of the Siberian Traps, represents global distribution or a more local affect. Further study of more widely distributed basins is required.

Geological Record of Mercury Contamination at the Latest Permian Extinction Event

Reconstruction of mercury deposition based on the geological sedimentary records in the Sverdrup Basin reveals significant mercury loading occurred immediately before and at the LPE extinction boundary. This elevated mercury input, interpreted as the product of volcanism and associated thermal metamorphism of coal at the LPE event (Sanei et al. 2012), may have contributed to severe environmental stress and shift in marine biogeochemical cycles at that time.

Background Mercury Loading Prior to the LPE: Initial Volcanic Mercury Loadings into the Ocean

The sediments below the LPE horizon contain normal marine organics, as shown by blue circles in Fig. 2, superimposed by organic-rich char and coal fly-ash layers, shown in red squares (Grasby et al. 2011). The episodic coal fly-ash loading events are identified by sudden spikes in TOC (total organic carbon), coal ash is recorded as high TOC layers—shown by red squares, superimposed on background TOC levels (blue circles) that are controlled by primary marine bioproductivity (Fig. 2; Grasby et al. 2011). Sediments below the extinction boundary do not show any signatures for anoxia that might explain preferential metal draw down (Proemse et al. 2013, Grasby and Beauchamp 2009).

Mercury concentrations progressively increase towards the LPE boundary (Fig. 2c). Three spikes in mercury concentration (up to four fold increase above background levels of <0.2 mg/kg; Fig. 2c) clearly correlate to coal fly-ash layers (Fig. 2b). The correlation likely represents direct deposition of mercury encapsulated in fly-ash char particulates (particulate mercury). Moreover, volcanic

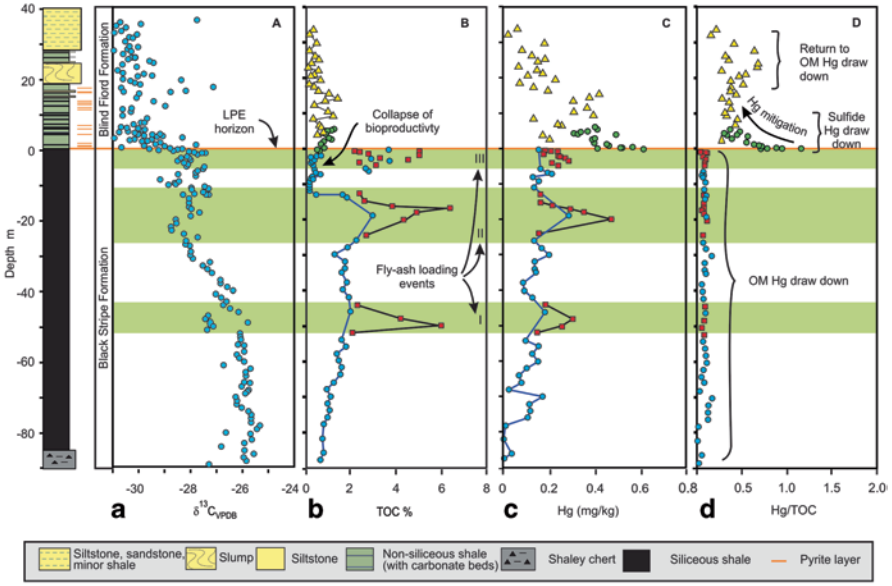

Fig. 2 Sedimentary records of the key geochemical parameters across the LPE horizon and the lithostratigraphic column of the shale-dominated environment (depths are relative to the Latest Permian extinction (LPE) horizon.). **a** stable isotope, and **b** per cent total organic carbon (TOC%) data (Grasby and Beauchamp 2009) is shown along with temporal trends of, **c** mercury (Hg), and **d** Hg/TOC ratio. (Figure reproduced from Sanei et al. 2012)

eruptions release significant amounts of gaseous mercury (elemental Hg° and reactive Hg(II)). Incorporation of this mercury into the marine environment involves wet/dry deposition of gaseous Hg°/Hg (II) and subsequent exchange of dissolved Hg(II) onto marine particulate organic carbon (POC) to become entrained by downward flux and ultimate burial by ocean sediments (Andren and Harriss 1975; Cranston and Buckley 1972; Gehrke et al. 2009; Lindberg et al. 1975; Outridge et al. 2007; Lindberg et al. 1975). This drawdown process, mediated by organic carbon production within the aquatic system, operates simultaneously with Hg loading as driven by increasing atmospheric flux. In modern sediments, this process is commonly preserved as temporal records that show a well documented strong positive correlation between Hg and TOC in sediments (Gehrke et al. 2009; Outridge et al. 2007). We observe a similar positive correlation between Hg and marine derived organics below the LPE (blue circles) (Fig. 3a). This suggests that, despite episodic Hg loading, an effective organic-mediated Hg drawdown process was operating in Late Permian oceans prior to the extinction event. This would have mitigated any build up of Hg in sea water due to prolonged volcanic activity. The marine system thus maintained a relative balance between Hg and organic carbon production during this period (Fig. 2d).

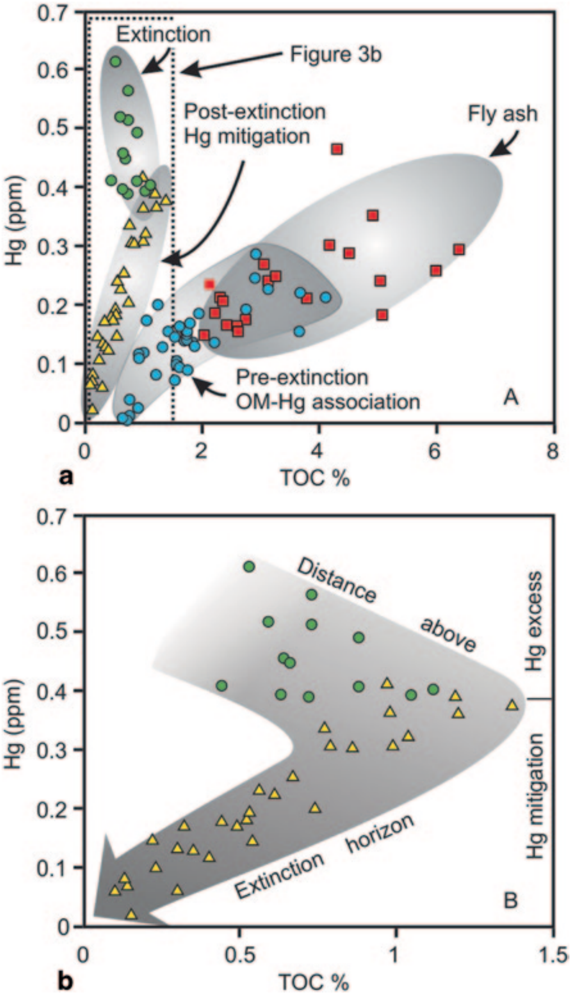

Fig. 3 Relationship between total mercury (Hg) content in the sediments and total organic carbon (TOC wt.%). **a** Samples below the Latest Permian extinction (LPE) horizon show a positive relationship and are defined as either normal marine organics (*blue circles*) or coal fly-ash dominated organics (*red squares*). Above the LPE horizon samples all represent normal marine organics but are distinguished by those that show a negative (*green circles*) or positive (*yellow triangles*) correlation between Hg and TOC. **b** A detail of the post extinction samples shows a progressive trends moving up from the LPE horizon whereby excess Hg decreases in response to increasing TOC until a return to a 'normal' positive correlation is achieved and normal marine mitigation of Hg loading is possible. (Figure reproduced from Sanei et al. 2012)

Mercury Toxicity: Collapse of Bio-productivity, Disruption of Organic Drawdown, and Catastrophic Accumulation of Dissolved Mercury in Ocean Water

About 10 m below the LPE horizon, and immediately above the coal fly-ash loading layer II, there is a significant drop in background TOC levels during a period of increasing marine anoxia, as demonstrated by trace element geochemistry, pyrite framboids, and Mo isotope data (Grasby and Beauchamp 2009; Proemse et al. 2013). Under the strongly developed anoxic to euxinic (i.e. stagnant, anoxic, and sulfidic) conditions right above the extinction boundary preservation of organic matter should be enhanced. Thus, the drop in TOC may indicate a reduction in primary productivity. Sanei et al. (2012) interpret this as a first sign of dramatic decline in bio-productivity as a response to initial ash loadings, increasing ocean anoxia, as well as a series of other environmental stresses placed on the global ecosystem at that time. Reduced bio-productivity would make oceans much more susceptible to the stress caused by Hg loading in the absence of sufficient organic buffering of the ocean. Under these conditions, further volcanic eruption phases would further increase the fugacity of atmospheric Hg, and in concert concentration in ocean water, until it progressively exceeds the capacity of autochthonous organic matter to draw down Hg to bottom sediments (Andren and Harriss 1975; Cranston and Buckley 1972; Lindberg et al. 1975; Outridge et al. 2007). In other words, the organic-mediated sediment fixing process (algal scavenging process) is no longer capable of effectively fixing the rapid increase in Hg deposition by flocculating particulate organic matter (Andren and Harriss 1975; Outridge et al. 2007; Cranston and Buckley 1972; Lindberg et al. 1975). This would result in the dramatic buildup of dissolved Hg in ocean water just prior to the LPE horizon, leading potentially to widespread ocean toxicity. While Hg is regarded as the most toxic element, other metals (e.g., Cr, As, etc.) typically associated with burning of coal and carbonaceous rocks show a similar trend (Grasby et al. 2011).

Tipping Point: Mercury Mitigation by Sulphide Drawdown, Ocean's Alternative Emergency Mechanism to Mitigate Toxic Mercury

Loss of productivity after fly ash loading occurred when the degree of anoxia was increasing through development of an oxygen minimum zone as defined by Mo and N isotope proxies (Proemse et al. 2013; Kniess et al. 2013). This resulted in euxinic (H_2S rich) conditions being developed. Euxinic condition is associated with formation of a large quantity of pyrite framboids within the water column (pyrite rain down—Grasby and Beauchamp 2009), that form a pyrite layer at the LPE boundary.

The strong Hg-OM association normally prevents highly insoluble mercury sulphide from precipitating in marine sediments (Lindberg et al. 1975). In the absence of adequate organic fixing capacity and a continued accumulation of dissolved Hg, a tipping point would be reached where development of euxinic conditions allows sulphide deposition to become the dominant Hg fixation process to compensate for the failing OM Hg draw- down process. This is supported by the observation that at the LPE level, the 'normal' Hg-OM relationship breaks down and instead a significant negative correlation between Hg and TOC develops (Fig. 3a and b—green circles), and is also shown by a significant increase in the Hg/TOC ratio (Fig. 2d). In this condition, there is a dramatic increase in Hg concentration in pyrite-rich sediments at this time (Fig. 2c), up to 0.6 mg/kg Hg. Values up to 0.6 mg/kg Hg are much greater than 0.1 mg/kg found in modern marine sediments which are considered to be affected by pollution (Camargo 2002), and are the same level as those observed in modern aquatic environments contaminated by major Hg emitting sources such as smelters (Outridge et al. 2011; Sanei et al. 2010).

Post-extinction Recovery; Re-establishing Hg OM-drawdown

After the LPE extinction, Hg concentrations decrease gradually upwards (Fig. 2c), away from the extinction level, until reaching the pre-extinction background level (Sanei et al. 2012). This suggests that the sulphide draw-down processes progressively reduced the excess dissolved Hg to a level that a normal Hg-OM relationship was re-established. This is shown by an eventual return to a positive correlation between Hg and OM with increasing distance above the LPE level (yellow triangles, Fig. 3a and b). This shows a return to effective Hg scavenging by surviving autochthonous OM and a movement of the system towards back towards the pre-extinction Hg-OM equilibrium (Fig. 2d) that continued at least for the next 5 million years (Grasby et al. 2013).

Summary

In summary, a long sedimentary archive obtained from the Canadian Arctic Archipelago can be regarded as the first geological record of Hg contamination in response to major volcanism coincident with Earth's greatest mass extinction event. The most important evidence obtained from this record is the observation that there is a breakdown of the positive correlation between Hg and TOC at the extinction level. Sanei et al. (2012) proposed that deteriorating environmental conditions suppressed organic productivity, which in turn limited the marine Hg draw-down process, as mediated by organic matter sequestration. Further Hg loading by Siberian Trap volcanics then overwhelmed the failing marine Hg-OM buffering system, leading to catastrophic build up of dissolved Hg in world oceans. By transition to extreme euxinic conditions, oceans switched to an alternative mitigation process driven by sulphide-Hg drawdown that removed excess dissolved Hg. The oceans then progressed towards recovery that eventually allowed re-establishment of the normal Hg mediation by organic matter. It is unlikely, however, that Hg loading is the sole cause of the LPE extinction, as the global ecosystem was already under stress by ocean anoxia (Grasby and Beauchamp 2009; Wignall and Hallam 1992), depletion of bio-essential elements (Grasby and Beauchamp 2009), coal fly-ash loading (Grasby et al. 2011), and rapid climate warming (Kidder and Worsley 2010; Rampino and Stothers 1988; Wignall 2001). The Earth's ecosystem was thus already stressed by the time the Hg contamination event occurred at the LPE level, making this one of a chain of events that leads to the greatest extinction in Earth history. The relative severity and global nature of this Hg event needs to be further assessed. In addition, Hg toxicity events associated with other major eruption phases in Earth history should be examined.

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Lake Sediment Records of Preindustrial Metal Pollution

Colin A. Cooke and Richard Bindler

Abstract The extraction of mineral resources has been occurring for millennia in both the Old and New Worlds. Lake sediments can archive the environmental legacy of these preindustrial activities, offering an independent method for understanding the magnitude and spatial extent of metal pollution through time. A number of geochemical records of past metal pollution within lake sediments have now been completed across especially Europe and the South American Andes, revealing histories of metal pollution that extend back over millennia. The use of paleolimnological techniques is refining our understanding of spatial and temporal differences in mineral resource extractions and use, and offers the opportunity to understand the degree to which human activities have mobilized metals from geologic stores into the biosphere.

Keywords Geochemistry · Mining · Metallurgy · Pollution · Lead · Mercury · Metals

Introduction

Human industrial activities have become one of the most important mobilizing mechanisms in the global biogeochemical cycling of many trace-metals. Yet humans have extracted trace-metals from the Earth's crust throughout history in pursuit of riches, useful metals, and energy. Indeed, many of the richest precious metal deposits on Earth were effectively exhausted prior to the advent of large-scale industrial mining operations. There is therefore considerable interest in understanding how, and to what degree, these preindustrial mining and metallurgical activities have contaminated the environment.

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Natural archives, including lake sediments, can be exploited to provide information about past environmental conditions, including the past biogeochemical cycling of many trace-metals. One of the first scientists to realize this was Clair Patterson, who with his seminal work on environmental lead (Pb) pollution, laid the groundwork for future efforts in this important field of research (Flegal 1998). The work of Patterson and his colleagues provided the impetus for subsequent efforts, some of which are summarized in this chapter. Our focus here is on the use of lake sediments as recorders of preindustrial metal pollution in Europe and the Andes of South America, as these regions have witnessed greater study than most other parts of the globe; however, research into this topic is accelerating, and new discoveries are undoubtedly forthcoming from other, less intensively studied regions with long histories of human occupation and mining and metallurgy, such as China (Lee et al. 2008).

Early Investigations into Ancient Metal Pollution

As part of his burgeoning interest in the contributions from human activities to the global biogeochemical cycling of lead, Patterson came to recognize the historical dimensions of metal pollution. Through the 1970s, Patterson developed estimates of the global production of lead and other metals from ancient to modern times, which culminated in an estimate of historical global lead production (Fig. 1; Settle and Patterson 1980). This seminal work, which has been reproduced in many publications since and was refined further by Jerome Nriagu (1983, 1996), correctly predicted what ultimately would be found in lake sediment and peat records throughout much of Europe as well as in the record from the Greenland ice sheet.

The early focus on lead proved useful for other reasons as well. First, as alluded to above, lead is a common component of many polymetallic ores. For example, many of the richest silver deposits in the Andes occur as argentiferous galena [(Pb, Ag) S]. As a result, lead aerosols were released to the atmosphere during smelting, even when lead itself was not the direct metal of interest. Second, because lead is released to, and transported within, the atmosphere as an aerosol, it is rapidly deposited across the landscape. The result of this is higher levels of atmospheric lead deposition in regions that have long histories of mining and metallurgy, as we detail below. Third, lead tends to be geochemically stable within lake sediment. This means that lead tends to undergo little, if any, diagenetic (i.e., vertical) mobilization within the sediment column after deposition (Gallon et al. 2004). Finally, lead has four stable isotopes, namely ^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb. Whereas ^{204}Pb is primordial, the latter three are the final daughter products following the radioactive decay of uranium-238, uranium-235 and thorium-232, respectively (Brown 1962; Faure 1986). When lead-containing ores are formed, they are separated from the host rock and thus also uranium (U) and thorium (Th). Consequently, the isotopic composition of the ores no longer develops. This is in contrast to lead contained within the original host rock, which continues to evolve isotopically over geologic time. Thus,

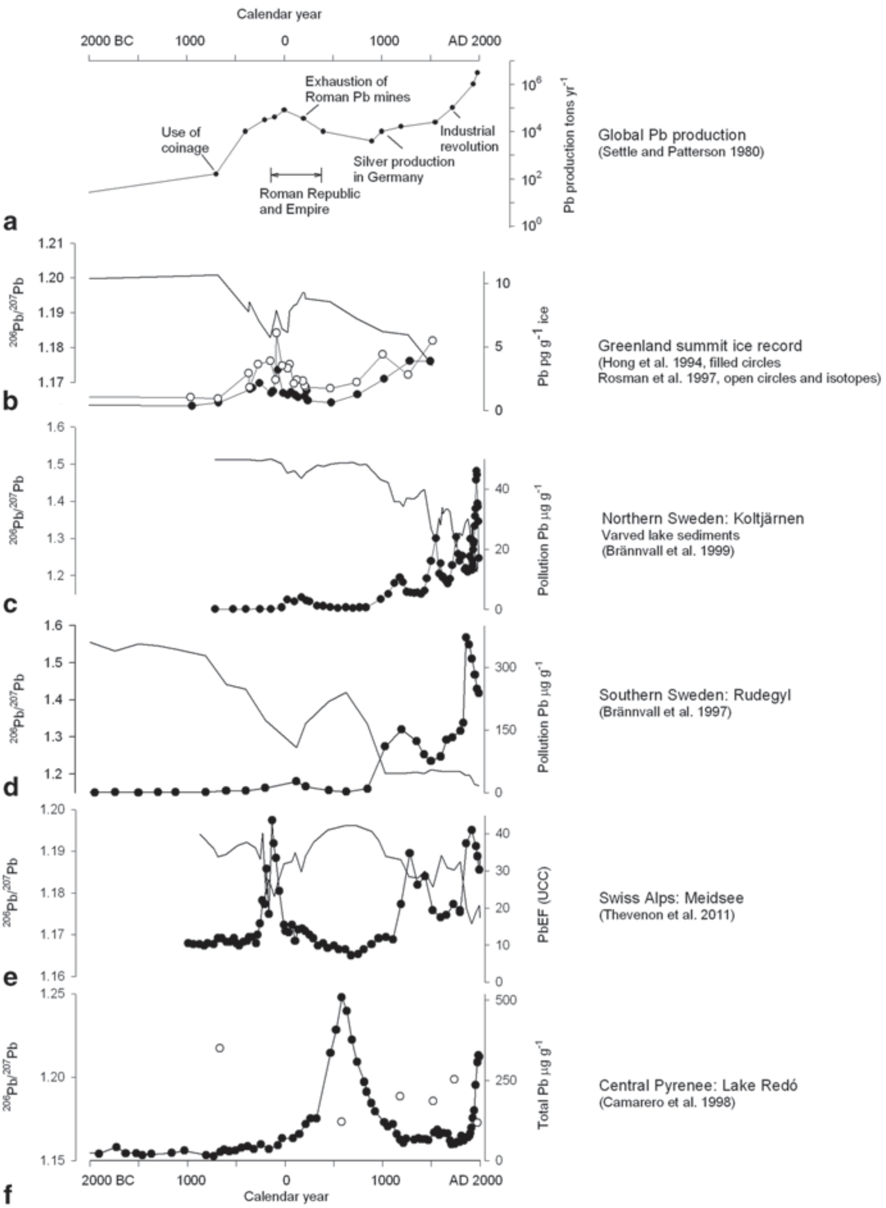

Fig. 1 **a** Global lead (Pb) production history (Settle and Patterson 1980), and pollution lead (Pb) records and ^{206}Pb/^{207}Pb isotope ratios from sediments of; **b** Greenland glacial summit (Hong et al. 1994; Rosman et al. 1997); **c**, annually laminated sediments of Koltjärnen in northern Sweden (Brännvall et al. 1999); **d** Rudgeyl in southernmost Sweden (Brännvall et al. 1997); **e** sediments of Meidsee in the Swiss Alps, bordering Italy (Thevenon et al. 2011), where Pb was calculated as an enrichment factor (PbEF) relative to the upper continental crust (UCC); and **f** sediments of Lake Redó in the Spanish Pyrenees (Camarero et al. 1998)

lead extracted from ores has a characteristic isotopic signature distinct from the surrounding bedrock, with the specific isotopic signature of an ore body depending in particular on the time of ore formation and the original U-Th composition of the bedrock. All of the reasons cited above make lead a particularly well-suited metal to reconstruct ancient metal pollution.

Preindustrial Metal Pollution in Europe

In the first study of its kind, Renberg et al. (1994) reported lead concentration records in well-dated sediment cores from 19 lakes in Sweden. These sediment cores showed a common pattern of changing lead concentrations through time (Fig. 1). Whereas lead concentrations were low in the lake sediments prior to 2500 years ago, typically just a few μg g^{-1}, there was a small, but distinct peak in lead about 2000 years ago with an increase in the range of a few to 10 μg g^{-1}. This concentration peak, which was coincident with Settle and Patterson's estimated peak in global lead production during the Roman period (Fig. 1), was highest in lakes in southernmost Sweden, lower in south-central areas, and, on the basis of concentrations alone, not as easily detected in lakes in the north. About 1000 years ago there was a larger, consistent increase, with lead concentrations as high as 200 μg g^{-1} in the south and about 20–50 μg g^{-1} in more northerly lakes. One month after publication of the Swedish study, Hong et al. (1994) revealed that the same temporal patterns in changing lead concentrations were found in the ice core record from the summit of the Greenland Ice Sheet; that is, a clear peak in lead about 2000 years ago and an increase from about 1000 years ago.

These early results from Swedish lake sediments as well as the Greenland ice sheet were subsequently reinforced by the addition of stable lead isotope analyses. Ores formed in areas underlain by Precambrian shield, such as Australia (Broken Hill mine), South Africa, Canada or Fennoscandia, often have low (i.e., radiogenic) ^{206}Pb/^{207}Pb isotope ratios in the range of 1.02–1.04 (^{206}Pb/^{207}Pb is the most commonly referred to isotope ratio in environmental studies). This is because these ores were isolated earlier (i.e., they are older), whereas ores in younger geologic terrains, such as in other parts of Europe, have evolved higher isotope ratios, mostly in the range of 1.16–1.18. Ore lead has been used in a wide range of applications from Antiquity to the present (Patterson 1971, 1972; Nriagu 1983, 1996), and this use does not impart isotopic fractionation. Thus, the original isotopic composition of the ore is retained.

Prior to human exploitation of lead-bearing ore resources, the ^{206}Pb/^{207}Pb isotope ratio of lake sediments reflected the ^{206}Pb/^{207}Pb isotope ratio of regional soils. This is because low concentrations of lead were delivered naturally to the lake through the erosion of watershed soils. Soils across much of Sweden (and thus also sediments) have evolved higher ^{206}Pb/^{207}Pb isotope ratios than many common ores because of the Precambrian origin of the bedrock. For example, parent soil material (C-horizon) and sediments older than 3000 years collected from sites throughout

Sweden as well as Finland have $^{206}Pb/^{207}Pb$ isotope ratios in the range of 1.3 to 2.0 (Brännvall et al. 1999; Bindler et al. 2001; Brännvall et al. 2001; Renberg et al. 2002; Klaminder et al. 2005; Meriläinen et al. 2011). However, $^{206}Pb/^{207}Pb$ isotope ratios in the studied sediment records in Sweden, Finland and as far north as the Kola Peninsula, Russia, show a decline about 2000 years ago at the same time as the small increase in concentrations originally described by Renberg et al. (1994). The isotope analyses provided clear evidence that the additional lead entering the lake sediment at this time had a non-local origin.

The input of lead to European lake sediments has commonly been simplified by using two isotopic end members: a local, soil lead; and anthropogenic lead, which was emitted during the mining and metallurgical processing of lead-bearing ores, transported atmospherically, and deposited on the lake and its watershed. A simple binary mixing model can then be constructed, comprised of the natural lead composition—which is based on deeper sediments for each lake, and an anthropogenic lead addition that has an isotopic composition similar to the average value of mainland European ores (Farmer et al. 1996; Brännvall et al. 1999). Based on this type of binary mixing model, the observed increase in lead can only be explained in terms of pollution, and not natural catchment processes, such as weathering (Bindler et al. 2008).

After the fall of the Roman Empire about 1500 years ago (~AD 500), lead concentrations and the lead isotopic composition of Swedish lake sediment records returned towards natural background values (Fig. 1). Thus, there was a decrease in anthropogenic lead emissions and deposition, which is not surprising given the decline in lead production at this time. However, about 1000 years ago, as lead concentrations again began to increase, so too did $^{206}Pb/^{207}Pb$ isotope ratios again decrease. This shift reflects a renewed flux of pollution lead inputs, this time in response to developments particularly in Germanic areas of Europe, as well as the start of significant mining in the Bergslagen region of south-central Sweden (discussed below).

This general long-term pattern of ancient and historical lead pollution has been observed in lake sediments from remote western Ireland (Schettler and Romer 2006), in peat records in areas outside of formerly glaciated terrains where lakes are less common (Hansson et al., this volume), and in lake sediments from upland (Currás et al. 2012) and high alpine areas (Arnaud et al. 2006; Guyard et al. 2007; Thevenon et al. 2011). Alpine lakes are especially well-suited for reconstructing ancient metal pollution for a few reasons. First, their watersheds tend to have experienced fewer disturbances than their lower elevation counterparts. Second, alpine lakes tend to be characterized by bowl-shaped bathymetries, which simplify deposition pathways. Third, alpine lakes tend to be characterized by small catchment to lake area ratios, which limits the importance of erosional inputs of soil-bound lead. In the Swiss Alps, for example, Thevenon et al. (2011) analyzed the sediment record from a small high-elevation lake, Meidsee (lake area 1 km^2; catchment area ~2 km^2; 2660 m asl), located near the border with Italy. As previously observed in Swedish sediments, peat bogs across Europe, and the Greenland ice cores, this alpine lake-sediment record shows a clear early enrichment in lead between 300

BC and AD 300 with a peak centered around 100 BC. Thevenon et al. could identify this peak both on the basis of concentrations and through stable lead isotopes (Fig. 1). At the peak, lead concentrations were five-times higher than background concentrations, and the stable lead isotope ratio ($^{206}Pb/^{207}Pb$) showed a sustained decline to ~1.18. This is in contrast to an average pre-anthropogenic ratio of about 1.19 for the several prior centuries. Similar to the Swedish lakes, pollution lead increases from AD 1100 to the present, with an early peak during 1200–1400. Only in the latter half of the twentieth century, with widespread usage of alkyl-lead additives in gasoline, did lead concentrations again reach the same levels as the peak recorded during the Roman period. Although the chronological development in this sediment record follows the general European pollution narrative, studies of other lake-sediment records from the French Alps provide increasing evidence for early mining that is regionally expressed across the alpine areas of Europe (Arnaud et al. 2006; Guyard et al. 2007).

Because this general stratigraphic pattern of lead pollution occurs in lake-sediment and peat records found throughout much of Europe, from the Iberian Peninsula west to the Alps and Germany and northwards to Scandinavia, Renberg et al. (2001) suggested that it can be used as an inferred dating tool, either as a proxy to estimate sediment ages or to support age-depth models. However, it is important to recognize that the specific pattern and timing of lead enrichment can vary regionally based on historical fluctuations in European economic and political history. For example, preindustrial mining activities peaked during the Roman period in the Iberian Peninsula but occurred during the Middle Ages in Germanic areas (Monna et al. 2000). There will also be specific variations in lead pollution records that will reflect local or regional histories of mining and metallurgy; for example, alpine sediment records from France and Switzerland record an early peak in lead ca. 100 BC (Arnaud et al. 2006; Guyard et al. 2007; Thevenon et al. 2011) where varved sediment records from central and northern Sweden preserve a lead peak somewhat later, ca. AD 80 (Brännvall et al. 1999; Bindler et al. 2011).

A clearer example of how local histories can be important is the lead record from Lake Redó (Spain), a high-elevation (2240 m asl) lake in the central Pyrenees. As observed in peat records from northwestern Spain (Kylander et al. 2005), Camarero et al. (1998) measured small increases in lead above the natural background range of 20–30 $\mu g\ g^{-1}$, which first began from ca. 670 BC in accordance with the early exploitation of ores in Spain (Fig. 1). However, rather than finding a distinct peak during the Roman period as seen in many other sediment and peat records in Europe, the largest peak in lead pollution in Lake Redó occurred later during the period from ca. AD 460 to 1105, with the peak concentration of 515 $\mu g\ g^{-1}$ occurring AD 660. This is a time period when most other sediment and peat records show that metal pollution conditions returned nearly to natural background conditions after the decline of the Roman Empire (Fig. 1). Although Camarero et al. did not discuss specific links to historical events regarding early mining in the region, their lead isotope analyses suggested that the lead was likely derived from mining in nearby areas of the Pyrenees; here, the lead stratigraphy must be a record of local or regional mining activity. Support for this interpretation of the lead record comes from the observation that lead deposition to Lake Redó during the twentieth century was linked in large part to specific mining activities in the surrounding region, such as the Cierco mine operating from 1930 until the end of the twentieth century Camarero et al. (1998).

Beyond Lead: Lake-Sediment Records of Historical Metal Pollution in the Bergslagen Mining Region of Central Sweden

Lead has been the most commonly studied of the ore-related metals, not least because lead is a ubiquitous pollutant from a wide range of sources, as well as that isotope analyses have made it possible to separate natural from anthropogenic sources. But lead is obviously not the only metal that was released into the environment from ancient and historical mining and metallurgy. Lake sediment records in some areas of Europe also trace early metal pollutants other than lead. More frequently the occurrence of a wider range of metal pollutants is from lake-sediment records that are geographically closely connected to mining and thus also mine drainage. A specific example of this is the sediment records from the Bergslagen region of central Sweden, which have been studied from the perspective of tracing the regional mining history (Wallin et al. 1987; Bindler et al. 2011), the regional impacts on metal pollution (Bindler et al. 2009, 2012) as well as early lake-water acidification (Ek et al. 2001; Ek and Renberg 2001).

In a historical context, the Bergslagen region of south-central Sweden was specifically defined as 23 mining districts, which received royal charters or concessions mostly during the fourteenth century. Geologically the Bergslagen region is a metallic rich mineral province with iron ores (banded, skarn and massive ores) and massive polymetallic sufide ores that are derived from intrusives and metavolcanic rocks, mostly in the age range of 1.7–1.9 Ga (Stephens et al. 2009). Amongst the historical districts were the Norberg mining district, which was the oldest of the districts focused on the mining of iron ores, and Falun, whose copper mine accounted for half to two-thirds of the global copper production during the seventeenth century (Lindroth 1955; Hong et al. 1996).

In the lake sediments from Kalven and Noren (Bindler et al. 2011), two adjoining lakes in Norberg, a similar pattern for lead occurs as seen in Rudegyl in southernmost Sweden as well as Koltjärnen in northern Sweden (Figs. 1 and 2). As typically found for lakes throughout Sweden (Renberg et al. 1994; Brännvall et al. 2001), there is a small peak in pollution lead ca. AD 80 and an increase from ca. AD 1000. In lakes located within the Bergslagen region, however, the sediment ^{206}Pb/^{207}Pb ratio indicates that beginning between ca. AD 1000 and 1200 pollution lead being was also added to the sediment from local (i.e., Begslagen; ^{206}Pb/^{207}Pb: 1.023) sources in addition to the well-established long-range atmospherically transported lead from mainland Europe. (^{206}Pb/^{207}Pb: 1.16–1.18).

The lake sediment cores Kalven and Noren also record differences in how metals (other than lead) were delivered to individual lakes (Fig. 2). Whereas Kalven once

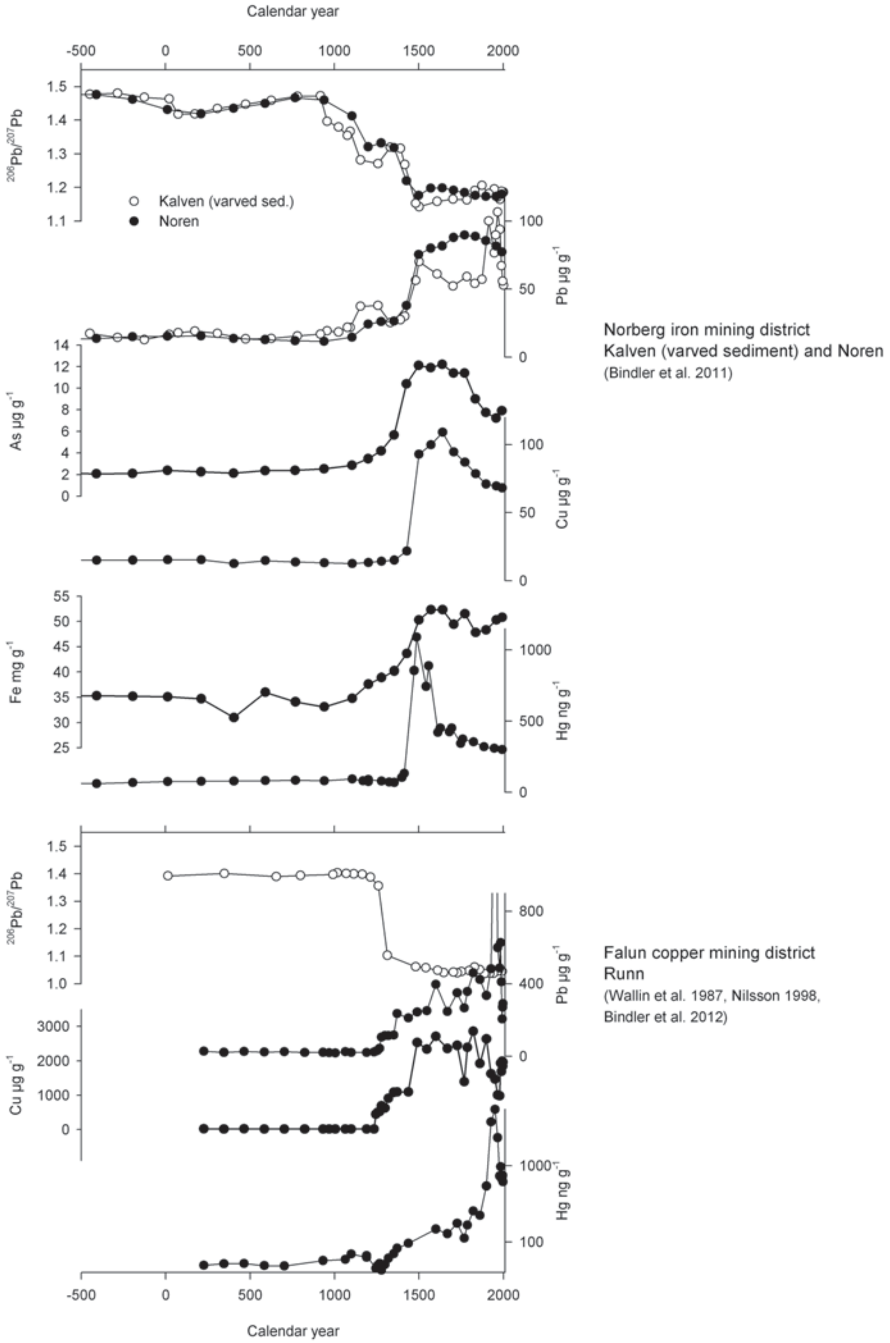

Fig. 2 Pollution metal records from lakes in the historical Bergslagen mining region in south-central Sweden, including concentrations of iron (*Fe*), copper (*Cu*), lead (*Pb*), mercury (*Hg*), and zinc (*Zn*) from the lake sediments of Noren in the Norberg iron mining district (Bindler et al. 2011). Also shown are concentrations of copper, lead (and ^{206}Pb/^{207}Pb isotope ratios) and mercury from the lake sediments of Runn, which is the main recipient lake receiving run-off from the copper mine in Falun (Wallín et al. 1987; Nilsson 1998; Bindler et al. 2012)

had two small iron blast furnaces on a small inlet stream feeding into the western half of the lake, the Norberg iron ore field passes across Noren. Archaeologists have registered more than 180 mine pits, ranging in size from small solitary pits to the multiple deep shafts of, for example, the Kolningsberg and Klackberg mine fields (Petterson 1994). Although all but a few of the pits or shafts entailed the extraction iron ores, intrusions of metal sulfides are common. Consequently, the sediment record of Noren reflects not only a combination of long-range and local/regional lead pollution as in Kalven, but from AD 1500 also includes arsenic, copper, zinc, and, possibly most critically, mercury, which increased ten-fold (Bindler et al. 2012; Fig. 2). These metals first increase in Noren's sediment record when mining in the area transitioned from working shallow pits to digging deeper shafts to access the ores buried below. Because these other ore-related elements do not increase in nearby Kalven, the source to Noren must have been mine drainage directly to the lake and not atmospheric deposition.

About 80 km to the north of Norberg is the Great Copper Mountain at Falun, which along with the burgeoning export of iron from the Middle Ages helped to finance the foundation of the Swedish state. The oldest known text documenting mining or metallurgy in Sweden is a deed of exchange from AD 1288, which concerned the reacquisition of a one-eighth share in the mine. Besides containing 1–7 % copper, the polymetallic sulfide ore contained also about 30 % sulfur and a few percent of lead and zinc. This composition is reflected in lake sediment records found throughout the area surrounding Falun, where there were also numerous smaller mines as well as smelters and forges. As part of a project aimed at studying acidification and recovery in response to the mining history of the Falun area, Ek et al. (2001) analyzed the metal records from fourteen lakes, and found elevated concentration of cadmium, copper, lead, sulfur, and zinc. The specific combination of metals that increase in the sediment record of each lake largely reflected the mining or metallurgical activities that occurred in closest proximity to the particular lake. To exemplify the historical impacts of mining of polymetallic sulfide ores on Falun lakes, data from a sediment record from Lake Runn are shown in Fig. 2. Lake Runn is the main recipient for surface waters draining from Falun, and in particular the river Faluån that flows through Falun. Thus the sediment record here is an integrated history of mine drainage for the Falun region. Qvarfort (1984) analyzed eight sediment cores from the 64 km^2 lake and found elevated concentrations of a large suite of ore-related elements, including antimony, cadmium, chrome, cobalt, copper, iron, lead, mercury, silver, tin, and zinc. The concentrations of copper, lead, and zinc at some locations were in the range of 1000–3000 $\mu g\ g^{-1}$. Subsequent analyses of the annually laminated sediments occurring in much of the lake by Wallin et al. (1987) showed that the increases in metals began shortly prior to AD 1345.

Subsequent work on Lake Runn, which was based on the varve record and radiocarbon dating (Nilsson 1998; Bindler and Renberg, unpublished data), demonstrated that the increases in ore-related elements began in the period beginning AD 1230–1245. This is about 50 years prior to the deed of exchange from AD 1288 mentioned above. In the sediment there was a rapid 20–40 % increase in all elements associated with mineral matter and an accompanying decline in organic matter content. More significant from a pollution perspective, there was an abrupt increase in the concentrations of ore-related elements from one sample (175 cm; AD 1230) to the next (174 cm; AD 1245): sulfur increased 1.5 fold; lead 1.6 fold; nickel 4.4 fold; zinc 4.6 fold; and copper 34 fold, for which concentrations increased from 15 to 445 µg g^{-1}(Fig. 2). After AD 1300 the sediment includes not only these metals, but also mercury (Bindler et al. 2012). These increases also included a large change in the lead isotope composition of the sediment that occurred between AD 1230 and AD 1275. During this interval, the $^{206}Pb/^{207}Pb$ isotope ratio declined from ≥ 1.356, which is characteristic of background sediment, to 1.103. After the natural lead contribution was subtracted, the additional lead must have a $^{206}Pb/^{207}Pb$ isotope ratio of about 1.04—i.e., the approximate isotopic signature of Falun ores. These historical concentrations are more commonly associated with twentieth century metal pollution levels.

The metal records summarized above reveal nearly 3000 years of lead production and pollution across the European continent. But there was clear variability in the timing and magnitude of preindustrial lead emissions between geographic regions, connected with local or regional histories. As new lake sediment records are developed, our understanding of how lead pollution varied geographically and temporally will undoubtedly improve.

Preindustrial Metal Pollution in the South American Andes

Mining and metallurgy developed independently in the New World. Yet despite a richly documented history of metallurgy following Hispanic conquest of the Inca, which occurred in AD 1532, little is known concerning the loci and intensities of earlier metallurgical activities. Abbott and Wolfe (2003) were the first to realize the potential lake sediments offered for understanding the mining, metallurgy, and heavy-metal emissions in the New World. They used the temporal stratigraphies of lead, silver, and other metals in a sediment core recovered from Laguna Lobato, a small headwater lake in southern Bolivia (Figs. 3 and 4), to infer a millennium of silver extraction at Cerro Rico de Potosí, Bolivia. This pioneering work initiated an interest in using paleolimnology and geochemistry to better understand past metal releases to the biosphere in the Americas. Research on this topic has only just begun, but the results so far indicate a legacy of metal pollution that rivals the European results summarized above.

Most efforts aimed at reconstructing preindustrial metal pollution in the Andes have relied upon the stratigraphy of two elements: lead and mercury. The advantages of relying on lead have been described in detail already. But in the Andes, lead and mercury were also uniquely representative of the two predominant ore-processing techniques employed during preindustrial times: lead-based smelting and mercury amalgamation. Preindustrial silver production relied upon the use of argentiferous galena [*soroche*; (Pb, Ag)S] as a flux during smelting, which was conducted in charcoal-fired, wind-drafted furnaces lined with clay (*huayras*) (Bakewell 1984;

Fig. 3 Map showing the location of lake sediment cores and archaeological sites from the Peruvian and Bolivian Andes that are discussed in this review

Van Buren and Mills 2005). The use of *soroche* led to excessive lead volatilization, resulting in lake sediment concentrations that are typically orders of magnitude higher than other trace elements. Lead-based smelting was largely replaced by mercury amalgamation of silver during the middle of the sixteenth Century AD. Mercury amalgamation was a cheap and simple method to extract silver from even the lowest grade ores, and it solved the problem of fuel scarcity, which had plagued the various mining and smelting centers of the Americas (Brading and Cross 1972; Nriagu 1993, 1994).

Profiles of lead, mercury, and (less frequently) stable lead isotopes have been generated from sediment cores recovered from a number of alpine lakes in the Peruvian and Bolivian Andes (Fig. 3). High-altitude headwater lakes have been the typical targets for the same reasons as in Europe: minimal watershed disturbance, small lake to catchment area ratios, and simply lake bathymetries. Many of these lakes are located near important preindustrial mining centers. For example, the Andes host two of the largest silver deposits in the world: Cerro Rico de Potosí in southern Bolivia, and Cerro de Pasco in central Peru. Peru also contains the world's second largest deposit of mercury, which is located near the city of Huancavelica. Sediment cores have been recovered from lakes located proximal to all of these mines with the goal of reconstructing the timing and magnitude of local ore extraction (e.g., Abbott and Wolfe 2003; Cooke et al. 2009a, b). Other, more recent efforts have focused on reconstructing patterns of preindustrial metal pollution from locations not directly impacted by regional mining activities (e.g., Beal et al. 2013).

In many of the Andean lake sediment cores investigated to date, the concentration and flux (accumulation rate) of lead prior to ca. AD 500 are typically 20 $\mu g\ g^{-1}$ and 5 $mg\ m^{-2}\ y^{-1}$, respectively (Fig. 4). This represents background or natural conditions prior to human activities in the region. However, in many Andean lake sediment cores, increases in lead concentration and flux are noted after AD 500 or sometimes after AD 1000 (Abbott and Wolfe 2003; Cooke et al. 2007, 2008, 2009b). For example, lead concentrations within Laguna Llamacocha (Peru) increased from a stable background of 2 $\mu g\ g^{-1}$ to ~10 $\mu g\ g^{-1}$ between ca. AD 400

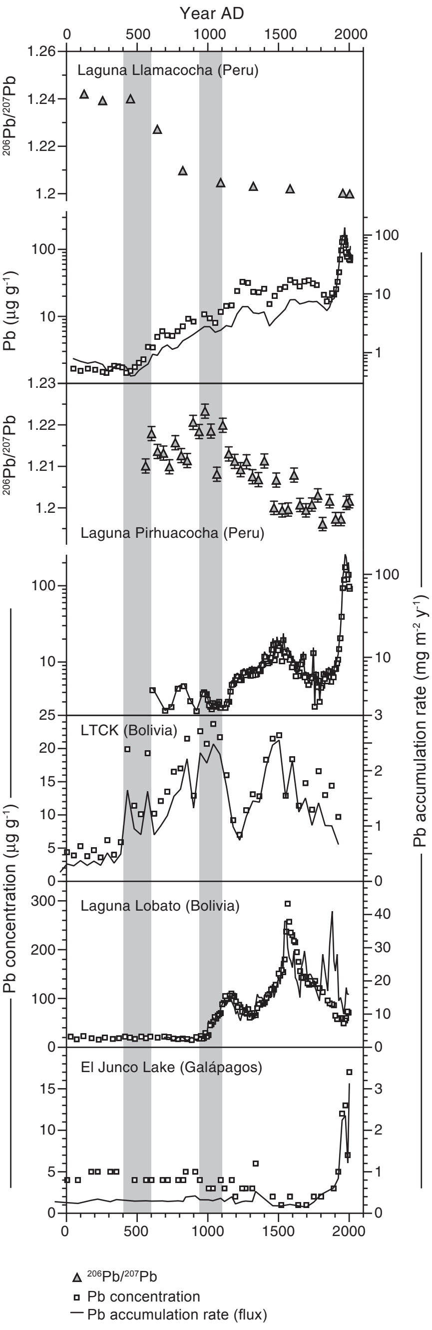

Fig. 4 Profiles of lead (Pb) concentration and accumulation rate (flux) for five South American study lakes. Also shown are ^{206}Pb/^{207}Pb isotopic ratios for Lagunas Llamacocha and Pirhuacocha. The *vertical grey bars* denote two ~ 200 year time periods, spanning AD 400–600 and AD 900–1100, in which lead pollution is first detected in Andean lakes. In contrast, mercury pollution is not detected on the Galápagos archipelago (El Junco Lake) until after ca. AD 1900

and 600; a similar increase in lead at the same time is also recorded by Laguna Taypi Chaka Kkota (Bolivia) (Fig. 4). In contrast, elevated lead deposition to Lagunas Pirhuacocha and Lobato are not evident until after ca. AD 1000. Thus, increased rates of lead deposition to Andean lake sediments appear to have been initiated either ca. AD 500 or AD 1000.

At the same time that lead concentrations and accumulation rates start to increase in Andean lake sediment cores, ^{206}Pb/^{207}Pb isotope ratios decrease. As in Europe, Andean ore deposits containing lead are characterized by lower ^{206}Pb/^{207}Pb isotope ratios than host rocks. Thus, increasing inputs of lead—due to mining or smelting of lead-bearing ores—will decrease the ^{206}Pb/^{207}Pb isotopic ratio of regional lake sediments. This is exemplified here using the sediment records from Lagunas Llamacocha and Pirhuacocha, where ^{206}Pb/^{207}Pb values shift from 1.23 to 1.26 down to ~ 1.20 at the same time as lead concentrations and flux begin to increase (Fig. 4). Lead isotopes thus offer a complimentary approach for delineating the onset of preindustrial lead pollution.

As mentioned above, preindustrial lead deposition to many of the Andean lakes investigated to date seems to begin at either ca. AD 500 or AD 1000. This variability has been interpreted to reflect regional differences in the timing and expansion of mining and metallurgy across the Andes (Cooke et al. 2008). These time periods were also important culturally. AD 500 marks the expansion, and AD 1000 the collapse, of the two largest pre-Inca Andean empires: the Wari and the Tiwanaku (Fig. 3). The emergence of these two empires increased demand for precious metals increased demand for precious metals (especially silver), thereby triggering the rise in lead pollution noted at this time in, for example, Lagunas Llamacocha and Taypi Chaka Kkota (LTCK). However, other Andean lake sediment records (e.g., Laguna Lobato) suggest another expansion of mining and metallurgy just as these two empires were collapsing around AD 1000. A recent hypothesis suggested that the collapse of the Wari and Tiwanaku Empires initiated a large-scale dispersal of people across the Peruvian and Bolivian Andes (Owen 2005). The movement of people away from the Wari and Tiwanaku heartlands, which is supported by archaeological evidence, may have similarly dispersed the knowledge and technology necessary to conduct mining and metallurgy across the Andes (Cooke et al. 2008).

Using lake sediment cores to infer past metal deposition rates makes the assumption that metals are loaded in direct proportion to local metal emission rates. Provided this is true, they can offer insight into the expansion of mining and metallurgy across the Andes. But sediment geochemistry can also be used to infer changes in the metal(s) being produced. For example, in the sediment core from Laguna Pirhuacocha both zinc and copper increased to a larger degree than lead prior to ca. AD 1450; after that time lead increases to a larger degree than either copper or zinc (Cooke et al. 2007). In addition, both bismuth and antimony first appear at detectable levels in the sediment record after this time. Because local silver-bearing ores are known to be enriched in bismuth, it was suggested that this change in inferred metal emissions reflected a switch from copper to silver metallurgy. This emphasis on silver production was maintained during the Colonial era, when lead levels within Laguna Pirhuacocha sediment again increase. A similar change in extractive technology was inferred at Laguna Lobato, where a Colonial-era increase in inferred atmospheric

Hg deposition signaled the transition for lead-based smelting to Hg amalgamation (discussed below). Thus, mining priorities appear to have changed with time, and these changes are reflected within regional lake sediment records.

Early Cinnabar Mining and Mercury Amalgamation in the Andes

Cinnabar (HgS) is a bright red mineral and the principal source of mercury. Once mined, cinnabar can be ground into a powder to make a bright red pigment known as vermillion, which was one of the earliest pigments used widely during prehistoric times in both the Old and New Worlds. Alternatively, cinnabar can be smelted, which releases the mercury as a gaseous elemental mercury (Hg^0) that can then be cooled and condensed to yield liquid elemental Hg. European alchemists believed that liquid mercury was a primary ingredient in all metals and could be transmuted into gold. Although we know this is not the case, liquid mercury will extract and dissolve fine flakes of gold and silver. This process, known as mercury amalgamation, was (and still is) a relatively easy and inexpensive process for extracting silver from low-grade ores.

Mercury amalgamation was first deployed on a large scale in the Americas during the mid-sixteenth century. Mercury was lost at all stages of amalgamation, and because of this an unprecedented demand for mercury was stimulated globally. In two papers published in the 1990s, Jerome Nriagu (1993, 1994) suggested that colonial mercury mining and amalgamation had left "…an unparalleled legacy of massive mercury pollution". Nriagu calculated that mercury amalgamation had emitted large quantities of mercury to the atmosphere, with cumulative emissions totaling over 100,000 t over a relatively short 250-year period (AD 1520–1870). These preindustrial mercury emissions were thought to have occurred as gaseous elemental mercury (Hg^0). The species emitted is important because gaseous elemental mercury is characterized by an atmospheric residence time of over a year, which allows for a global distribution. Other species of atmospheric mercury, including gaseous oxidized mercury (Hg^{2+}) and particulate mercury (Hg^P), are rapidly scavenged from the atmosphere and thus have much shorter atmospheric residence times and deposition patterns more typical of other trace metals emitted by human activities (e.g., mining and metallurgy).

To better constrain the timing, magnitude, and geographic distribution of preindustrial mercury emissions, Cooke et al. (2009a) recovered sediment cores from two lakes (Lagunas Yanacocha 1 and 2, hereafter simply LY1 and LY2); both lakes are located within 10 km of the large cinnabar deposits at Huancavelica in central Peru. Cinnabar (HgS) Cinnabar deposits at Huancavelica supplied much of the mercury supplied much of the mercury used to amalgamate silver during the Colonial era.

Somewhat surprisingly, Cooke et al. found that atmospheric mercury deposition to LY1 and LY2 increased as early as 1400 BC, and by 600 BC mercury accumulation rates within both lakes exceeded background by a factor of 10 or greater (Fig. 5). This early rise in mercury was attributed to the onset of cinnabar mining because of the widespread use of vermillion by pre-Incan cultures.

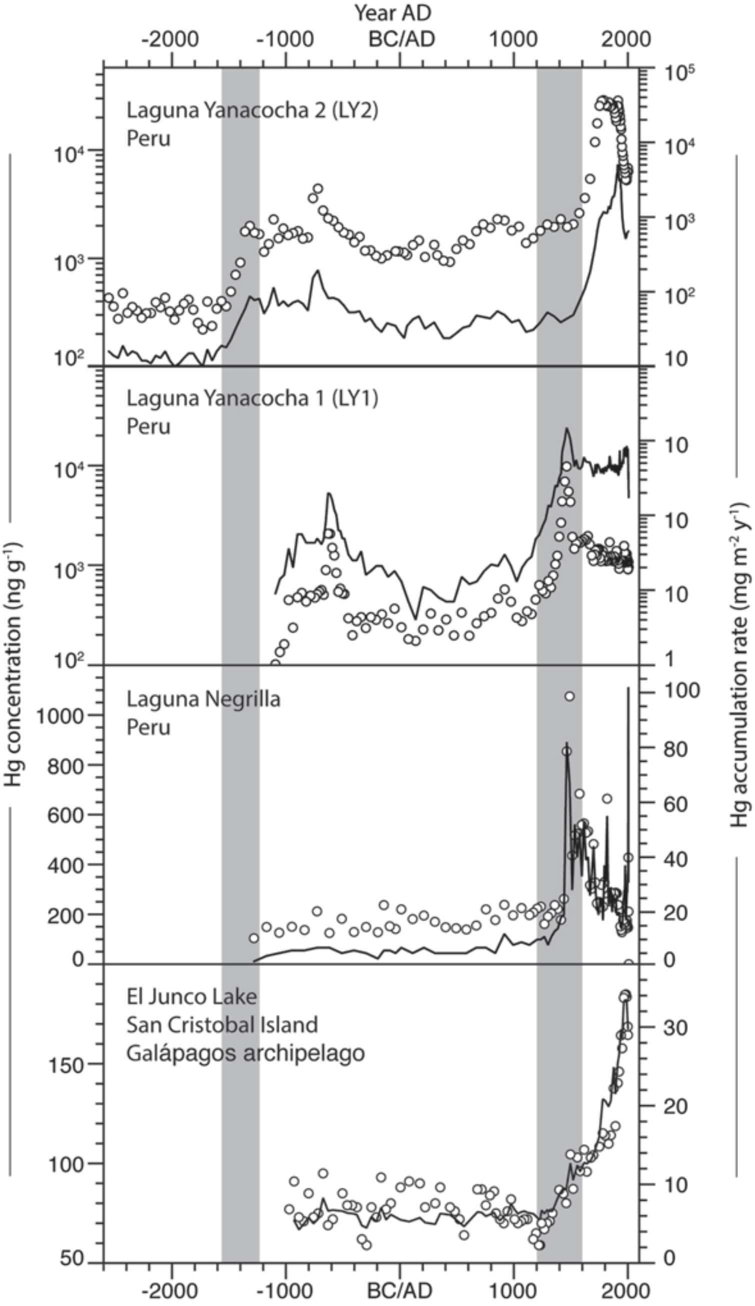

Fig. 5 Profiles of mercury (*Hg*) concentration and accumulation rate (flux) for four South American study lakes. The *vertical grey bars* denote two ~ 400 year time periods, spanning 1600–1200 BC and AD 1200–1600, of increasing mercury deposition to Andean lakes

Mercury concentration and flux within LY1 and LY2 sediments increased again between AD 1400 and 1600, with mercury concentrations reaching nearly 10,000 ng g^{-1} in LY1 and 30,000 ng g^{-1} in LY2 (Fig. 5), which are about 10-fold higher than the mining-contaminated lakes in Sweden (Fig. 2). These exceptionally high mercury concentrations were driven by regional cinnabar mining, which expanded dramatically after the introduction of mercury amalgamation to the Andes.

The impacts of amalgamation were not limited to lakes located directly downwind of the cinnabar mines. For example, a coeval increase in mercury at this time is noted as far away as El Junco, a crater lake on San Cristobal Island, Galápagos archipelago (Cooke et al. 2013). At the same time, other sediment cores recovered from lakes located in the Southern Peruvian Andes, record no preindustrial increases in mercury deposition (Beal et al. 2013). Thus, mercury emitted during the era of amalgamation was not uniformly distributed across the landscape.

There is general agreement that massive amounts of Hg were mined and lost in the amalgamation of precious metals, particularly silver. Considered collectively, however, Andean lake sediment cores suggest considerable spatial and temporal heterogeneity in anthropogenic emissions of mercury during the preindustrial era. Such a high degree of variability implies that, in contrast to Nriagu's original hypothesis, the majority of preindustrial mercury emissions to the atmosphere did not occur as gaseous elemental mercury. Instead, preindustrial mercury emissions more likely occurred as either reactive gaseous mercury or particulate mercury (most likely cinnabar dust).

Future Directions and Remaining Questions

This review of lake sediment archives of preindustrial metal pollution has been focused on Europe and the South American Andes, two regions with which we are most familiar and for which there have been a number of studies conducted to date. But preindustrial mining and metallurgy was by no means restricted to these regions. Indeed, new efforts using lake sediment cores from China are beginning to expand our understanding of the environmental impacts of early Asian mining and metallurgy. For example, Dearing et al. (2008) document an increase in regional metal pollution beginning as early as ca. 2200 years ago (200 BC) in the Yunnan region of Southern China, and Lee et al. (2008) have suggested increases even as early as 3000 BC. In addition, paleolimnological techniques have recently been applied to understand the timing and magnitude of ancient copper mining in the Great Lakes region of the United States and Canada. Using well-dated sediment cores collected from lakes located on the Keweenaw Peninsula in Michigan (United States), Pompeani et al. (2013) generated high-resolution records of past metal deposition spanning the Holocene. Pompeani et al. found that lead concentrations within the cores increased as early as 8000–7000 years ago, which predates the regional appearance of agriculture and ceramics. Interestingly, this (so far) appears to be the earliest evidence for preindustrial metal pollution, albeit at a very limited geographic scale. Future efforts using lake sediment cores from metal-rich regions around the world will undoubtedly offer new insight into the temporal and spatial scope of past human-environment interactions and resource exploitation.

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Lacustrine Archives of Metals from Mining and Other Industrial Activities—A Geochemical Approach

John Boyle, Richard Chiverrell and Dan Schillereff

Abstract Since the first studies reporting recent stratigraphic changes of metal concentration in lake sediments, many hundreds of studies have been published in the peer-reviewed literature. It is an impossible task to do justice to all of these works here; instead we: (1) examine recent methodological advances and place these in the context of the historical development of the discipline; and (2) explore the various purposes to which such methods have been applied. Such a historical emphasis may appear in conflict with the needs of a review of new approaches; however, this is not in fact the case for two main reasons. First, most new advances supplement rather than replace traditional methods, such that a thorough understanding of the practical and theoretical issues impacting these is still essential for reliable interpretation of palaeolimnological data. Second, while many of the new methods purport to circumvent problems, they achieve this only under favourable conditions, not dissimilar to the conditions that influence the earlier methods, so the same lesson must be learned anyway. Consequently, we use this historical narrative to address the fundamentals of the discipline.

The chapter comprises two main parts; methodology and applications. The methodological section has three subsections: (1) Introduction to processes controlling natural variations in metal fluxes and concentrations in lake sediments; (2) Measurement of metal concentrations in sediments; (3) Calculation of enrichment or fluxes from sediment metal concentration data.

There are four main applications subsections focusing on the value of lake sediment records of metals derived from mining or industry. They are: (1) Geochronological markers in sediments providing chronology for other research goals; (2) Lake sediment heavy metal records to quantify pollution loading histories, or to

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identify pollutant sources; (3) Identifying and quantifying pre- and post-mining baseline conditions; (4) Identifying pollutant pathways or environmental processes regulating heavy metals.

Keywords Lake sediment · Metal · Contamination · Mining · Industry · Geochemistry

Part I. Review of Methods

A number of issues impact the measurement and interpretation of metal concentrations in lake sediment depending on their natural dynamics within a lake's catchment. So important are these to the reliable interpretation of metal pollution records that we provide a brief introduction to natural processes before proceeding to measurement and data processing. We then describe analytical approaches for the evaluation of metal pollution records preserved in lake sediments, dividing these into two categories: methods for measurement of metal concentrations, and methods to obtain useful information from such measurements.

Processes

Parent Material Heterogeneity

Natural materials are highly variable in elemental composition. Though biological entities such as plant tissues have relatively limited variability in major element concentrations, most soil or rock types are classified in terms of function (e.g., crop types, or drainage in the case of soil) and/or physicochemical characteristics, and may exhibit a wide range of elemental compositions. Even the better-defined igneous rock classification terms, such as "granite", actually have multiple meanings (with various strict and broad definitions), and even when strictly specified are defined in terms of their component minerals, which in turn may be highly variable in composition. Other terms, such as "sandstone", convey very little compositional meaning at all; though likely dominated by quartz, they may contain any other minerals including calcite, provided the detrital particles fall in the size class for sand. Even when qualified by terms like "volcaniclastic", the type of volcanic rock comprising the sandstone is commonly not mentioned, and thus an extremely wide compositional range is possible.

To make matters worse, geological maps may be chronostratigraphic in purpose, accurately reflecting what is known of rock age, but saying little or nothing of what the mapped units are made of. Even lithostratigraphical maps typically distinguish heterogeneous groupings of rock types that show great local variability. An additional problem arises from the loose material, commonly referred to as drift, which lies above the bedrock. The vast preponderance of lakes in the northern hemisphere owe their existence to glaciations. Consequently, a great deal of detritus delivered to lakes is derived from the weathering of glacial materials (dominantly till, but including sand, gravel and loess). Some of this is locally derived, and may reflect the underlying bedrock, but much has been transported great distances. Thus geological maps may provide little compositional information to the palaeolimnologist in terms of natural metal concentrations in the parent rock types. Consequently, direct assessment of parent material composition is required if natural heavy metal contributions are to be fully understood. Without this, it may be very difficult to separate a pollutant signal from natural variation. Nevertheless, some geological maps list specific rock types, particularly maps that represent small areas, and thus rock classification may be used as a starting point. Table 1 shows the element concentrations of a small number of selected rock types. It is highly incomplete and, more importantly, represents only the average condition and thus may be a very poor guide to the composition of a specific instance of one of the listed types. Nevertheless, the values in the table serve to illustrate likely between-rock type differences in element concentration given some knowledge of the geological make-up of the catchment. Some elements differ little across the rock types (except in the case of carbonates, in which all elements except Ca, Cd, Mg, Mn, Sr and Zn—have low concentrations). However, most heavy metals show substantial differences. Thus, Cu, Cr, Ni and Zn are enriched in mafic (Mg-Fe rich) rock types, Cr and Ni strikingly so in ultramafic rocks, whereas As, Hg, and Cd are most enriched in shale (and other fine-grained rocks, commonly with abundant clay) and their metamorphic equivalents such as slate and schist). Pb is depleted in mafic rock types, but enriched in granite and shale. Such information is useful when choosing study sites as careful screening of bedrock type improves the chance of finding the low natural heavy metal concentrations and fluxes, and thus improving signal to noise ratio when evaluating atmospheric metal pollution.

Table 1 provides the average compositions for rock types that may underlie a catchment. However, several processes cause a lake's sediment to be quite different in composition to its parent rock. This is partly because little if any of the sediment comprises fragments—termed lithoclasts—of that rock. In the case of coarse-grained rock types such as granite, no lithic fragments are small enough to be transported to deeper parts of lakes. Thus, most lithogenic particles in the sediment comprise individual minerals. This would matter little to interpretation of the sediment composition if the mineral assemblage in the sediment comprised an unbiased sample of the rock minerals; the particles would then have the same composition as the bedrock. However, this is certainly not the case for coarse parent rock, as the finer-grained primary crystals are preferentially transported to the lake centre, and these are generally atypical in composition (Fig. 1). In the case of fine-grained rock types, such as siltstone, shale/mudstone/slate or volcanic rocks, the lake sediment particles may include rock fragments, but even those are unlikely to be identical to the parent material. These lithogenic particles will have been altered by chemical weathering prior to erosion, except in cold or rapidly eroding settings (such as alpine, tundra and periglacial landscapes). Weathering may have removed

Table 1 The elemental composition of some common rock types

		Granite	Granitic rocks,high Ca	Granitic rocks, low Ca	Syenite	Basalt	Mafic	Ultra-mafic	Shale	Shale	Sand-stone	Lime-stone
	Source	1	2	2	2	1	2	2	1	2	2	2
Si	Mg g^{-1}	323	314	347	291	230	230	205	238	273	368	24
Al	Mg g^{-1}	77	82	72	88	84	78	20	92	80	25	4.2
Fe	mg g^{-1}	27	29.6	14.2	36.7	86	86.5	94.3	47	47.2	9.8	3.8
Ca	mg g^{-1}	16	25.3	5.1	18	72	76	25	25	22.1	39.1	302.3
Mg	mg g^{-1}	4	9.4	1.6	5.8	45	46	204	14	15	7	47
K	mg g^{-1}	32	25.2	42	48	8	8.3	0.04	25	26.6	10.7	2.7
Na	mg g^{-1}	28	28.4	25.8	40.4	19	18	4.2	9	9.6	3.3	0.4
Ti	Mg g^{-1}	2100	3.4	1.2	3.5	9000	13.8	0.3	4500	4.6	1.5	0.4
Mn	µg g^{-1}	500	540	390	850	1700	1500	1620	850	850		1100
As	µg g^{-1}		1.9	1.5	1.4		2	1		13	1	1
Ba	µg g^{-1}		420	840	1600		330	0.4		580		10
Cd	µg g^{-1}	0.1	0.13	0.13	0.13	0.2	0.22		0.3	0.3		0.035
Cr	µg g^{-1}	20	22	4.1	2	200	170	1600	100	90	35	11
Cu	µg g^{-1}	12	30	10	5	100	87	10	50	45		4
Pb	µg g^{-1}	20	15	19	12	3.5	6	1	20	20	7	9
Hg	µg g^{-1}	0.03	0.08	0.08		0.01	0.09		0.3	0.4	0.03	0.04
Ni	µg g^{-1}	0.8	15	4.5	4	150	130	2000	80	68	2	20
Rb	µg g^{-1}	150	110	170	110	30	30	0.2	140	140	60	3
Sr	µg g^{-1}	300	440	100	200	450	465	1	400	300	20	610
Zn	µg g^{-1}	50	60	39	130	100	105	50	90	95	16	20
Zr	µg g^{-1}	180	140	175	500	140	140	45	180	160	220	19

1 Krauskopf 1982, *2* Turekian and Wedepohl 1961

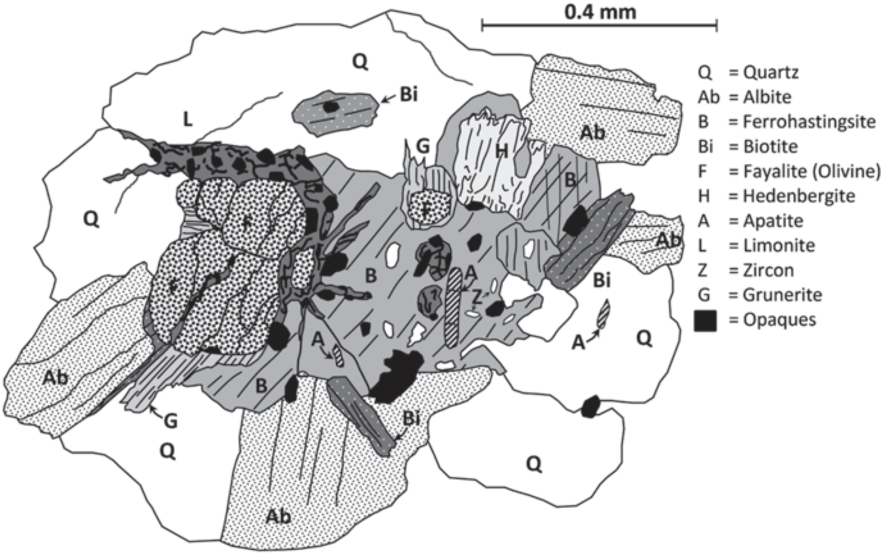

Fig. 1 A sketch thin-section of granitic rock is reproduced here with permission of Kurt Hollocher. This alkali fayalite granite illustrates the mix of crystal sizes. Mainly large crystals of quartz, feldspar (*albite*), amphiboles (*ferrohastingsite* and *grunerite*), pyroxene (*hedenbergite*), olivine (*fayalite*) and biotite, enclose an assemblage of smaller crystals of apatite, zircon and opaques (mainly ilmenite and magnetite). Other common small crystals are various oxides of Ti (rutile, anatase and brookite). During weathering, micas readily disintegrate to smaller particles; *quartz* and feldspar tend to remain intact

the least stable minerals (such as sulphides, carbonates, and apatite) from the regolith, and may have partially removed minerals of intermediate weatherability such as plagioclase and chlorite (and other mafic minerals such as olivines, amphiboles and pyroxenes). The weathered regolith will not just have lost minerals, it will have acquired secondary "clay" minerals too. Thus, to understand the range of likely compositions for lithogenic sediments, derived from variably weathered parent materials, it is necessary to know something of the composition of the rock forming minerals; those that make up the bulk of the common rocks; and of the commoner secondary minerals. Clearly, in mining regions we may find rarer minerals in abundance, but we do not review them.

Table 2 shows the compositions of a selection of individual mineral analyses. This table must be interpreted with caution for two reasons. First, to simplify the table, only single examples are given. This was done even for the very large mineral families, such as the pyroxenes, amphiboles and chlorites. Averages of common types within these families are presented, but even these types commonly show great natural variability. The values serve to distinguish difference in typical mineral compositions, but may be incorrect in any specific case. Second, the mineral data set on which the trace element analysis is derived is incomplete, likely comprises an unrepresentative sample, and displays great variability in composition. The val-

Table 2 Elemental composition of some common rock-forming minerals

	Source		Albite	Amphibole	Andesine	Apatite	Biotite	Chlorite	Garnet	Illite	Kaolinite	K-feldspar	Labradorite	Magnetite	Muscovite	Oligoclase	Olivine	Pyroxene	Quartz
Si	1	$\mathrm{Mg\ g^{-1}}$	317	220	271	0	175	125	177	241	214	302	247	1	202	299	147	236	468
Al	1	$\mathrm{Mg\ g^{-1}}$	104	42	140	0	81	108	87	145	209	104	157	1	145	120	2	9	0.0
Fe	1	$\mathrm{Mg\ g^{-1}}$	0.4	128	1.4	0.2	181	183	149	22.4	5.4	0.9	7.0	721	77.0	2.3	436	178	0.0
Ca	1	$\mathrm{Mg\ g^{-1}}$	0.0	58.6	56.0	399	4.7	0.9	152	6.5	2.9	3.2	87.7	0.0	0.4	23.3	9.8	52.2	0.0
Mg	1	$\mathrm{Mg\ g^{-1}}$	0.2	89.4	0.2	0.1	48.8	98.7	16.2	7.7	0.8	0.0	0.0	0.0	15.0	1.5	49.7	93.1	0.0
K	1	$\mathrm{Mg\ g^{-1}}$	2.4	5.1	9.1	1.1	66.1	0.2	0.0	54.6	0.2	97.3	1.1	0.0	84.1	0.4	0.0	1.0	0.0
Na	1	$\mathrm{Mg\ g^{-1}}$	82.1	7.3	48.1	31.2	3.1	0.4	0.0	3.3	0.0	25.0	31.2	0.0	3.5	73.4	0.0	3.5	0.0
Ti	1	$\mathrm{Mg\ g^{-1}}$	0.0	7.8	0.0	0.0	19.5	2.9	1.2	2.9	0.0	0.0	0.0	0.0	6.5	0.0	2.7	1.8	0.0
Mn	1	$\mathrm{Mg\ g^{-1}}$	0.0	2.4	0.0	0.0	0.8	1.0	8.5	1.4	0.0	0.0	0.0	0.0	0.6	0.0	13.2	4.3	0.0
As	2	$\mathrm{\mu g\ g^{-1}}$		1.7		0.4	1.4							3.6		0.71	0.11	0.4	0.9
Ba	2	$\mathrm{\mu g\ g^{-1}}$	16	214	471	248	1198	83				957	168		1057	355		75	
Cd	2	$\mathrm{\mu g\ g^{-1}}$				0.15	1.51						0.15	0.12			0.37	0.4	
Cr	2	$\mathrm{\mu g\ g^{-1}}$																	
Cu	2	$\mathrm{\mu g\ g^{-1}}$	5	29			57	100	19		23	3		89	32	53	71	72	2
Pb	2	$\mathrm{\mu g\ g^{-1}}$		13			26					45		7	27	22		6	0.1
Hg	2	$\mathrm{\mu g\ g^{-1}}$				0.05								0.65		0.27			
Ni	2	$\mathrm{\mu g\ g^{-1}}$						700	116							15	1280	250	
Rb	2	$\mathrm{\mu g\ g^{-1}}$		3.5			612					280			339	0.63		2.2	
Sr	2	$\mathrm{\mu g\ g^{-1}}$	482	59	906	1512	18					210	1013			1002			
V	2	$\mathrm{\mu g\ g^{-1}}$		174		80	186		2			2		1965		3		69	
Zn	2	$\mathrm{\mu g\ g^{-1}}$		507			412	512	451	120	59	5		204	24	14	60	139	10

1 Deer et al. (1966), *2* Wedepohl (1969) ues are log means of highly skewed data, so any particular specimen of a mineral may differ greatly from these. Nevertheless, as in the case of the rock compositions in Table 1, the generalities are useful. Thus the strong association of V with magnetite, of Cu and Zn with mafic minerals, of Pb with potassium bearing minerals, particularly the K-feldspar minerals, is reliable and this information is useful when interpreting natural concentrations and fluxes of heavy minerals.

Pedogenic Materials

In general, lithogenic particles in lake sediments are derived from soil rather than directly from bedrock. Thus the compositional transformations that occur within soils must be fully understood if we are to understand the composition of lake sediments. Weathering of many rock-forming minerals generates secondary solid phases. As these secondary phases generally occur as very small particles, they may contribute disproportionately to profundal lake sediments. Unfortunately, relatively little is known about the heavy metal content of these materials. While the minerals they are composed of are commonly well-studied, specimens studied are typically from unweathered bedrock. In soils, the same secondary phases are typically mixed with other materials, particularly humic substances that coat their surfaces and control their adsorption properties. This is particularly important in the case of secondary oxides, hydroxides and oxyhydroxides of Fe, Mn and Al. Thus, secondary minerals have not only inherited elements directly from their parent minerals, but have also adsorbed some elements released from the chemical weathering of other minerals. Thus Cu, Cd and Zn released from parent material sulphides, and Pb released from partial dissolution of micas and feldspars, are partially or wholly retained in the soil, chemically bound to the pedogenic phases. It is unclear just what proportion of Cu, for example, is held this way rather than released to the exported runoff from soil. However, some preliminary modelling using the Windermere Humic Acid Model (WHAM), which assesses binding of metals to humic substances coating sediment particles (Steve Lofts, Pers. Comm.) suggests a high degree of retention. In the event that heavy metals are also being supplied to the soil by pollution, they will be fixed in the sediment by the same secondary phases that hold the natural component. This similarity of process is highly significant when it comes to the characterisation of pollutant metals because there need be no difference between the natural and pedogenic metal in terms of chemical speciation in the soil, though both may readily be distinguished from any metal bound with the lattices of lithogenic minerals.

Element Fractionation During Transport from Parent Material to Lake Sediment

The heterogeneity of parent materials described above, in rock type, their component minerals, and by pedogenic transformation, contributes to fractionation of elements as they make their way from the catchment to the lake bed, and this impacts the interpretation of natural baseline element fluxes, enrichment factors, and other concepts or methods used to understand heavy metal pollution using lake sediment records. Three factors influence this fractionation: (1) contrasts in element "solubility" between the soil environment and lake water column; (2) hydrodynamic sorting of compositionally heterogeneous particulate matter, and (3) solubility contrasts between buried sediment and the sediment surface. All three must be properly understood if stratigraphic changes in element composition are to be correctly interpreted.

Fractionation by Solubility Contrast The ease by which an element may be dissolved in the catchment soil, and the ease by which it may be re-precipitated with the lake or sediment, are both fundamentally important to understanding sediment composition (Mackereth 1966). Mackereth contrasts elements such as K, Na, and Ca (he was not considering marl lakes), which are readily leached from the soil and transferred to the lake, but which are poorly captured by the sediment (in soft-water systems at least), in contrast to elements such as P and heavy metals, which may be readily dissolved in soil but readily retained by sediment within the lake (Ca will fall in this category in the case of marl lakes). In the former case, the element concentrations in the sediment are unaffected by the dissolved load, and are controlled instead by the supply of eroded soil particles. In the latter case, a more complex pattern of variation is expected arising from both allogenic (eroded particles) and authigenic (formation of or capture by particles in the water column) delivery.

This useful conceptual system can be extended in two ways. First, relatively insoluble elements such as Ti and Zr, not considered by Mackereth (1966), can be treated as a third case. In their mechanism of delivery to the lake bed they resemble K, Na, and Ca. However, while the latter are subject to gradual source-area depletion (neglecting calcite, which would be rapidly depleted) through time by leaching (Boyle 2007; Boyle et al. 2013), Ti and Zr are not, and thus potentially remain at relatively invariant concentrations throughout a long (~10^3 plus years) sediment record (neglecting dilution by organic matter). Second, a significant proportion of easily dissolved P delivered to a lake may exit with any out-flowing water (Kirchner and Dillon 1975) while the proportion of heavy metals captured is generally very high, though varying among metals (Boyle and Birks 1999; Rippey 2010). This last point is crucial for quantitative interpretation of heavy metal sedimentation fluxes, which may be quite different from short-term supply fluxes, particularly in deeper lakes (Boyle et al. 1998). However, changing solubility is also relevant to the interpretation of long sediment records of heavy metals. First reported by Mackereth (1966), the strong early Holocene sediment enrichment by Cu and Zn has been attributed to changing metal solubility within soil and sediment brought about by warming-induced increases in dissolved organic carbon fluxes (Wolfe and Hartling 1997).

Fractionation by Size Effects The data in Table 2, revealing widely differing element concentrations across the common minerals, shows the potential for hydrodynamic sorting of allogenic particles to change sediment metal concentrations. Clays, micas, and chlorites are all enriched in Cu and Zn such that sediment fining, whether due to enhanced mobilisation of fine sediment or reduced mobilisation of

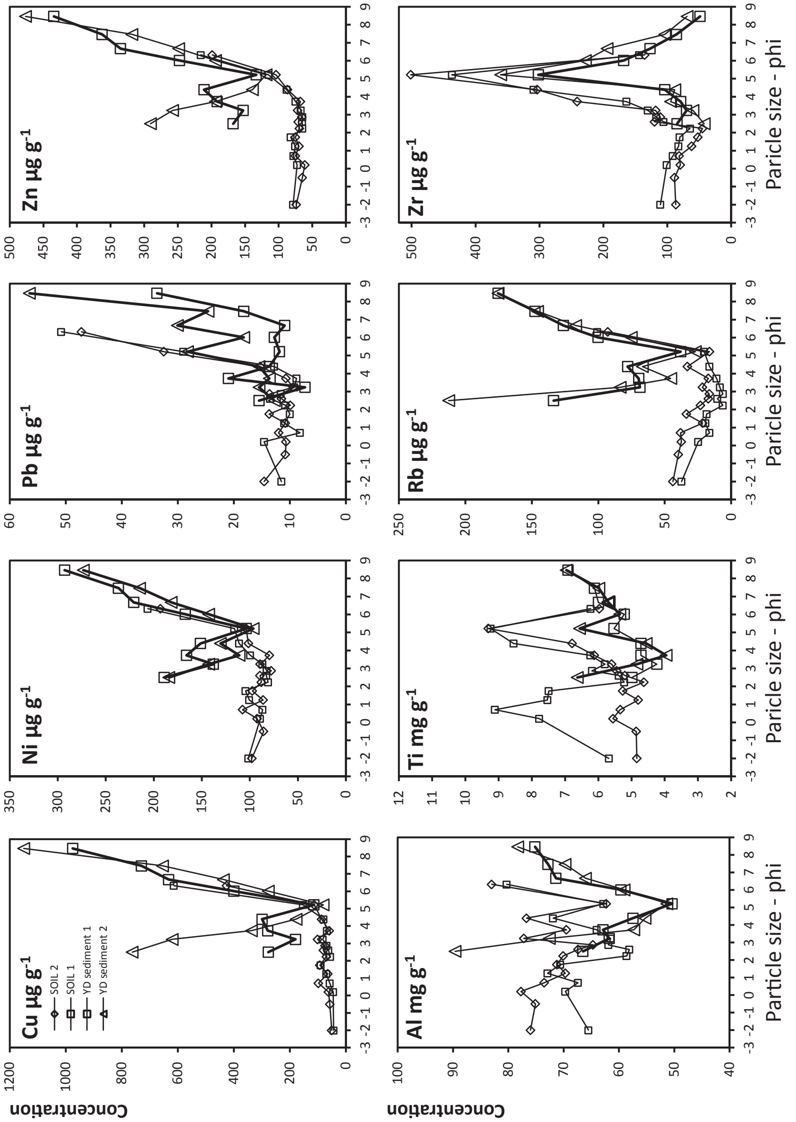

Fig. 2 Soil and sediment particle size fractions at Kråkenes Lake, western Norway

coarse sediment, will cause elevated Cu and Zn concentrations. The strength of the particle size effect is illustrated for two soil and two Younger Dryas sediment samples from Kråkenes Lake, Norway (Fig. 2, unpublished data and Boyle et al. 2013). Derived from till, here a mixture of schist, granitic gneiss, and amphibolite, Cu, Ni, Pb and Zn are strongly enriched in the finest size fractions. As the soil and sediment samples were treated to remove the organic matter and adsorbed ions, this particle size effect is a property of the allogenic particles. For comparison, Al, Ti, Rb and Zr, all elements proposed for use as passive tracers of the natural heavy metal flux, show widely varying size dependence. Rb is similar to the heavy metals, particularly to Cu and Zn, in showing both a strong enrichment in the fine fraction, and a degree of enrichment in the coarse sediment, dominated by weathered biotite. At the other extreme is Zr which is depleted in both coarse and fine sediment but strongly enriched in silt. Aluminium occurs across all size fractions, with a tendency to enrichment at the fine end. Ti is similar but with a peak in the silt size reflecting primary Ti oxide minerals. Clearly, at this site changing hydrodynamic sorting will strongly impact the heavy metal ratios to Al, Ti, and Zr but much less so for Rb. At other sites, however, very different results might be expected. Where Al and Ti are dominantly in clays rather than primary oxides, they may provide good analogues to the heavy metals. Crucially, it is clear that such size sorting effects may invalidate enrichment factor calculations (see below), which must therefore be assessed carefully.

Fractionation of Elements by Diagenesis If element solubility can change after sedimentation then post-deposition change can also occur. The effect is best seen for Fe, Mn, As, Co, Cr, and V because changes in oxidation state so profoundly change the solubility (Boyle 2001a; b). It is less certain whether elements that occur in a single oxidation state (under natural conditions) are also subject to such powerful migration. Based on a simple process model Boyle (2001a) argued that Cu, Zn and Pb profiles might indeed be modified by changing Fe and Mn sediment concentrations, but only to a noticeable degree in very slowly accumulating sediments (sediment mass accumulation rate <50 g m^{-2} year^{-1}). Empirical studies comparing known heavy metal pollution histories with the sediment record support the view the records are generally reliable for Cu, Cd, Pb and Zn (Couillard et al. 2004) and Hg (Lockhart et al. 2000). However appropriate caution should always be applied in considering possible causes of metal migration (See Outridge and Wang, this volume). For example, in the exceptionally acidic lakes near Sudbury (Canada) the combination of elevated lake-water Cu and Zn concentration and sulphate reduction in the sediment causes diagenetic enrichment of the sediment with these elements (Carignan and Tessier 1985; Tessier et al. 1989).

Concentration Versus Flux

The debate about whether sediment geochemical records should be expressed as fluxes rather than concentrations is addressed in detail by Engstrom and Wright (1984), and further visited by Boyle (2001b). The broad conclusion of both is that concentration is the primary form being more precise, less open to interference and generally easier to interpret. However, accumulation rate data are invaluable for the interpretation of the elemental concentrations, and a case can be made for displaying both where needed. Concentration and flux are not unrelated. If concentration is viewed in terms of relative flux—that is, the flux of the element of interest divided the total sediment flux—it is easier to conceptualise possible causes of the compositional variation. An increase in heavy metal concentration is frequently mistaken for an increase in heavy metal flux, while it may be equally well explained by a decrease in the total sedimentation rate. Perry et al. (2005) present a thorough analysis of sediment accumulation rate effects in relation to lake sediment Hg records.

It is worth reiterating that if sediment accumulation rate is critically important, then it is unlikely that a single core will be sufficient to characterize a lake and its pollution history. Rowan et al. (1995a, b) discuss this at length and propose an approach to estimating the optimum number of cores. Dillon and Evans (1982) demonstrate the value of multi core studies of Pb loadings in Ontario, Canada.

Measurement

Two main approaches exist (Boyle 2001b): (1) determining elemental concentrations of the solid material directly and (2) determining the elemental concentrations of metals extracted from the solid material. The decision regarding which approach to employ depends on the research question being asked and whether there is a need for non-destructive analyses. In general, analysing sediment directly yields values that reflect a total concentration, and some methods are non-destructive, conserving sediment and minimising the risk of contamination. However, for elements that are abundant both in loosely bound form and within primary mineral lattices, total concentrations can be difficult to interpret. In such cases, analysing extracts can be more versatile as total or partial components can be considered as required. However, such procedures are always destructive resulting in a loss of sample, though the sample size required may be very small. Furthermore, hazardous reagents are used in many of the chemical extraction methods, particularly hydrofluoric and perchloric acids. Completing appropriate risk assessments prior to commencing the work and employing safe working practices are essential.

Extraction Methods

Total Digestion Using Acid Digestion Where the total extraction of mineral-bearing material is desired, the preferable method is acid attack using a mixture of nitric (HNO_3), perchloric ($HClO_4$), and hydrofluoric (HF) acids (Boyle 2001b; Couillard et al. 2004). Two broad approaches are used. Allen et al. (1974) used open vessels, enabling HF acid to be fumigated along with silicon, reducing matrix interferences in the subsequent analysis. More commonly sealed acid pressure vessels are used which ensure more complete dissolution (Jackwerth and Gomiscek 1984; Garçon et al. 2012), but which then requires greater care in the management of matrix effects. Boric acid (H_3BO_3) is added to make the solution safe.

Partial or Sequential Extraction The aim of applying partial extraction techniques to sediment samples is to separate readily available elements from immobile ones. One recommended procedure (Engstrom and Wright 1984) initially uses 0.3 M HCl as an extraction reagent followed by oxidation by adding hydrogen peroxide (H_2O_2). Alternative acid digestion methods include *aqua regia* (HCl + HNO_3 mixture, Skierszkan et al. (2013)). A comparative study by Peña-Icart et al. (2011), investigating the relative extraction efficiencies of *aqua regia* and EPA Method 3050B which applies a mixture of nitric acid (HNO_3), hydrogen peroxide (H_2O_2) and HCl, concluded that both methods extracted similar amounts of Cu while Ni and Pb showed different levels of extraction. Importantly, both of these methods are effective at minimising the dissolution of the silicate component.

Sequential extractions are time-consuming, so it is important to assess the value of the information gained this way. Boyle (2001b) points out that little evidence exists that the components separated by sequential extraction, using methods developed and tested for freshly deposited sediments or soils, are preserved in lake sediment cores. Furthermore, there is no evidence suggesting that such extractable metal is necessarily pollutant in origin (See *Pedogenic Materials*, in the Methods section). Nevertheless, partial dissolution can separate the insoluble primary mineral component from the rest, and this is both useful and likely preserved in the sediment record. These reasons lend support to the conclusion of Arain et al. (2008) who argued that a single extraction for a number of heavy metals (Cd, Cr, Ni, Pb and Zn) was as useful as more complex multiple extractions, greatly reducing the total preparation time.

Some elements may require special extraction procedures which are detailed below for specific instruments or are cited in Boyle (2001b).

Analysing Solid Samples

The two most widely used methods for direct analysis of solid sediment samples are x-ray fluorescence analysis (XRF) and neutron activation analysis (NAA). These are underpinned by different physical processes, nuclear and atomic, where a sample is irradiated by neutrons or x-rays, respectively. More recently, laser ablation has been added to various instruments. These methods and some others are described here.

X-ray Fluorescence Spectrometry All XRF techniques are based on the irradiation of solid material by an x-ray source. This triggers the photoelectric fluorescence of secondary x-rays with energies characteristic of the elements present in the sample. Signal processing by the XRF system converts count rates into element concentrations. The x-ray count rate is primarily controlled by element concentration, excitation and detector efficiency and instrument geometry, but must be corrected for x-ray absorption by the material. XRF systems deliver x-rays either from an isotope source or x-ray tube source and may also differ in their method of x-ray detection. Wavelength dispersive instruments (XRF-WD) are more precise, but more time consuming, while energy-dispersive instruments (XRF-ED) are more rapid but commonly have lower detection limits, and for some elements yield less precise results.

For a number of elements the detection limits of XRF techniques are poor relative to the various solution analysis techniques described below. For two widely studied pollutant metals, Hg and Cd, only exceptionally polluted soils and sediment are measurable by XRF (Boyle 2001b). However, for most palaeolimnological applications, observed concentrations vastly exceed XRF detection limits, especially for many mining-related elements (e.g. As, Ba, Cr, Cu, Fe, Mn, Ni, Pb, Zn) elements. Recent advances in XRF technology, particularly the use of polarised x-ray sources, are greatly improving detection limits.

Traditional XRF equipment has been designed for use in laboratories, being large in size with helium or other coolant gases required. More recently, field portable XRF guns (e.g. Thermo-Niton, Olympus Delta, and Bruker) have come into common use. They generally have poorer detection limits than bench top instruments, but nevertheless offer high-precision and good accuracy. These offer the advantages of rapid data acquisition in the field or laboratory, either on split cores or sub-samples in bags. Beneficial implications for field expeditions include identifying preferred locations for extraction of master core(s) based on immediate, on-site geochemical assessment.

Scanning XRF The development of X-ray fluorescence core scanning in the last decades is proving a valuable addition to palaeolimnological research (as well as in marine or other sedimentary settings). These technologies offer rapid, non-destructive acquisition of geochemical data on wet sediment cores at resolution down to sub-millimetre scale (Croudace et al. 2006; Richter et al. 2006).

Two main types of core scanner are regularly used. The Geotek Multi-core logger measures elemental concentrations directly using an Olympus Delta portable XRF gun mounted on a mechanised arm that tracks along the core. This applies XRF measurements and returns total concentrations after applying a series of algorithms to convert count rate into total concentrations. This instrument has low resolution (~ 5 mm). A critical assessment of instrument accuracy and calculation of dry mass concentration values is presented by Boyle et al. (2014).

The ITRAX (Croudace et al. 2006) and Avaatek (Richter et al. 2006) systems operate differently, using a fixed dedicated Energy-Dispersive XRF (using a Mo or Cr x-ray tube) under which the sediment core is passed. This configuration has the disadvantage that the instrument occupies a space twice the length of the core track. Compared with the Geotek system, these systems have the additional disadvantage of reporting only x-ray count rates rather than element concentrations. Conversely, the exceptionally high analytical resolution (~ 200 µm) and measurement speed are great advantages.

Despite the recent substantial volume of research using XRF core scanning, potentially significant measurement uncertainties have been highlighted only recently.

Hennekam and de Lange (2012) identified problems which may cause unpredictable deviations in measurements, including the heterogeneous nature of the wet sediments, grain size variability, uneven core surface, interstitial water content, and the formation of a water film between the sediment surface and covering polypropylene film. The x-ray tubes can also change with age, meaning measurements performed with significant time gaps should not be compared directly (Löwemark et al. 2011).

Sediment water content can negatively impact measurement reliability in two ways: water dilution reduces the element mass concentration, reducing the intensity and thus sensitivity of the x-ray signal (Hennekam and de Lange 2012); and variable water content causes variation in element concentration that is indistinguishable from changing dry mass concentration. Some potential solutions have recently appeared, focusing on accounting for variable water content and verifying effective x-ray operation. Normalising the raw data to the ratio between incoherent and coherent backscatter to account for changes in water content along a core appears sufficiently rapid to offer a practical solution (Kylander et al. 2011; Boyle et al. 2014). Using elemental ratios can be an effective solution. However, a good understanding of the chemical properties being analysed is crucial to ensure signal is not lost and that the ratios reflect true values (Löwemark et al. 2011; Hennekam and de Lange 2012).

The undesirable absorption of secondary x-rays by water predominantly influences weaker energies (Tjallingii et al. 2007) and therefore poses a greater problem to the precision of measuring elements with a lower atomic number. The heavier elements associated with industrial effluent are likely to be less affected by this source of error (Hennekam and de Lange 2012).

Laser Ablation ICP Mass Spectrometry (LA-ICP-MS) Detailed discussion of ICP procedures is contained in the following section (analysis of solutions). The recent development of laser ablation (LA) techniques has enabled solid, powdered samples to be analysed by ICP-MS for a number of major elements, the trace metals Ba, Cr, Cu, Zn, and As (Shaheen and Fryer 2011), and Pb isotopes (Sheppard et al. 2009). This technique shows great promise for minimising the complications inherent to ICP analyses of extracted solutions introduced by pre-treatment, sample handling and spectral interference (Shaheen et al. 2012). LA-ICP-MS enables sub-millimetre resolution analyses, although, where water content is high or the core surface has been disturbed, effective laser profiling may be more problematic.

A number of methods have been proposed for creating an effective flat surface for scanning by the laser system. Powdered samples can be compressed into small disc-shaped briquettes using a styrene-wax binder (Sheppard et al. 2009). Rauch et al. (2006) proposed using thin-sections sub-sampled 1.5 cm below the surface of frozen sediment cores and dried at low temperature (40 °C) to ensure sediment structure is maintained. Alternatively, dried sediment can be directly impregnated with epoxy resin (Shaheen and Fryer 2011). The LA system operates by placing samples in a sealed cell through which a stream of Ar gas is pumped. A narrow laser beam (50–100 µm) is focused on the sediment surface and moves incrementally (5–10 µm) causing ablation along a linear transect. These ablated particles are carried under Ar flow to the plasma torch for analysis by ICP-MS. Usefully, instrumental setup parameters are published by Rauch et al. (2006) and Shaheen and Fryer (2011) for their particular systems and enabling a degree of inter-laboratory data comparison.

Direct Mercury Analyser This equipment offers a simple method for determining total Hg concentrations from solid material with no pre-treatment required. Quoted measurement precision is 1 ng g^{-1}. The instrument performs all necessary procedures including drying and oxidation of the original sample, reduction of elemental Hg and the measurement of the resultant total Hg in vapour (Couillard et al. 2008).

Instrumental Neutron Activation Analysis (INAA) Different procedures and system setups exist which irradiate samples by neutrons adjacent to a nuclear core, initially forming highly-excited nuclei before subsequent gamma ray emission upon de-excitation. Decay energies of the gamma emissions are a function of elemental composition, enabling elemental speciation and concentrations to be measured (Li et al. 2012). INAA is useful as both short-lived and long-lived isotopes, including many trace elements and heavy metals, can be measured with high degrees of precision by exposing samples to differing irradiation time intervals (from a few seconds to 30 days). Li et al. (2012) noted that Cu and Pb were below detection limits on their system.

Measurement uncertainties associated with neutron flux mean this method is not in common use (Negi et al. 1997). However, a number of recent papers have successfully used NAA to measure concentrations of heavy metals in sediments (Matsapaeva et al. 2010; Waheed et al. 2010; Li et al. 2012).

Thermogravimetry Analysis (TGA) Thermal analysis, in which solid sediment samples are heated at a controlled rate (5–20 °C/min) across a specified temperature range (usually 30–950 °C) under an oxygen or nitrogen atmosphere, has been demonstrated to contain signals of heavy metal pollution in marine sediments (Rodríguez-Barroso et al. 2008; Rodríguez-Barroso et al. 2010). Provided geochemical data obtained using a secondary technique is available for correlation purposes, applying their procedures to lake sediments offers an automated and low-cost methodology.

Analysis of Solutions

Atomic Absorption Spectroscopy (AAS) Measuring the absorption of light at a specific wavelength by an atomised sample preparation is the basis for AAS, each element having a small number of narrow absorption bands that are linearly related to concentration (Boyle 2001b). The method is relatively free from spectral interferences, and calibration is linear over a wide concentration range. However, each element must be measured separately, reducing sample throughput rate.

The atomization of a sample can be achieved in two ways. In flame atomic absorption spectrometry (FAAS) the solution containing the target element is aspirated into a flame, while in electrothermal atomic absorption (EAAS) an aliquot of the sample is injected into a graphite tube, which is briefly heated by a high-current electric supply. In general, EAAS delivers lower detection limits but is prone to greater matrix interference than FAAS and significant technological advances in FAAS now enable a number of trace metal elements to be measured more effectively. For example, using a flow injection or sequential injection method enables ultra-trace concentrations of heavy metals to be determined (Zhang and Adeloju 2008). Furthermore, the cold-vapour AAS technique enables very low concentrations of Hg in the parts-per-billion range to be determined.

Cold-Vapour Atomic Fluorescence Spectrometry (CVAFS) Coupling the cold-vapour principle with atomic fluorescence spectrometry, which involves exciting electrons using a beam of ultraviolet light, is particularly effective for measuring trace amounts of mercury (Ma et al. 2013). Most studies use EPA method 1631, initially involving oxidation by bromine monochloride (BrCl) and subsequent two-step reduction procedure using hydroxylamine hydrochloride ($NH_2OH.HCl$) and stannous chloride ($SnCl_2$) prior to collection of the Hg vapours in a gold trap. An experimental setup to achieve picogram detection levels is described by Bloom and Fitzgerald (1988). A comprehensive review of different techniques for the speciation and measurement of Hg in environmental samples is provided by Leermakers et al. (2005).

Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) Subjecting atoms to thermal excitation causes radiation lines to be emitted at particular wavelengths according to the elemental composition of the solution. The wavelength intensity should be proportional to concentration of each element within the sample. The integration of ICP and AES systems promotes greater emissions than traditional AES and hence is capable of measuring a wide range of elements simultaneously at detection levels reaching parts-per-billion. A similar digestion procedure is usually employed involving sequential $HClO_4$-HF-HCl treatment (Couillard et al. 2004), though HNO_3 extracts are also widely used. The high number of emission lines from multiple elements (i.e., spectral interference) presents a significant challenge to robust interpretation of highly heterogeneous materials like lake sediments. In addition, high operating costs limits the number of samples that can feasibly be run. This is particularly problematic if the spatial distribution of mining pollution across a lake is being assessed using many sediment cores.

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) The accuracy and detection limits of these techniques are superior, in general, to both ICP-AES and AAS methods. ICP which uses high-temperature plasma to atomize samples for analysis by mass spectrometry is coupled with mass spectrometry (Boyle 2001b). However, the high equipment cost and greater sample handling for sediment samples are disadvantageous when compared to AAS and XRF.

Sample preparation prior to ICP-MS usually follows USEPA Method 3501, which involves leaching the sediment via microwave-assisted HNO_3 digestion to liberate adsorbed and other loosely bound elements, and to digest sulphides, carbonates, and some clays while avoiding the dissolution of primary silicates (Parviainen et al. 2012). Conducting sample preparation in the sealed microwave environment minimises vaporisation of certain pollutant elements which are highly volatile at temperatures $<60\,°C$ (As, Hg, Cr).

Isotopic Determination (Hg and Pb)

Using a multi-collector ICP-MS permits isotopes of pollutant elements including mercury (^{199}Hg, ^{200}Hg, ^{201}Hg or ^{202}Hg) and lead (^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb) to be determined (Garçon et al. 2012; Ma et al. 2013). Analyses of isotopic composition are a powerful tool for detecting provenance of pollution fluxes (Farmer et al. 1996; Renberg et al. 2001). Komarek et al. (2008) provide a detailed overview of Pb isotope analyses on environmental samples.

Solution preparation for Pb isotopes also involves digestion using HF, $HClO_4$ and HNO_3 before Pb is isolated using an anion exchange technique involving HCl and phosphoric acid (H_3PO_4) following Manhes et al. (1984).

Quality Control

All instruments must be calibrated, samples must be prepared (though minimally in the case of XRF), and commonly quite elaborate signal processing is required to correct for matrix effects and inter-element interferences. How sure can we be that all of this is being performed correctly? A full treatment of quality control procedures is beyond the scope of this chapter; each instrument and manufacturer generally has comprehensive guidance. However, the role of blanks and certified reference materials is critical.

Analytical Blanks Perhaps counter intuitively, an instrument is unlikely to yield a zero signal for an element that is effectively at zero concentration. Spectral background and inter-element interferences lead to a measurable signal even in the absence of the element of interest. Therefore, to prove that an observed signal does indeed indicate the detectable presence of an element it is essential that analytical blanks have been correctly prepared and measured as unknowns. These must have the same matrix as the samples being measured; generally this means treating an aliquot of nothing (empty crucible, for example) identically to the samples, with the same reagent additions and treatments. Measuring such a blank as if it were an unknown sample serves to assess simultaneously both instrument calibration and any introduced contamination (from reagents or environment). Measuring a suite of such analytical blanks provides a statistical characterisation of the zero measurement, and is essential for calculation of the true detection limit.

Analytical blanks are problematic for solid sample methods, such as XRF, for two reasons. First, it is practically impossible to create a solid material whose matrix is similar to lake sediment but which contains none of a particular metal—even spectrographically pure reagents contain trace contamination. Second, the matrix (major components such as quartz, organic matter, etc.) of lake sediment is highly variable; thus a large number of analytical blanks would be needed to cover all possibilities. Generally the best option is to seek Certified Reference Materials (see below) that have low concentration of specific elements and a range of matrices, from which the zero condition can be reliably approximated.

Certified Reference Materials (CRMs) Many organisations exist that manufacture large batches of homogenised sediment that have been analysed for specified elements by multiple laboratories using multiple methods. Statistical analysis of the suite of values obtained this way is used to generate certified values (meaning the most probable value) for element concentrations. These materials provide the corner stone of reliable sediment analysis. Small subsamples of CRMs must be included with each batch of unknowns, and treated identically. The readings obtained can then be compared with the certified values, and any problems can be identified and addressed. The choice of CRM, and the number of different ones to include, will depend on the purpose of the analysis. Ideally, the matrix of the CRM should be similar to the unknown. This is problematic for highly organic sediments, particularly for mineral-poor peats as only a single peat CRM is available (Yafa et al. 2004). Various plant tissue CRMs provide a partial solution, but these are mineral-poor compared with typical highly organic lake sediments.

Approaches to Calculation

Accurate and precise measurement of heavy metal concentrations in lake sediment is a prerequisite to reliable interpretation. However, it is not enough. Heavy metals are present in unpolluted sediments, and may naturally show stratigraphic variation. How certain are we that any metal enrichment derives from pollution? A series of procedures have been developed to address this question; these are reviewed here starting with the methods used in the earliest studies.

Raw Concentrations

The earliest studies to use lake sediment records to infer recent changes in heavy metal pollution explored variations in the concentrations of Hg and Pb (Thomas 1972; Aston et al. 1973; Kemp and Thomas 1976). Their interpretations are based on the trends and timing of concentration changes, allowing them to infer an increasing pollution load. This simple approach succeeded because the signal was strong; Hg and Pb have very low natural concentrations at the studied sites, so a pollution contribution added substantially to the total, leaving a clear signal. In cases where these conditions are met, this simple approach is still applicable and widely used. Hammarlund et al. (2008), for example, applied this approach in Sweden at a location where the pollution signal is strong. This situation is illustrated

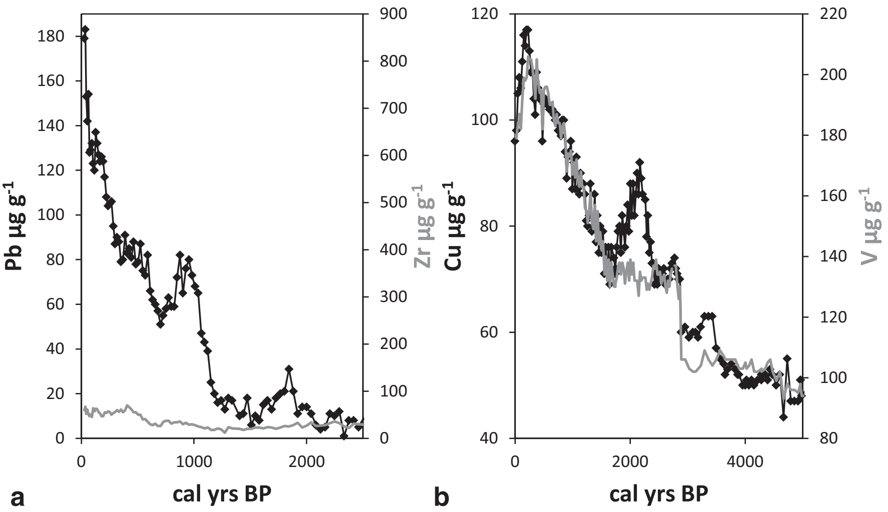

Fig. 3 **a** 2500 years of Pb concentration variation at Lilla Öresjön, Sweden, shows a series of abrupt increases. These are far in excess of any passive tracers (only Zr shown). **b** At Er Hai (Dearing et al. 2008) Cu concentrations also increase steadily. However, V, which is supplied via erosion of basaltic soils, closely follows the Cu increase except for two episodes of elevated Cu concentration which are considered to reflect Cu mining

in Fig. 3a for the Pb sediment concentration record at Lilla Öresjön (John Boyle and Richard Chiverrell, unpublished data). However, where pollution signals are weak, or in the case of elements that have strong natural components, separating the natural component from any pollutant contribution is more difficult. Mackereth (1966) demonstrated that Cu, Ni and Zn displayed strong systematic concentration changes through the Holocene; and while he did not investigate modern pollution, it is clear that the patterns he revealed must be allowed for if pollution is to be identified. This situation is illustrated in Fig. 3b for Cu in Er Hai, Yunnan Province, China. The Cu concentration rises strongly over the last 3000 years; however, most of this rise can be attributed to changing patterns of soil erosion (erosion of basaltic soils rich in magnetite), as is shown by the V concentration signal. Only at a limited number of time intervals does Cu vary independently of V, evidencing episodes of Cu pollution.

Ratio to Passive Tracer

On the basis that lithogenic element fluxes should remain constant during pollution, expressing heavy metal concentrations as ratios to a lithogenic tracer element should correct for any changes in concentration arising from mutual dilution effects (by, for example, organic matter). Thus, Bruland et al. (1974), interpreting sediment heavy metal records from near-shore marine sediments in California, use ratios to

Al concentration to support their case for enhanced pollution (using Al, assumed to have a uniform flux to the sediment, to correct for the effect of high and variable natural supply of $CaCO_3$ and organic matter). Kemp and Thomas (1976) develop this approach for their Great Lake records, applying a normalisation that retained the original concentration units. Norton and Kahl (1987) formalised this approach, using Eq. 1,

$$M_{a,x} = M_{total,x} - M_{total,bg} \frac{[T_x]}{[T_{bg}]} \tag{1}$$

where M = a heavy metal, T = passive tracer element, suffix a = anthropogenic, x is any depth, bg = background (usually, basal sediment values).

They also switch from Al to Ti as the passive tracer. Does this matter? Indeed, is either one of these elements suitable for this purpose? Renberg (1986) showed for sites in Sweden that loss on ignition (LOI, a proxy for organic matter concentration) provided a better tracer than any of the lithogenic elements. Ochsenbein et al. (1983) showed that for Bleham Tarn (English Lake District) natural Cu variation was controlled by the mineral chlorite, such that Mg made a good passive tracer for it. At Er Hai, Yunnan, as described above (Fig. 3b), V is an excellent passive tracer for natural Cu owing to the enrichment of both in catchment-derived primary magnetite (Dearing et al. 2008). Such strong associations, however, are rare. Boes et al. (2011) compared Ti, Zr, Rb and Al as passive tracers in Swedish lakes. They find substantial differences between these and recommend using all four to inform a critical interpretation. How can this diversity be reconciled? The element concentrations shown in Table 2 help explain why different passive tracers are needed for different heavy metals, and that the choice of tracer must vary with parent material composition. Combining the information in Table 2 with the data in Fig. 1 (Kråkenes, Norway) is still more informative; choice of passive tracer must take particle size into account. Most heavy metals, even under natural conditions, are strongly enriched in the finest particle size fractions. At Kråkenes Lake, most possible passive tracers fail to match the size-composition properties of the heavy metals; only Rb is at all suitable. Zr, enriched in the silt fraction, is wholly unsuitable, and would only yield accurate results if there are no changes in particle size associated with recent human impacts. Rb, Ti, and Al are enriched in the fine sediment, though not so strongly as the heavy metals, but they are also enriched in the coarse sediment. If sediment particle size and chemistry are unrelated, all three could make usable tracers. Such issues are of great practical importance. Boyle et al. (2004) recorded large stratigraphic variations in heavy metals concentrations in six cores from Svalbard, but ruled out natural causes for these at only one site, and only for Pb. The literature is full of examples where a less cautious approach has led to potentially erroneous (unsafe) inference of human impacts.

A useful empirical approach for the numerical optimisation of passive tracer methods is given by Hilton et al. (1985). While this improves the precision of the method, and tests its numerical validity, it does not avoid the conceptual pitfalls described above.

In conclusion, the passive tracer approach constitutes a valuable empirical approximation but one that should be approached cautiously and critically. The information discussed above provides a framework for identifying likely passive tracers, but this is no substitute for critically testing the suitability of any candidates. That said, the method has wide effective application, as illustrated by a number of recent case studies, each using different passive tracers. Thus, Ahmed et al. (2005) (Dhaka City, Bangladesh) normalise their concentration to Fe, von Gunten et al. (2009) (Chile) normalise to Rb and Zr, and Krom et al. (2009), studying pollution signals in Sea Lochs, normalised Pb and Zn to Al.

Enrichment Factors

Enrichment factors may be problematic and should be approached with caution. Numerically, they are essentially the same as the passive tracer ratio methods described in the preceding section. The reality is that no matter the extent to which a statistical analysis demonstrates that one part of a sediment sequence has a greater metal quotient than another part, this does not demonstrate that enrichment has occurred. Nevertheless, these methods are so widely used that a brief review is necessary.

Various enrichment factors have been proposed, each intended to show whether or not sediments have been enriched in a specific element due to pollution. The approaches fall into two general classes depending on the nature of the benchmark against which enrichment is judged, this being either local or global.

The Anthropogenic Factor (AF) of Szefer and Skwarzec (1988) is directly analogous to the normalisation procedure of Kemp and Thomas (1976), Eq. 2:

$$AF = \frac{C_{s,M} / C_{s,Zr}}{C_{d,M} / C_{d,Zr}} \tag{2}$$

where C = concentration, suffix s refers to surface sediment (0–5 cm, quasi modern) and suffix d to deeper sediment (below 15 cm, pre-industrial revolution). M is the metal under investigation, and Zr is the normalisation element.

This approach is classified as local (perhaps even intra-core) because the benchmark is older sediment from the same location. Note also that this differs from the method of Kemp and Thomas (1976) only in its genetic nomenclature. The alternative is to normalize against a global reference material, commonly the Wedepohl (1995) estimate of average crustal rock. Thus the Enrichment Factor (EF) of Sinex and Helz (1981) uses the same formulation as for AF, but with D referring to crustal average values rather than deep sediment. Other methods normalise to crustal average values but avoid additional normalisation to passive tracer elements. One influential implementation of this is the Geoaccumulation index of (Müller 1979). This is based on the logarithm of the element concentration (c) normalised to global

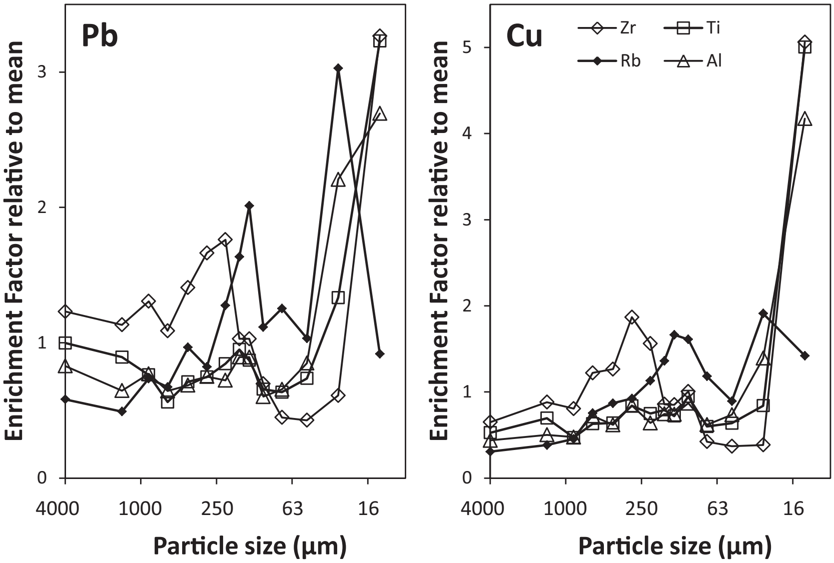

Fig. 4 Enrichment factors by particle size fraction relative to mean concentrations (data from Kråkenes, unpublished data and Boyle et al. (2013). These are calculated according to Eq. 2, substituting size fraction for depth (s) and mean concentration for the deep sample (d). This serves to show the potential for particle size sorting to lead to changes in enrichment factor values

shale concentration (B), adjusted slightly to allow for uncertainty in natural concentrations (Eq. 3). Such methods are assessed by Das et al. (2008),

$$I_{Geoaccumulation} = log_2\left(\frac{c}{1.5B}\right) \tag{3}$$

Both of these approaches are in widespread use, though the terms used vary substantially. Thus the EF of Camarero et al. (2009) is identical to the AF of Szefer and Skwarzec (1988), though with Ti as a normalising factor rather than Zr. Both are locally referenced. Local reference methods are useful where element concentration varies due to changing dilution by biogenic or authigenic sediment. However, there are two issues that weaken this approach. First, just as in the case of ratios to passive tracers, EF normalisation only corrects for natural fluctuations if there is no change in the sediment particle size characteristics. The magnitude of this effect is illustrated for the Kråkenes particle size fraction data (see Fig. 2), converted to enrichment factors relative to the mean concentrations (Fig. 4). Across the four normalising elements (Al, Ti, Rb and Zr), the apparent EF values range from 0.3 to 5.1 for Cu and from 0.4 to 3.3 for Pb. Given the pervasive character of most human impacts on catchments, changes in sediment particle size must occur often. Second, the term Enrichment Factor conveys a causal mechanism which cannot be readily tested. If its magnitude is significantly higher in the surface sediment, then

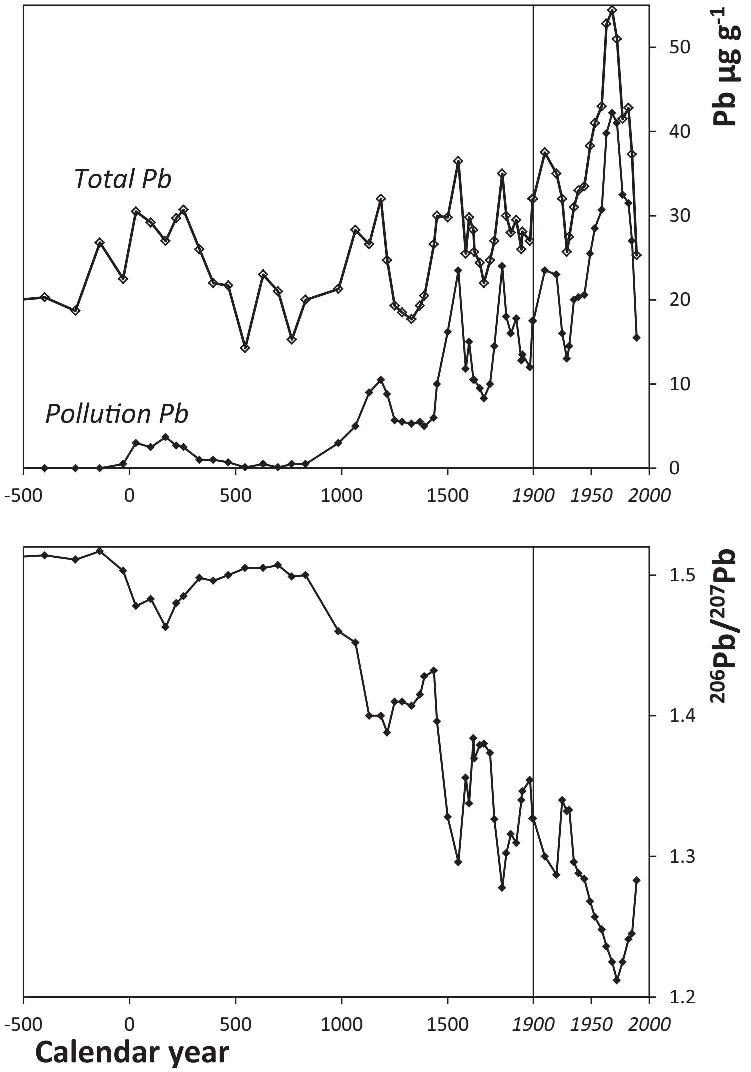

Fig. 5 Combining Pb concentration data with Pb isotope values greatly increases confidence in interpretations (Data from Renberg et al. 2002). The small Roman enrichment at Koltjärn (Northern Sweden) would be difficult to detect in the total Pb concentration without the corresponding excursion in isotopic ratios (which have been used to correct total Pb for the natural contribution)

the pattern is consistent with enrichment. However, there is no way of rejecting the alternative explanation, that the normalising element is depleted in the surface sediment while the metal flux remains constant (Fig. 5).

Globally referenced enrichment factors suffer because local compositions are generally very different from the global average, due to very great natural local heterogeneity. Tapia et al. (2012), for example, demonstrated that average crustal concentrations are of no use in assessing heavy metal enrichments in the mineralised regions of Bolivia.

Enrichment factors, whether locally or globally referenced must always be treated cautiously. A high or low EF tells us no more about local pollution than about local bedrock characteristics. If weathering does indeed also come into play, as suggested by Das et al. (2008), then the EF values depend on even more unknowns and unrelated properties and must be interpreted only with the very greatest of caution. To illustrate this point one need only look at the widely varying preindustrial sediment concentrations seen for Cu, Ni and Zn in Arctic Canada (Wolfe and Hartling 1997), the English Lake District (Mackereth 1966), the Alps (Koinig et al. 2003) and in Er Hai, Yunnan Province, China (Fig. 3b), and for Hg in Greenland (Lindeberg et al. 2006). All of these would be revealed as pollution according to any of the published EF schemes, and yet are of wholly natural origin.

Fluxes and Mass Balance

The methods described above are wholly empirical, and referenced to local benchmarks that smooth out geographical factors, or to global benchmarks that are generally a poor guide to actual catchment materials. This means that there is no theoretical framework by which to interpret the results, and no interpretation can be judged more reasonable than any other as there is no mechanism for assessing reasonableness. An alternative approach is to apply a mass balance method which provides externally referenced estimates of an expected result. Thus Gallagher et al. (2004), studying six lakes from British Columbia, used not just concentrations but mass fluxes to assess plausible sources. With quantitative estimates of fluxes, though they cannot rule out natural change, they can at least compare observed with expected pollutant loading, allowing plausibility to be established. Conversely, Boyle et al. (2004) in failing to observe any clear anthropogenic heavy metals signal in five of size cores in Svalbard are able to show that the likely anthropogenic atmospheric fluxes are too weak to be detected. Curiously, this powerful approach, put to great effect by Garrels and Mackenzie (1971) in application to global fluxes, has been little used in the analysis of sediment heavy metal records. Two exceptions to this are with the increasing use of Pb isotopes, discussed below, and some mass balance modelling of lake sediment heavy metal fluxes (Boyle et al. 1998; Boyle and Birks 1999; Rippey 2010). A powerful argument in favour of this approach has been presented recently by Engstrom and Rose (2013).

Normalisation to ^{210}Pb

Quantitative treatment of heavy metal fluxes in lake sediment raises the problem of interpreting sediment accumulation rates. A measured sediment mass accumulation rate for a single core partially reflects the average lake-wide sedimentation flux, and partly local factors that result in sediment focussing. In general, it is the lake-wide flux that is needed (to assess pollution loading, for example), so any focussing effects must be quantified and corrected. Various predictive models have been developed over the years (Håkanson 1977, 1981; Rowan et al. 1992; Håkanson 2003), but while the general trends are well known, prediction of focussing at specific coring location remains highly uncertain (Terasmaa 2011). The alternative is to use ^{210}Pb inventories as a direct measure of focusing (Rowan et al. 1995a), improving estimation of lake-wide sediment fluxes from single cores. While not as good as using multiple cores, 5–10 cores being recommended (Rowan et al. 1995b) sensible values can be obtained with single cores, as was shown by Krom et al. (2009) in Scottish sea lochs in their assessment Zn and Pb pollution.

Isotopic Signature and Mixing Models

Studies in which heavy metal isotopes are used in conjunction with their concentration values (e.g., Fig. 6) show far greater interpretational value than either alone (Brännvall et al. 1997, 2001, Renberg et al. 2002). The more recent application of binary mixing models to these data are proving very powerful (Brugam et al. 2012) as a tool in source quantification.

The long established Pb isotopes method has more recently been added to by isotopic studies of both Cu and Zn (Thapalia et al. 2010), showing similar power for discrimination of heavy metals sources.

Part II: Applications

Lake sediment records of heavy metals have been used for nearly 50 years (Thomas 1972), and have been applied to an extraordinarily wide range of environmental questions. The topics listed here represent the breadth and depth of this work.

Chronological Markers for Other Research

Where pollution histories are well known, either from extensive palaeoenvironmental research or from documentary records, the stratigraphy of heavy metals in lake sediments can provide a method for establishing, or contributing to the establishment of, sediment chronologies. Indeed, many studies use sediment records of heavy metal pollution solely to obtain chronological information, typically relying on mining/industrial production data to secure the chronology. Such an approach may be regional in scope, as with the exemplary nation-wide investigation of Pb concentration and isotopic character in Sweden (Renberg et al. 1994; Brännvall et al. 2001), leading to concepts that are applicable at least as far away as Britain (Eades et al. 2002; Yang et al. 2002; Oldfield et al. 2003). Or it may be local in character, exploiting the known history of specific mines or industries. This latter may

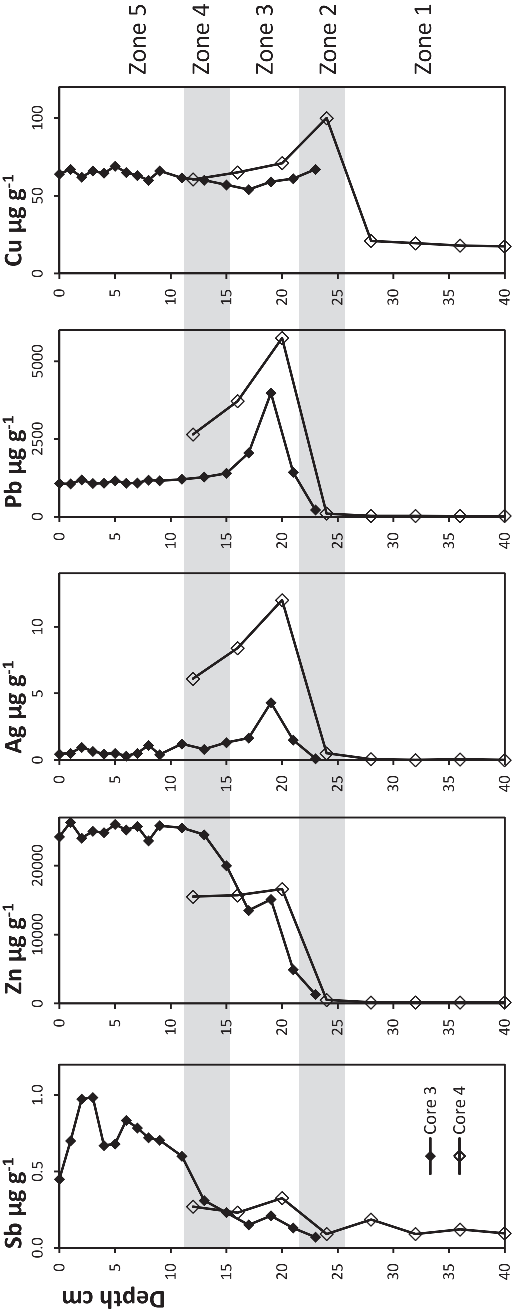

Fig. 6 Complex heavy metal record at Verkasjön (Data from Backstrom et al. 2006). Zone 1: pre-mining; Zone 2: Cu smelting from 1830–1860; Zone 3: onset of Zn mining at Zinkgruven (1863), and ore dressing at Mårsäter (1877–1881); Zone 4: continued mining at Zinkgruven until 1945; Zone 5: long transported pollution

take the form of chronological links between single elements and specific events in the mining record (Dearing 1992; Grayson and Plater, 2009), or may include multiple elements and multiple phases of mining as illustrated in Fig. 7 for Lake Verkasjön, Sweden. Bäckstrom et al. (2006), by relating different elements to stages in the industrial development of the Salaån River catchment, are able to provide a far more robust chronology for Verkasjön than would be possible for a single metal or phase of mining. In another example, where the main objective was to document the impacts of mining and the subsequent recovery on mine closure, the Pb pollution record was used by Hammarlund et al. (2008) to improve their sediment chronology. Once established, a metal pollutant history that is well constrained in time provides an excellent means for chronologic correlation of cores in an individual lake basin. These chronological markers can then underpin assessment of spatial patterns of lake sediment accumulation. For example at Brotherswater (NW England) correlation of 12 cores shows there are sharp reductions in sediment accumulation rate with distance from the inflow delta (Schillereff, unpublished data).

Identifying and Quantifying Pre- and Post-mining Baseline States

Industrial activity has contaminated the terrestrial ecosystem to an extent that ecological harm has occurred. Such contamination predates any attempt at environmental monitoring. As governments have come to accept the need to restore soils, rivers, and lakes to their pre-contamination state, the question has arisen of exactly what this means. Palaeoecology is well suited to this task, as amply demonstrated in the cases of acidification (Battarbee et al. 1996, 2005) and eutrophication (Battarbee 1997; Bennion et al. 2004, 2011). More recently, several research groups have started the task of characterising background environmental heavy metal concentrations. Catalan et al. (2013) review evidence for metal pollution (and other substances) at lake sites across Europe and North America remote from local disturbance, stressing their role in providing benchmarks against which to evaluate current trends. Bindler et al. (2011a) used lake sediment records of Cd, Cu, Hg, and Pb to assess the meaning of the European Union's Water Framework Directive "reference conditions", and concluded that it is important to distinguish between "natural background conditions" which are those existing prior to human disturbance, and "reference conditions" which may constitute any well-defined point of comparison. They show that far deeper levels in the sediment must be sought for Pb natural conditions than is the case for Hg and Cd. Wei and Wen (2012) present a thorough analysis of sediment from Dianchi and Taihu to determine baseline conditions for central China. Tapia et al. (2012) do the same for a mineralised region of Bolivia. This is a field of research needing further development; it offers the potential to go beyond simple characterisation of "natural" or "reference" conditions, to assessment of mechanisms that might help assess the feasibility of achieving specific remediation targets. This is addressed in Sect. 2.4.

This generalising research builds on a longer history of identifying the dates and environmental characteristics of pre-industrial conditions at specific sites. For ex-

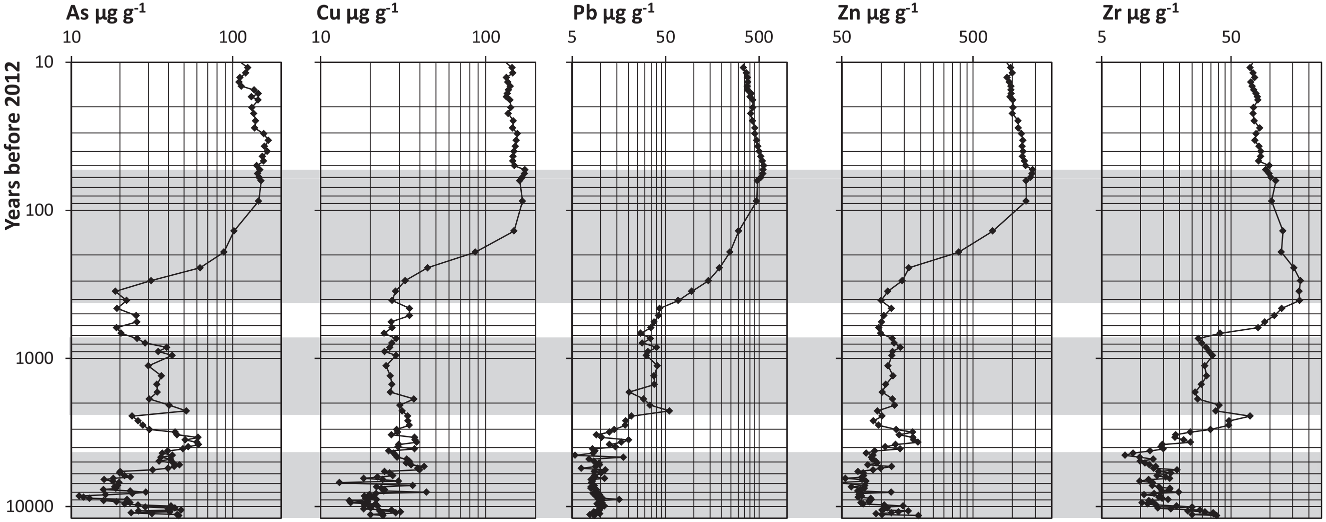

Fig. 7 Mining and metal working pollution at Hatchmere, Cheshire, UK (unpublished data, D. Alderson). This reveals erosion (Zr) and Zn mining in Bronze Age (4 ka), Pb mining Iron Age (2.7 ka), enhanced soil erosion (1300 AD), onset of recent Pb pollution (1600 AD), and onset of Zn and Cu pollution (ca. 1700 BP), peaking in the mid-twentieth century

ample, Farmer et al. (1997) use lake sediment records of Cu, Pb and Zn to provide a benchmark for the onset of renewed mining on the Scottish Highlands at Tyndrum. Audry et al. (2004) show strong enrichment in Cd and Zn in three reservoirs of the Lot River (southwest France) due to smelting and mining. They use their data to determine pre-mining baseline Cd and Zn concentrations for the Lot-Garonne fluvial system, using the Geoaccumulation Index (see Eq. 3) of (Müller 1979) to classify the state of metal pollution. Ahmed et al. (2005) assess pre-pollution conditions in Dhaka City for Pb and Zn using two lake sediment records.

Lake Sediment Heavy Metal Records to Quantify Pollution Loading Histories, or to Identify Pollution Sources

With due care in choice of lake site, coring location, number of cores, and independent sediment chronologies, and with an informed approach to understanding natural heavy metal dynamics, lake sediments provide a uniquely high quality source of historical information about heavy metal pollution. The earliest studies focussed on known regional pollution hotspots, on metals known to be scarce in nature, and aimed to establish the pollution history or demonstrate the importance of local factors within the broader story. The studies of Hg and Pb (Thomas 1972; Aston et al. 1973; Kemp and Thomas 1976) broadly fit this category. Such work continues, but increasingly studies address specific local questions or the impact of long-transported heavy metal pollution at sites remote from industry. A particularly fruitful area has been the establishment of reliable pollution records in areas of historic and prehistoric mining or industry.

In Britain, Farmer et al. (1997) studied the historical Cu, Pb and Zn mining legacy of the southern Scottish Highlands in Loch Tay, showing the link to metal mining in the wider catchment. Eades et al. (2002) used both concentrations and isotopic composition of Pb to extend this analysis more widely across Scotland, showing stages in evolving contamination starting with coal burning before 1820, through local mining and smelting during the nineteenth century, to international sources of Pb for fuel later. Further south, the impact of nineteenth century Cu mining on the composition of sediment in Coniston, English Lake District, was studied by Davison et al. (1985). It was shown that Cu was transported in particulate sulphide form in surface water, and dispersed quite efficiently throughout the lake, though most concentrated near the source. Investigations at both Brotherswater (Schillereff, in prep) and Bassenthwaite Lake (Chiverrell, Sear, Dearing, Warburton and Schillereff, unpublished data) show a strong match between historical mining production metrics (e.g. Tylmann 2005) and metal concentrations preserved in the lake sediment record. In the case of Bassenthwaite Lake this recorded successive phases of Cu, Zn, Pb and Ba extraction. For lowland Britain, the magnitude of Pb and Zn pollution from heavy industry was demonstrated by Foster and Charlesworth (1996). This is illustrated for a small rural lake, Hatchmere (Cheshire, UK, Fig. 7), showing a suite of changes starting in the Bronze Age, but which are dominated by the legacy of the Industrial Revolution that dwarfs even the impact of leaded fuel.

In Sweden, a number of large studies have investigated long and complex mining histories. Ek and Renberg (2001) used a multi-lake study of the region around the Falun copper mine in west-central Sweden, demonstrating acidification in the early seventeenth century associated with a rapid expansion of the already ancient mine. More than 300 years later, the region remains severely polluted. Later, Bindler et al. (2009) used a large multi-lake study of an entire catchment draining this region to show that water transport dominated the local signal for Cu, Zn, Pb and Hg. In the same area, but looking at the whole Holocene, Hammarlund et al. (2008) used the Fe, Pb and Zn sediment records to link to the Cu and Fe mining of region, and to long transported Pb. Bindler et al. (2011b) focused more specifically on the 1000 year history of Swedish Fe working using lake sediments. The detailed study at Lake Verkasjön, farther south in Sweden (Bäckstrom et al. 2006), has been addressed above. Together, these studies build up an accurate record of the industrial history and the environmental consequences for a large area of central Sweden. Across the Baltic in Estonia, the legacy of oil shale mining and power generation in terms of heavy metal fluxes was assessed by Punning et al. (1997), distinguishing direct pollution effects and indirect disturbance of the hydrology.

In a rather different setting and with a far shorter pollution history, a suite of studies has investigated the legacy of heavy industry in North America. Sprenke et al. (2000) provided a quantitative characterisation of late nineteenth and early twentieth century heavy metal contamination in lateral lakes along the Coeur d'Alene River, Idaho, a legacy of upstream mining. Further east, at St Louis, Missouri, Vermillion et al. (2005) evaluated the impact of Pb smelting, active since the late eighteenth century. Combining concentration data, Pb/Ti ratios and Pb isotopes, they successfully demonstrate a progressive intensification of smelting impacts leading to a peak around 1950s. Recycling of battery lead after 1950 then led to a distinctive change in the isotopic signature demonstrating the power of the method for source discrimination. Across the Great Lakes region Drevnick et al. (2012) showed a pattern of variation in Hg accumulation reflecting both an interplay between local point sources and atmospheric deposition, and document the impact of emission reductions over the last few decades. Further south, in Colorado, Gray et al. (2005) used sediment records of the late twentieth century to assess possible sources of Hg contamination. They showed that coal burning is the most likely explanation. At a larger spatial scale, detailed analysis of Cu and Hg in multiple short cores from Lake Superior show the complex interplay or early mining and metal working, followed by later long transported atmospheric pollution (Kerfoot et al. 1999; Kerfoot et al. 2004). This work also revealed high natural baselines, as might be expected for a region suitable for mining.

The preceding examples all depend on good chronological control for the sediment record in order to link to the documented environmental data. A subset of studies into sediment records of heavy metal impacts, though using sediment chronology for other reasons, used the same sediment core to measure both the disturbance (increased heavy metal contamination) and ecological response, thereby avoid the problem of synchronising records. For example, Kauppila (2006) assessed Ni loadings near smelters in western Finland to assess whether cessation of activity has changes the loading, and whether this in turn reduced ecological stress. Salonen et al. (2006) did this for diatoms and chrysophytes near a Cu mine in Finland. Effects of mine tailings from gold mining, including large qualities of Hg, were assessed in Nova Scotia (Wong et al. 1999).

Many other such studies exist, far too numerous to list here, much less describe and discuss. These range from regions in central Europe with long mining histories such as (Tylmann (2005); Thevenon et al. (2011); Thevenon and Poté (2012), areas with current rapid expansion of industrial activity (Rose et al. 2004), and polar regions where long-transported pollution is surprisingly evident (Muir and Rose 2004). It is this field of geochemical palaeolimnology which has proved the most successful, a consequence of its sound theoretical basis; its continuing application seems certain.

Identifying Pollutant Pathways or Environmental Processes Regulating Heavy Metals

The applications described in the preceding sections are essentially empirical in purpose: studies designed to generate evidence needed to define system states and test for change. However, these same, or similar, studies can be used to formulate, parameterise or test process models describing the fluxes and fate of heavy metals in soils, rivers, and lakes. The following studies illustrate this approach to assess the migration of heavy metals through soil to watercourses. Shotbolt et al. (2006) used reservoir sediment records of Pb and Zn to demonstrate delayed supply of Pb to the lake from its catchment. The delayed delivery of Pb and Hg from catchments to lakes was clearly shown for both long transported contamination of mountain soils (Yang et al. 2002; Yang and Rose 2005) and localised Hg pollution associated with the weaving industry in Diss, UK (Yang 2010). Data of this type have been used to generate a conceptual model of transfer mechanisms for Pb and Hg (Rose et al. 2012).

At the still longer time scale, Bindler et al. (2008) developed a conceptual model of pollutant supply, storage, and fate in Sweden over the last 4 millennia. They showed that even following current emissions reductions, atmospheric Pb fluxes are still 2 to 3 orders of magnitude above the natural baseline, and that despite this recent aggravation, more than half the total atmospheric loading in Sweden was deposited prior to modern industrialisation. This allows them to provide robust estimates of recovery rates for catchment soils, finding the legacy of the last 150–500 years of deposition dominates topsoil inventories, greatly reducing the benefit of recent regional emission reductions.

The above-described delay effect is still more striking in mining districts. For example, Wong et al. (1999) found no decrease in the export of As, Hg, Pb to lakes from gold mine tailings at the Goldenville, Nova Scotia, 50 years after mining ceased. At Bassenthwaite Lake and Brotherswater in the English Lake District, present-day lake sediment Pb concentrations are 300–400 ppm, down from the 19th century peak of 3000–4000 ppm, but still 10–15 times higher than the pre-mining values (Chiverrell and Schillereff, unpublished data).

Concluding Statement

The assessment of heavy metal pollution is one of the most successful and widely used applications of palaeolimnology. It holds this position owing to its sound theoretical basis, and straightforward procedures. Provided sediment mass accumulation rates are well constrained and natural heavy metal fluxes can be reliably established, then chemical palaeolimnology provides accurate and reliable quantification of environmental heavy metal fluxes.

Nevertheless, there is much potential for error. Natural variation in heavy metal fluxes can be large relative to pollution fluxes. In such cases, reliable interpretation of heavy metal concentration records requires a thorough understanding of natural processes. The various enrichment factor methods, all validly applicable under suitable conditions, may readily lead to misinterpretations where their underlying assumptions are invalid. This is particularly likely where there are changes in sediment particle size and thus particularly likely in recent sediments over the time frames over which heavy metal contamination records are of interest.

It might be supposed that Pb-isotope approach would avoid this problem. However, this need not be the case. Pb-isotopes are fractionated between rock forming minerals, and so are also subject to particle size sorting effects. It is preferable then that particle size effects are properly investigated and correctly handled.

All existing methods for the interpretation of heavy metal pollution records in lake sediment would be more reliable if appropriate mass balance modelling were done in conjunction. This would serve to assess the geochemical plausibility of any interpretations. This field of research is ripe for improvement, as there is both wealth of good quality data and a well-developed theoretical basis for quantitative modelling.

Isotopes procedures, though not without their methodological issues, have revolutionised heavy metal sediment record interpretations by avoiding dilution effects when assessing potential sources. Further development of these methods has great potential for the future.

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Organic Pollutants in Sediment Core Archives

Jennifer B. Korosi, Wenhan Cheng and Jules M. Blais

Abstract Organic contaminant profiles in lake and marine sediment cores are important for understanding the persistence of pollutants in aquatic ecosystems, as well as for evaluating the success of emission restrictions and regulations. Several different classes of organic contaminants can be reconstructed from cores. The earliest studies measured PCBs, DDT, and polycyclic aromatic hydrocarbons, but paleolimnological approaches are now common for a suite of organochlorines and brominated flame retardants, as well as emerging studies on fluorinated persistent organic pollutants and historical sewage indicators (fecal sterols). In order for the history of organic contaminant inputs to be successfully reconstructed from sediment cores, the contaminant must have a high affinity for sedimentary particulates and low water solubility, ensuring its rapid delivery and incorporation into the sediment record, and minimal porewater migration once it is deposited. In addition, the compound must be resistant to microbial degradation and post-depositional transformation, so that any changes in composition and abundance down-core may be confidently attributed to changing contaminant inputs to the aquatic environment. Using several independent lines of evidence, we review the reliability of sediment cores as historical archives for organochlorines, brominated flame retardants, perfluoroalkyl substances, polycyclic aromatic hydrocarbons, and fecal sterols. The objective of this chapter is to provide a framework for researchers to critically evaluate the reliability of sediment cores for reflecting historical inputs of legacy and emerging organic contaminants.

Keywords Organochlorine compounds · Polychlorinated biphenyls (PCBs) · Dichlorodiphenyltrichloroethane (DDT) · Dechloranes · Flame retardants · Polybrominated diphenyl ethers (PBDEs) · Perfluorooctane sulfonate (PFOS) ·

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Perfluorooctanoic acid (PFOA) · Perfluorocarboxylic acid (PFCA) · Polycyclic aromatic hydrocarbons (PAHs) · Fecal sterols · Coprostanol

Introduction

Since the pioneering studies of the late 1970s (e.g. Hites et al. 1977; Müller et al. 1977; Frank et al. 1979), there has been a rapid increase in the number of studies utilizing organic contaminants preserved in lake sediment cores to reconstruct the input history of chemical pollutants to lakes, rivers and coastal zones. Many persistent organic pollutants of environmental concern are strongly hydrophobic, with a high affinity for sorption onto organic matter and suspended particles through which they eventually become incorporated into the sediments of aquatic ecosystems. The ultimate distribution of organic contaminants in sediment cores is determined by a range of factors, including those that influence inter-media transport to the sediments (e.g. sorption onto organic particles, tendency to revolatilize to the air), and factors influencing their preservation over decades (e.g. resistance to biodegradation). Site-specific factors such as sedimentation and resuspension rates, organic matter content, and redox conditions at the sediment-water interface all influence the preservation of organic contaminants in a sediment core, as well as the characteristics of the compound itself that determines its mobility in the porewater and vulnerability to degradation. In general, chemical compounds that have low water solubility, a high organic carbon—water partition coefficient (K_{oc}) and a long half-life (years to decades) that are resistant to post-depositional transformation are likely to be well preserved in the sediments, allowing trends in their historical deposition to be reconstructed from sediment core chronologies.

Sediment cores have the potential to provide critical insights on the environmental fate of persistent organic pollutants, including whether recent production and emission controls have been successful in reducing their environmental impacts. Therefore, critical examinations of the reliability of sediment cores for reflecting depositional histories of organic contaminants are essential for the success of this approach. Some examples of methods that can be employed to evaluate the reliability of sediment cores in elucidating depositional histories of organic contaminants include: (1) comparisons of sedimentary profiles against known histories and/or modeled chemical profiles; (2) mass balance analysis to compare recorded deposition rates against known historical fluxes to a water body; (3) comparisons with profiles of inorganic contaminants that have a similar emission history; (4) evaluation against radioisotopic dating profiles, for example matching down-core trends in organic contaminants with peaks in ^{137}Cs released during atmospheric nuclear arms testing; and (5) examinations of compositional changes over depth to assess degradation rates. Although the question of the reliability of sediment cores as contaminant archives is crucial, limited attempts have been made to systematically examine their preservation in lake sediments, and the ability of sediments to archive anthropogenic contaminant deposition in the environment. Using the multiple lines of evidence outlined above, we critically examine the reliability of sediment cores as archives for several legacy and emerging natural and anthropogenic organic pollutants commonly measured in sediment cores, including chlorinated and brominated persistent organic pollutants (POPs), fluorinated POPs, polycyclic aromatic hydrocarbons, and fecal sterols. We focus mainly on post-depositional processes, and only briefly touch upon the processes that may alter organic contaminants before their burial in the sediments.

Chlorinated Persistent Organic Pollutants

The anthropogenically-derived organochlorines are a diverse group of (mainly) synthetic compounds produced as industrial chemicals, pesticides, or as unintended byproducts of manufacturing. Many organochlorines have been identified as persistent organic pollutants, including the original "dirty dozen" listed under the Stockholm Convention on Persistent Organic Pollutants in 2001. These compounds are now either banned or regulated in many countries, resulting in well-defined histories of production (Fig. 1). For example, widespread market production of dichlorodiphenyltrichloroethane (DDT) as an agricultural insecticide began in the 1940s after World War II (Hassall 1982), as a result of an improved global economy in many industrialized countries and new scientific research into insecticides to improve agricultural production for a rapidly expanding global population. It was banned in the United States in 1972, followed by a worldwide ban in agricultural use under the 2001 Stockholm Convention on Persistent Organic Pollutants. Likewise, a technical hexachlorocyclohexane (HCH) mixture became widely used in the 1940s and was restricted in Canada and the USA around 1970, although the gamma HCH isomer (an insecticide called lindane) was still used until a global ban took place in 2009 under the Stockholm Convention (Secretariat of the Stockholm Convention 2009). The polychlorinated biphenyls (PCBs), which consist of 209 separate congeners possessing anywhere from one to ten chlorines on its biphenyl ring (Fig. 2), were first introduced as lubricants and insulators starting in the 1920s. They were produced extensively from 1930 until the mid-1970s, with peak production and usage in the USA occurring in 1970 (Oliver et al. 1989), followed by a gradual decline until its global ban in 2001 under the Stockholm Convention.

Chlorinated persistent organic pollutants are semi-volatile, and have the unique character of exhibiting a global distribution and relatively uniform history of deposition. They can be delivered to aquatic ecosystems in many ways, including through effluent release (e.g. wastewater treatment plants), atmospheric deposition, or run-off. High affinity for organic matter, strong hydrophobicity, long half-life, and resistance to biodegradation is characteristic of the halogenated persistent organic pollutants, and leads to their accumulation in sediments. For example, the half-life of DDT in lake sediments has been estimated at 14–21 years, while its breakdown products DDE and DDD are also highly persistent with similar chemical and physical properties (CCME 1999). As a result, most paleolimnological studies

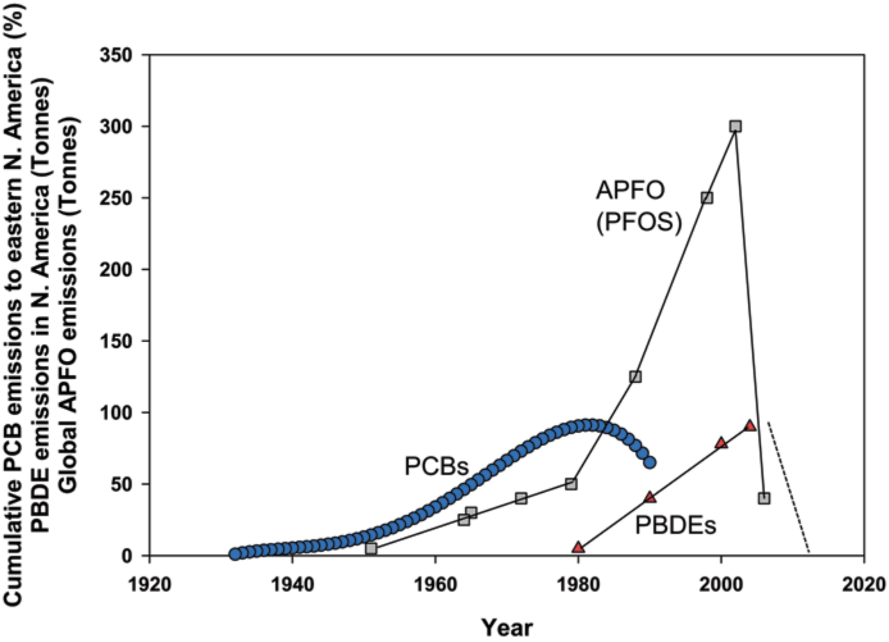

Fig. 1 Emission histories of PCBs, PBDEs, and APFO (a derivative of PFOA). Data sources are: PCBs, Rapaport and Eisenreich (1988); PBDEs, Li et al. (2006); APFO, Prevedouras et al. (2006) The *dashed line* represents the decline in PBDE emissions in North America based on expected phase out of deca BDE by end of 2013 (U.S. Environmental Protection Agency DecaBDE Phase-out Initiative). (See: http://www.epa.gov/oppt/existingchemicals/pubs/actionplans/deccadbe.html)

on DDT will measure ∑DDT, the sum of DDT, DDD and DDE. Triclosan, an antimicrobial agent used in personal care products that has also been measured in sediment cores (Cantwell et al. 2010), has an estimated half-life of 540 days, has a log K_{ow} (octanol-water partition coefficient) of 4.8, and a log K_{oc} of 4.26 (Halden and Paull 2005). For PCBs, water solubility and resistance to biodegradation tends to be inversely related to the degree of chlorination (Borja et al. 2005). The most commonly studied organochlorines in paleolimnological studies are PCBs and ∑DDT (e.g. Eisenrich et al. 1989; Santschi et al. 2001), but dioxins (e.g. Baker and Hites 2000), dechloranes (e.g. Hoh et al. 2006), hexachlorocyclohexanes (HCH) (e.g. Kim et al. 2007), polychlorinated naphthalenes (PCNs) (e.g. Helm et al. 2011), and chlorinated paraffins (e.g. Iozza et al. 2008) are also frequently measured in lake sediment cores. In contrast, other important organochlorines are not as readily deposited in the sediment record. For example, kepone has higher water solubility relative to other organochlorines, and was not detected in the sediments of the Laurentian Great Lakes (Yang et al. 2011). Similarly, lindane (γ-HCH) was only present in low concentrations in the sediments of the Great Lakes, and has a much lower tendency to partition to the sediments than would be predicted based on its K_{ow} (Oliver et al. 1989).

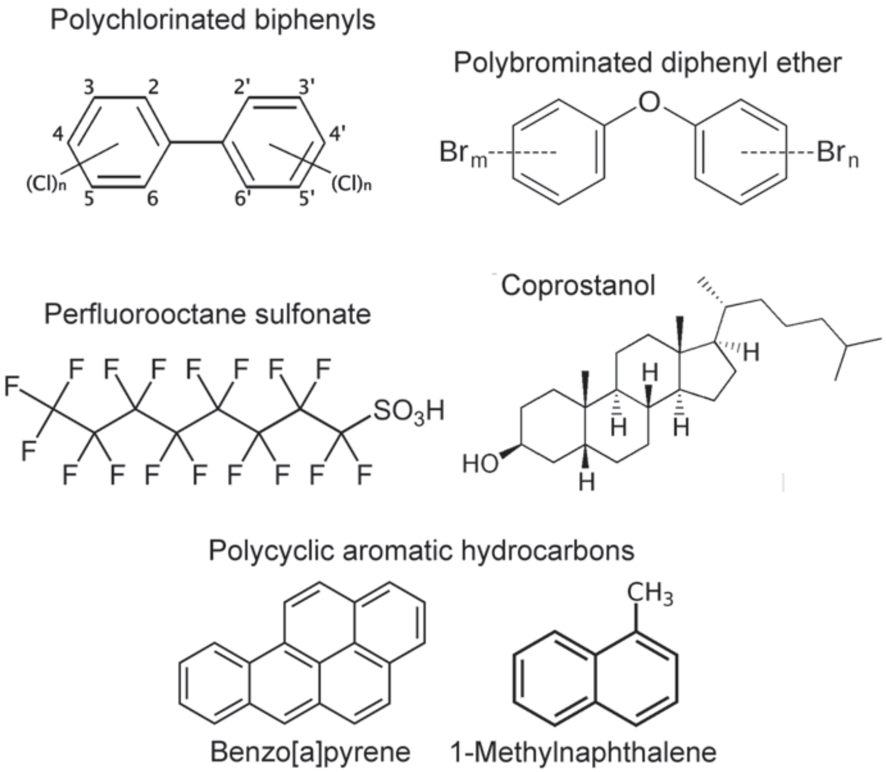

Fig. 2 Examples of the chemical structures of some of the organic contaminants discussed in this chapter

Well-defined histories of chemical production are advantageous for assessing the reliability of sediment cores as archives of pollution, and temporal sediment-based studies of DDT and PCBs provided some of the first evidence that sediment cores could be used to reconstruct the history of organic contaminant deposition in lakes (e.g. Frank et al. 1979). Numerous studies have shown excellent agreement between the chronology of chemical deposits (e.g. PCBs, DDT, Mirex, dibenzo-p-dioxins, and HCB) in dated sediment cores and the actual histories of chemical usage globally (e.g. Bopp et al. 1982 and Van Metre et al. 1998 for northeastern North America; Desmet et al. 2012 for Europe; Barra et al. 2001 for South America; Kim et al. 2007 for Asia; Muir et al. 1995 for the Arctic) (Fig. 3). For example, in Lake Thun, Switzerland, time trends for PCBs, PCNs, and DDT reconstructed from sediment cores were consistent with modeled emissions (Bodgal et al. 2008). PCBs reached peak concentrations in the 1960s, slightly later than the peak observed for PCNs (PCN usage declined following widespread production of PCBs), and the concentrations of PCBs and PCNs in sediment cores reflected the estimated production ratio of 10:1 (Bogdal et al. 2008). DDT concentrations peaked in 1952, 10 years after their introduction to the market as an agricultural pesticide (Bodgal

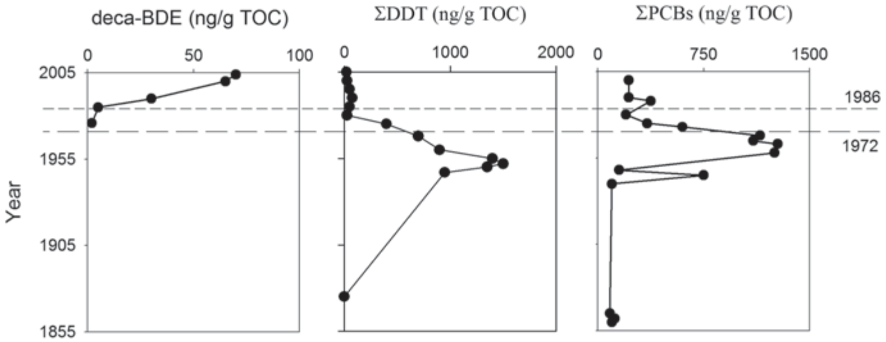

Fig. 3 A comparison of sedimentary chronologies for deca-BDEs, DDT, and PCBs in a sediment core from Lake Thun, Switzerland. Deca-BDE began to increase in the 1980–1990s and continue to increase in the surface of the sediment core, as fully brominated DecaBDE is still in use. PCBs reached maximum sedimentary concentrations in 1965, and showed large declines post-1972 when regulatory measures for PCBs were enacted in Switzerland. A complete ban on PCBs in Switzerland was put in place in 1986. The peak in DDT occurred in 1952, 10 years after its introduction to the market, and concentrations declined after its use was prohibited in 1972. (Data are from Bodgal et al. (2008))

et al. 2008). Decreases in sedimentary concentrations for PCBs, PCNs, and DDT were observed following 1970 emission regulations (Bogdal et al. 2008) (Fig. 3). In Kempenfeldt Bay (Lake Simcoe, Ontario, Canada), historical inputs of PCBs, dibenzo-p-dioxins, and PCNs increase from the 1930s to peak concentrations in the 1960s, consistent with emissions history as well as sediment cores from the nearby Laurentian Great Lakes (Helm et al. 2011). Similar to Lake Thun, a slightly earlier peak was observed for PCNs compared to PCBs (Helm et al. 2011). In White Rock Lake (United States), PCBs were not detected prior to 1950, reached peak concentrations of 21 µg/kg in 1961, and decreased to 3 µg/kg in the surface interval (Van Metre et al. 1997). Triclosan was measured in sediment cores from four urbanized estuaries along the Atlantic Coast of the United States, and its initial appearance in each core corresponded to the 1964 US patent issuance date for triclosan (Cantwell et al. 2010). This was verified by the 1963 sediment ^{137}Cs fallout maxima, representing the height of atmospheric nuclear arms testing (Cantwell et al. 2010).

There are several examples where sediment core profiles for organochlorines do not match historic usage patterns; however, these exceptions are often easily attributed to local factors (e.g. pollutant sources, sedimentation processes), and do not reflect poor preservation of organochlorines in sediment cores. For example, the lack of distinct maxima for chlorinated organics can sometimes be attributed to sediment mixing by comparison with radioisotopic dating profiles, corroborated by a similar lack of a clearly defined ^{137}Cs peak (Oliver et al. 1989). In particular, it is common to observe sedimentary profiles where peaks in organochlorines occur much later than peaks in historic usage. For example, in an investigation of PCBs in sediment cores from the Rhône River (France) downstream of the city of Lyon, peak PCB concentrations occurred in the 1990s, much later than regulations on PCBs enacted in the 1970s, while sediment cores taken upstream from Lyon and in an off-river, rural reference site showed PCB peaks in the 1970s and declines thereafter, as expected (Desmet et al. 2012). This suggests that industrial discharge from the city of Lyon is still a significant source of PCBs to the Rhône River (Desmet et al. 2012). In Lake Mead, a large reservoir in Nevada and Arizona, USA, DDT persisted in sediment cores for more than a decade after restrictions on DDT use, as a result of local sources of DDT from a manufacturing plant in Las Vegas (Rosen and Van Metre 2010, see Rosen, this volume). In comparison, where there was no local source of PCBs, PCB concentrations in the sediments peaked in the 1970s when the ban was enacted (Rosen and Van Metre 2010). Similarly, Santschi et al. (2001) recorded more dramatic decreases in PCBs compared to DDT after their ban in the early 1970s, and inferred that heavy application of DDT to agricultural crops in the lower Mississippi watershed prior to its ban still contribute diffuse sources of DDT in the Mississippi River Delta. The appearance of PCBs in High Arctic lake sediment cores was delayed by ~20 years compared to lower latitudes, with concentrations continuing to increase into the 1990s, consistent with the global fractionation model (Muir et al. 1996).

Collectively, the studies described above demonstrate that sediment cores can reasonably archive organochlorine pollution in aquatic environments. However, laboratory studies have also shown that, while these compounds are persistent, they can undergo dechlorination in the environment (summarized in Borja et al. 2005), potentially altering their composition down-core. In order to investigate the potential for dechlorination to occur following burial in the sediments, changes in chemical composition, for example PCB congener patterns, can be examined in surface sediment samples and down-core profiles to compare with commercial mixtures. For sediments, the most prevalent pathway of degradation occurs via anaerobic reductive dechlorination by microbes. In sediments from Woods Pond, Massachusetts (USA), mass balance analysis of PCB congeners demonstrated that the PCB congener distribution in the sediments most plausibly resulted from modest rates of dechlorination (mainly from the *meta* and *para* positions) of Aroclor 1260, which was released through effluent into Woods Pond; however, the extent of dechlorination was variable even for samples located close together (Bedard and May 1996). In general, rates of PCB dechlorination are lower for anaerobic degradation pathways compared to aerobic pathways, and degradation rates also increase as a function of temperature. Therefore, the cool, anaerobic conditions present in lake sediments should significantly reduce the rates of reductive dechlorination. In support of this, PCB composition in Lake Ontario sediment cores were observed to shift from less heavily chlorinated congeners to more heavily chlorinated ones downcore, which is the opposite pattern you would expect if dechlorination was occurring (Oliver et al. 1989). Moreover, this shift occurred at the same time interval (corresponding to different sediment core depths) in each core, suggesting that this shift is related to a changing PCB source and not diagenetic processes (Oliver et al. 1989). Although down-core degradation of organochlorines may be minimal, the PCB congener signal in the sediments will likely differ somewhat from that of suspended particles in the water column, which should be taken into account when using sediment cores to reflect historical organochlorine inputs.

In addition to legacy organochlorine contaminants such as PCBs and DDT, sediment cores continue to provide an important historical archive for many emerging chlorinated persistent organic pollutants. For example, Dechlorane Plus (DP) and other DP-like substances (e.g. Dec 602, 603, 604) have only recently been found in the environment despite a long production history as flame retardants (Hoh et al. 2006; Sverko et al. 2011). DP and DP-like substances have been identified by the European Commission as potential substitutes for polybrominated diphenyl ethers (PBDEs), but their global distribution and environmental persistence makes them potential candidates for evaluation under Annex D of the Stockholm Convention on POPs (Sverko et al. 2011). To date, down-core sedimentary investigations of DP and Dec 600s are limited to the North American Laurentian Great Lakes (Hoh et al. 2006; Shen et al. 2011; Sverko et al. 2010; Yang et al. 2011). In general, these studies tend to show maximum concentrations occurring in the 1980−1990s followed by decreases, although trends in post-1990s declines differ somewhat between sites. In a sediment core from Lake Ontario at the mouth of the Niagara River (the site of a manufacturing facility), a dramatic post-1980 decrease in DP was observed, likely related to the installation of an industrial wastewater treatment facility (Sverko et al. 2010). In sediment cores from Lake Superior where the main source is atmospheric deposition, DP and Dec 602 are still increasing (Yang et al. 2011).

Chlorinated paraffins (CPs) are a group of chemicals that have been produced since the 1930s, and still have widespread industrial applications. CPs were measured in a sediment core from Lake Thun (Switzerland) along with PCBs, and an increase in CP concentrations was observed in the 1980s, with concentrations stabilizing in recent decades (Iozza et al. 2008). There has also been a continuous increase in chlorine content of CPs over the last 20 years, but it is unclear whether this is indicative of down-core dechlorination or shifting industrial CP mixtures (Iozza et al. 2008). Sediment core studies on both legacy and emerging organochlorines have greatly contributed to our understanding of their pathways and persistence in the environment, and continue to provide critical information on the success of emission restrictions and government regulations.

Brominated Flame Retardants

Brominated flame retardants (BFRs) are chemicals used in consumer products to increase fire resistance, and have become a growing concern due to their expanded production in response to stricter fire regulations, especially in recent decades. As a result, production of flame retardants has increased dramatically in the last three decades. Major sources of flame retardants include plastics, textiles, furniture, clothing, and electronic devices. The brominated flame retardants are among the most frequently used due to their low cost and ease of manufacture (Birnbaum and Staskal 2004). Similar to the chlorinated aromatics produced earlier, the brominated flame retardants are hydrophobic (log K_{ow} generally 5-10), bioaccumulative, and extremely resistant to degradation (Alcock et al. 1993). These chemicals may either be incorporated in a chemical polymer or mixed into a substance as a chemical additive. It is these additives that are most likely to leach from manufactured goods and be released into soil, air, water, and ultimately sediment. Polybrominated diphenyl ethers (PBDEs) (Fig. 2) became widely used in commercial and domestic products since the 1980s, increasing from 40 kt/yr in 1990 to over 70 kt/yr by the late 1990s (Wania and Dugani 2003). By the early 2000s, the penta PBDE formulation was phased out of production, leaving the octa and deca formulations in continued use. The result was a shift toward more brominated formulations of PBDEs after the early 2000s, though the final phase out of deca-BDE in North America was expected for the end of 2013 (US EPA 2013) (Figs. 1 and 3).

Similar to the chlorinated POPs described above, there is a rich scientific literature available that uses sediment cores to track the history of BFRs as environmental pollutants, especially for the PBDEs. Also similar to the organochlorines, time-trends of BFRs reconstructed from sediment cores are mostly consistent with historical estimates of production and emissions (e.g. Bogdal et al. 2008; Helm et al. 2011; Johannesson et al. 2008). Chen et al. (2007) compared PBDE-209 flux to estuary sediment of the Pearl River Delta (PRD), the largest electronic and telecommunication equipment manufacturing base in China, against the gross industrial output of this industry in China. The doubling time of the telecommunications industry in China from 1987 to 2005 was 2.3 years, corresponding almost precisely with the doubling time of 2.6 years calculated for PBDE-209 in one of their sediment cores over the same time interval. A second core also exhibited a pronounced increase in PBDE-209 over the same time interval, but with a slower doubling time of 6.4 years, which the authors attributed to sediment resuspension at this location, resulting in sediment dilution and a slower response to the increased chemical burden by the industry. In the Clyde Estuary, U.K., PBDE-209 was the predominant congener increasing in the uppermost 10 cm, consistent with studies of U.K. house dust that was also dominated by PBDE-209 (Vane et al. 2010). In Lake Michigan and Lake Erie (Laurentian Great Lakes, North America), PBDE concentrations increased rapidly over the last 30 years (doubling times of 5–10 years), consistent with increasing market demand (Zhu and Hites 2005). In contrast, the polybrominated biphenyls, particularly BB-153, increased rapidly during the 1970s and peaked in the 1980s, approximately 5 years after the ban on BB-153 production and use in the USA (Zhu and Hites 2005).

PBDEs are made up of 209 congeners that are vulnerable to debromination in the environment, potentially influencing sediment core profiles. Many studies analyze changes in the ratios of deca-BDEs to all homologue groups to investigate the potential for debromination down-core. In general, congener patterns of PBDEs in sediment cores are stable over time, suggesting that *in-situ* debromination is minimal (e.g. Johannesson et al. 2008; Kohler et al. 2008). Wei et al. (2012) observed evidence of *in-situ* debromination for one water body in south-central Arkansas (USA) that received direct inputs of wastewater treatment sludge, but not in five additional, less impacted water bodies. In general, differences in PBDE congener patterns between sediments and technical mixtures are likely related to degradation pathways that occur prior to the incorporation of these compounds into the sediments (e.g. photodegradation of PBDEs in dust; Kohler et al. 2008), and therefore have minimal influence on the interpretation of down-core PBDE trends, although this bias should be considered when extrapolating sedimentary PBDE trends to infer historical inputs of PBDEs to the waterbody.

In the future, sediment cores will continue to be useful for evaluating the success of the recent phase-out of many brominated chemicals, and for evaluating whether emerging BFRs introduced to replace compounds such as PBDEs are having an environmental impact. For example, decabromodiphenylethane (DBDPE) was introduced in the early 1990s, and its production is projected to increase significantly following increased regulation and phasing out of PBDEs. Wu et al. (2012) analyzed DBDPE in sediment cores from three lakes in China, and first detected these compounds between 1980 (a result which may indicate vertical mixing in the sediment core) and 1998, with concentrations of DBDPE steadily increasing towards the surface of the cores, although DBDPE in the surface sediments is still lower than ∑PBDE. In 16 sediment cores from the Laurentian Great Lakes, emerging BFRs (e.g. DBDPE, 1,2-bis(2,4,6 tribromophenoxy)-ethane (BTBPE), hexabromocyclododecane (HBCD), 1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane (TBECH) and hexachlorocyclopentadienyl dibromocyclooctane (HCDBCO)) were analyzed alongside dechloranes and PBDEs, and as expected, the emerging BFRs had much lower sedimentary concentrations than the more established flame retardants (Yang et al. 2012). However, the doubling time was 3–7 years for DBDPE and 5–7 years for BTBPE, demonstrating that these compounds have the potential to contribute significantly to the contaminant burden of the Great Lakes in the future (Yang et al. 2012).

Fluorinated Organic Contaminants

Perfluoroalkyl and polyfluoroalkyl substances (collectively denoted as PFASs; Buck et al. 2011) are a group of manufactured organic substances that consist of a hydrophobic carbon-fluorine chain attached to a hydrophillic head (Fig. 2). PFASs display a number of unique chemical properties that result in their widespread industrial and commercial use as surfactants, including their thermal and chemical stability and dual lipid- and water-repellent properties. The extraordinary stability of these compounds leads to their persistence and bioaccumulation in the environment, and PFASs have been widely reported in humans and biota at several trophic levels in aquatic and terrestrial food webs across the globe (reviewed in Houde et al. 2006). The unique properties of PFASs (both polar and non-polar moieties) have implications for their preservation in sediment cores, in contrast to chlorinated and brominated organic contaminants that are highly non-polar and tend to be stable once deposited in the sediments. However, many different PFASs have been reported in lake and marine sediments (e.g. Alzaga et al. 2005; Higgins et al. 2005; Myers et al. 2012) and there is evidence that sediments are the most significant source of PFASs to the Lake Ontario food web (Martin et al. 2004). This suggests that sediment may be an important sink for PFASs, and that the potential exists to use sediment cores as a historical archive of PFAS deposition.

The sorption strength of PFASs onto particulates (and consequently their stability in sediment cores) varies depending on the compound of interest. For example, sorption onto sediments has been found to decrease with decreasing length of the hydrophobic carbon-fluorine chain (Ahrens et al. 2009), and short-chain PFASs were not detected in the sediments of Lake Ontario (Yeung et al. 2013). Conflicting results have been reported for perfluorooctane sulfonate (PFOS) regarding its sorption onto sediments: PFOS was not detected in the sediments of remote alpine lakes in Europe (Clara et al. 2009) and Canada (Benskin et al. 2011), but it was the dominant PFAS reported in Lake Ontario sediment cores (Myers et al. 2012; Yeung et al. 2013), and was also detected in Tokyo Bay (Zushi et al. 2010) and three remote High Arctic lakes (Stock et al. 2007). Sediment organic matter content may be important for determining the strength of PFOS sorption to sediments (Ahrens et al. 2009; Ahrens et al. 2010; Higgins and Luthy 2006).

To date, limited studies have been published in the scientific literature that analyze PFAS concentrations in dated sediment core profiles, and this represents an emerging field. Zushi et al. (2010) analyzed a sediment core from Tokyo Bay, and reported post-1990 decreases in PFOS and recent increases in perfluorooctanoic acid (PFOA), consistent with the historical shift from production of PFOS by electrochemical fluorination to PFOA production by telomerization (Fig. 4). Similarly, Myers et al. (2012) and Yeung et al. (2013) observed that sedimentary core profiles from Lake Ontario generally correlated well with early PFOS production (Fig. 4). Benskin et al. (2011) analyzed perfluorocarboxylic acid (PFCA) isomer profiles in sediment cores from remote alpine lakes in the Canadian Rocky Mountains in

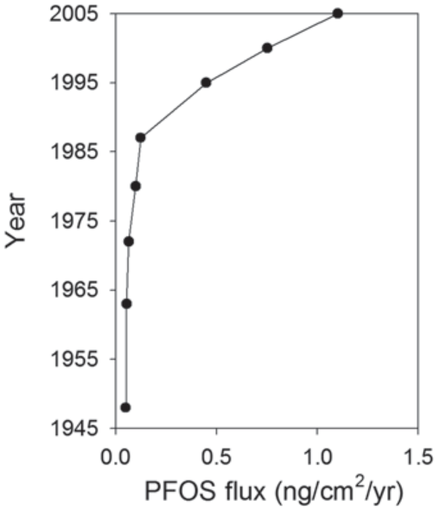

Fig. 4 Temporal PFOS flux in a sediment core from Lake Ontario, redrawn from Yeung et al. (2013). Although there is some uncertainty regarding the sorption of PFOS onto sediments and its long-term preservation in cores, this profile clearly shows post-1970 increases in PFOS in lake sediments

order to identify the source of PFCA emissions to the Rockies, as the electrochemical fluorination manufacturing process produces a mixture of structural isomers, while telomerization tends to produce linear compounds (De Silva et al. 2009). The predominance of linear isomer signatures in the sediments suggested that telomer-based compounds were the dominant source of PFCAs to the Rockies, although the authors caution that the possibility that branched isomers do not partition to sediments as effectively as linear isomers warrants further attention (Benskin et al. 2011). The study of PFAS chronologies in sediment cores is still in its infancy, and additional investigations into sorption mechanisms and sediment core migration are required to fully assess the potential for commonly studied compounds (e.g. PFOS, PFOA, PFCA) measured in sediment cores to accurately reflect historical deposition trends.

Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are a group of persistent organic pollutants characterized by two or more fused aromatic benzene rings (Fig. 2). They are typically classified as alkylated PAHs (having at least one alkyl side chain attached to the ring structure) or parent PAHs (unsubstituted). They are among the most ubiquitous contaminants measured in the environment due to a high diversity of sources that can be both natural (e.g. oil seeps, forest fires) or anthropogenic (e.g. fossil fuel emissions) in origin. Since the industrial revolution, human activities have greatly enhanced PAH loading to the environment, with many PAH compounds having been identified as toxic to aquatic biota and probable human carcinogens (Newstead and Giesy 1987; Xie et al. 2006). Due to the semi-volatile nature of many PAH compounds, they are susceptible to global dispersion through long-range atmospheric transport, where they can accumulate in regions otherwise remote from human influence such as the High Arctic (Wang et al. 2010; Halsall et al. 1997; De Laender et al. 2011). As a result, PAHs are included in the Convention for Long-Range Transboundary Air Pollution's Persistent Organic Pollutants protocol (UNECE 1998). In general, however, PAH concentrations in the environment tend to decrease with increasing distance from emission sources (Halsall et al. 2001; Maliszewska-Kordyback 1999).

PAHs accumulate in the environment due to their high affinity for particulate organic matter, recalcitrant nature, and low water solubility. PAHs in soils and sediments are typically found sorbed onto organic particles, rendering them mostly inaccessible to bacterial degradation (Johnsen et al. 2005). However, specific physio-chemical properties of different PAH compounds vary substantially based on molecular weight. High molecular weight PAHs with 4^+ aromatic rings are less water soluble, less volatile, and more lipophillic than low molecular weight PAHs, and water solubility decreases almost logarithmically as a function of increasing number of aromatic rings (Johnsen et al. 2005; Meharg et al. 1998). For example, log K_{ow} for naphthalene (two aromatic rings) is 3.29, compared to 4.45 for pyrene (four aromatic rings), and 6.58 for indeno(1,2,3-c, d)pyrene (six aromatic rings). PAHs with five or more aromatic rings are found almost exclusively in the solid phase; they tend to be rapidly deposited from the atmosphere and retained close to the emission source (Johnsen et al. 2005). Those with 2–4 aromatic rings can be found in the atmosphere in either a gaseous or particulate phase, resulting in their global dispersion and accumulation in polar regions (Wilcke 2000; Maliszewska-Kordyback 1999).

A high affinity for organic matter characteristic of the majority of commonly-studied PAH compounds facilitates their preservation in dated lake sediment cores, allowing them to be used as historical archives of PAH deposition (Hites et al. 1977). Unlike most man-made POPs, there is a long history of anthropogenic PAH emissions dating back to the industrial revolution in the mid-1800s. Thus, a longer time frame is provided by lake sediment cores over which to assess potential degradation patterns for PAH profiles. Early studies observed that PAH compositional profiles in sediment core intervals deposited after the industrial revolution have remained remarkably similar, and the compositional uniformity of PAHs provides evidence that diagenetic processes do not exhibit a significant influence over PAHs once they undergo sedimentation (Naes and Oug 1997; Readman et al. 1987; Simcik et al. 1999; Fernandez et al. 2000). Readman et al. (1987) modeled compositional changes in various PAH compounds in a sediment core from the Tamar Estuary, U.K., and concluded that PAHs appeared to be irreversibly bound to the sediments and largely unavailable for microbial degradation (although PAH-degrading *mycobacteria* have been detected in contaminated sediments of Lake Erie, Canada; DeBruyan et al. 2009). Good agreement between PAHs in the surface sediments of lakes/estuaries with aerosols or estimated atmospheric deposition has also been reported in various locations, for example in Norwegian Fjords (Naes and Oug 1997), and in lakes in the Pyrenees and Tatra Mountains of Europe (Grimault et al. 2004; Van Drooge et al. 2011).

Comparisons between sedimentary PAH profiles and historical socioeconomic data (as a proxy for PAH emissions) provide further evidence for the reliability of sediment cores as historical archives of PAH pollution (Fig. 5). There are numerous examples in the published literature from study locations across the globe that recorded increases in sedimentary PAH concentrations beginning in the latter half of the 1800s, consistent with the onset of the industrial revolution (e.g. Simcik et al. 1999; Eide et al. 2011; Elmquist et al. 2007). Several studies also recorded declines in sedimentary PAH concentrations beginning ~1950–1970, reflecting a shift from coal to oil/natural gas as an energy source, improvements in combustion technologies, and government regulations/emission controls (Van Metre et al. 2000; Cranwell and Koul 1989; Bogdall et al. 2011; Liu et al. 2012). Recently, Guan et al. (2012) analyzed PAHs in a sediment core from Sihailongwan Maar Lake and found that, as predicted, stratigraphical trends in total PAHs correlated well with Chinese socioeconomic data. The application of a chemical mass balance model (for delineation of PAH sources in environmental samples) to sediment cores from eight urban lakes in the USA showed that sedimentary PAH profiles accurately reflected an increased contribution of PAHs from coal-tar-based (CT) pavement sealcoat in

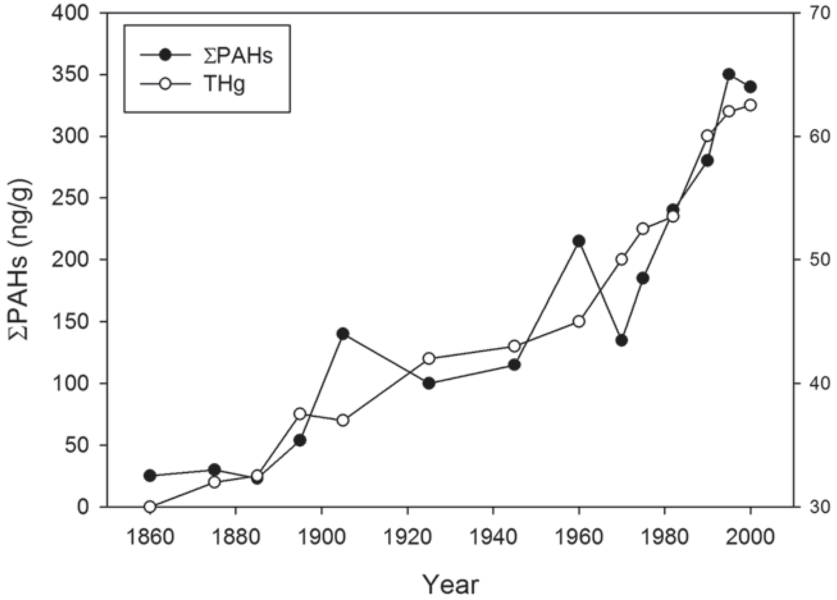

Fig. 5 USEPA priority PAHs and mercury (Hg) concentrations in a sediment core from a remote lake of the northeastern Tibetan Plateau are strongly correlated, and show steady increases since the industrial revolution. (Data are from Wang et al. (2010))

the 1960 and 1970s (Van Metre and Mahler 2010). For several lakes in the vicinity of the Athabasca oil sands region (Alberta, Canada), increases in PAHs and dibenzothiophenes were recorded after the extraction of bitumen resources began in 1960, and the composition of PAHs indicated a temporal shift from primarily wood combustion to petrogenic sources (Kurek et al. 2013a; b).

Pyrogenic PAH emissions are often associated with increased emissions of other pollutants such as lead (Pb) and other heavy metals. Therefore, analysis of both PAHs and metals in sediment cores can also provide insight on the use of sediment cores as records of atmospheric PAH deposition. Sediment cores taken from lakes subjected to atmospheric deposition of pollutants often show strong correlations between pyrolytic PAHs (resulting from decomposition of organic material at elevated temperatures in the absence of oxygen), Pb, mercury (Hg), and/or cadmium (Cd), with baseline depths for PAHs occurring at approximately the same depth as baseline for metals (Mikac et al. 2011; Wang et al. 2010; Müller et al 1977; Heit et al 1981). Independent confirmation from pollutant indicators, which behave very different chemically in the environment, increase confidence that PAH profiles in lake sediments are accurately reflecting anthropogenic PAH emissions (Fig. 5). However, for more remote lakes that have received minimal atmospheric pollution, the relationship between metals and PAHs is often less striking. For example, Loch Caire nan Arr in Scotland is thought to be among the least polluted lakes in the United Kingdom, with low concentrations of both metals and organic contaminants (Rose and Rippey 2002). The timing of the peak in PAH concentrations in the sediment core from this lake was not consistent with other forms of pollution (e.g. metals, PCBs), indicating that industrial emissions are not an important source of PAHs to this lake (Rose and Rippey 2002). Similarly, weak relationships between Hg and PAHs were observed for two remote northern lakes in Ontario, Canada (Lockhart et al. 1993). Pyrolytic PAHs that are particle bound are less susceptible to long-range transport compared to metals, which may explain why relationships between metals and PAHs are weaker in lakes that receive only minimal atmospheric pollution. While most multi-proxy studies on PAHs in sediment cores compare PAH profiles against other types of pollutants, many other paleolimnological proxies have the potential to strengthen PAH sedimentary profile interpretations. An interesting example is found in Hall et al. (2012), which applied paleohydrological reconstructions in flood-prone lakes in the Peace-Athabasca Delta downstream of the Athabasca oil sands development to interpret stratigraphic records of PAHs. They found that periods of flooding by the Athabasca River was associated with higher concentrations of bitumen-sourced PAHs to the sediments, demonstrating the importance of natural erosion of exposed bitumen along the banks of the Athabasca River as a vector for delivery of PAHs downstream (Hall et al. 2012).

Fecal Sterols

Sterols are natural, unsaturated steroid alcohols possessing a basic structure that consists of three cyclohexanes and one cyclopentane (Fig. 2). They usually have a hydroxyl at position 3, and an aliphatic side chain of eight or more carbons at position 17 (Fahy et al. 2005). Sterols may derive from protists, higher plants, or animals (Matsumoto et al. 2010; Nishimura and Koyama 1976; Wang et al. 2007), and those derived from animals are typically found as fecal sterols (Eneroth et al. 1964; Murtaugh and Bunch 1967). For example, coprostanol is formed from anaerobic microbial degradation of cholesterol in the intestines of higher animals and birds, and it is the most abundant sterol in human feces (Rosenfeld 1964). In contrast, livestock such as cows and sheep excrete much lower concentrations of coprostanol in their feces and higher proportions of 5β-campestanol and 5β-stigmastanol (Leeming et al. 1996). The differences in sterol composition between different types of species led to their widespread use as biomarkers in paleolimnological studies (D’Anjou et al. 2012; Huang et al. 2011; Wang et al. 2007); however, despite being produced naturally, fecal sterols such as coprostanol are also regarded as environmental pollutants. Unlike the persistent organic pollutants described in the preceding sections that have significant ecotoxicological implications, fecal sterols are mainly used as tracers of sewage contamination in aquatic sediments, since domestic sewage that incorporates fecal sterols is often a dominant source of water pollution in urban areas (Carreira et al. 2004; Jeng et al. 1996; Mudge and Duce 2005). That these compounds are often found associated with fecal bacteria in sediments further confirms their role as fecal indicators (Dutka et al. 1974). Still, coprostanol has been shown to bioaccumulate and induce estrogenic effects in mussels (Gagné et al. 2001; 2002), suggesting that it can be both an aquatic pollutant as well as a biomarker of sewage contamination. For the purposes of this chapter, we will be focusing on fecal sterols as indicators of sewage pollution in aquatic environments.

Coprostanol has low water solubility and is most often associated with the solid phase, thus it is readily incorporated into the sediment record. The stability of the aliphatic backbone and sterane ring in coprostanol and other sterols provides some resistance against microbial degradation in anaerobic sediments (Bartlett 1987), and fecal sterols recovered from a lake sediment core have been used successfully as a paleoenvironmental archive to track past human settlements and agricultural activities for thousands of years (D'Anjou et al. 2012). However, temperature and redox conditions that exist in the water column and the sediment-water interface can greatly affect the preservation of these compounds before their burial in the sediments. For example, the half-life of coprostanol in aerobic conditions at temperatures above 20 °C can be less than ten days, while it can be >400 days under anaerobic conditions (Ogura 1983). Enhanced microbial degradation under aerobic conditions at elevated temperatures may compromise the value of fecal sterols as sewage tracers in tropical systems (Brown and Wade 1984; Pierce and Brown 1984), potentially leading to the underestimation of sewage contamination (Santos et al. 2008; Seguel et al. 2001). This was determined to be the case for sediment cores recovered from Guanabara Bay, Brazil, where there was evidence of enhanced coprostanol decomposition in the upper sediment layer that was partly oxic due to resuspension from tidal currents (Carreira et al. 2004).

Coprostanol and other fecal sterols are currently underutilized as tracers of domestic sewage pollution, partly due to a limited understanding of the conditions that favor preservation of these compounds relative to the more commonly studied organic contaminants. Still, several studies document interesting relationships between temporal trends of fecal sterols in the sediment record and known information about anthropogenic sewage inputs to aquatic ecosystems, suggesting there is considerable promise for sediment cores to provide a historical archive of fecal pollution (Fig. 6). D'Anjou et al. (2012) documented the arrival of prehistoric humans and their grazing animals to an archaeological site at Lake Liland, Norway 2250 years ago by measuring increases in coprostanol and 5β-stigmastanol in a lake sediment core. Müller et al. (1979) recorded a steady increase in coprostanol from ~1800 to present in Lake Constance (Europe), and no coprostanol was detected in the pre-1800 sediments. In a sediment core from the Macao Estuary, a sharp decrease in coprostanol was observed at the surface of the core, corresponding to the beginning of operations at a new wastewater treatment plant in 1996 (Peng et al. 2002). Fecal sterol profiles were used to track the impacts of municipal sewage input to Ross Lake (Manitoba, Canada) over an 80-year period (Tse et al. 2014). Ross Lake received direct inputs of raw municipal sewage for ~20 years until the construction of a sewage treatment facility in 1951. This was clearly reflected in the sedimentary coprostanol record, as a dramatic increase was observed in coprostanol ~1930, followed by striking post-1950 declines (Fig. 6). The maximum concentration of coprostanol in the sediments was 22 μg/g dry weight (~250 μg/g

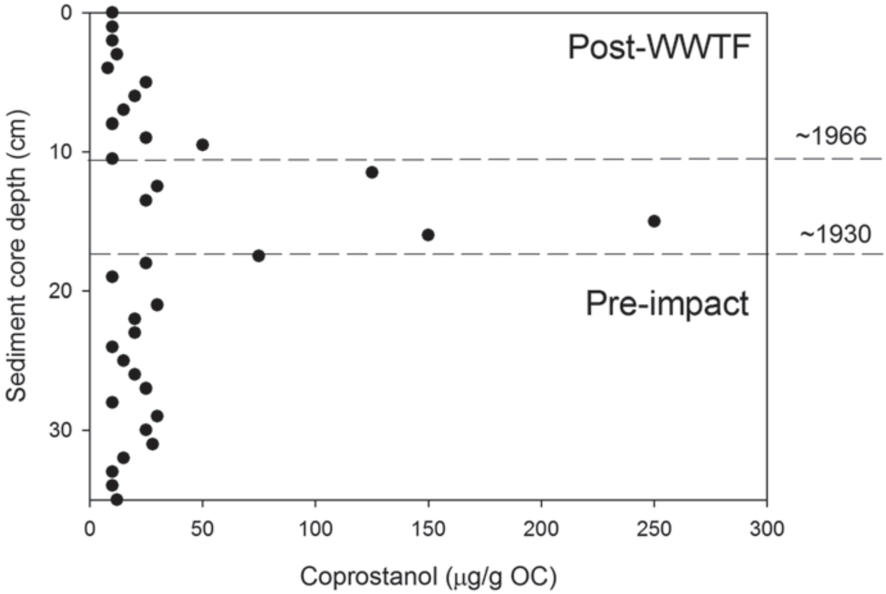

Fig. 6 Coprostanol concentrations in a sediment core from Ross Lake, Manitoba, Canada tracks municipal sewage inputs from the mining community of Flin Flon. Raw and minimally treated sewage was released into the lake for >20 years beginning in ~1930, and coprostanol concentrations in sediments from this time period indicate a lake heavily contaminated by domestic sewage. Sedimentary coprostanol concentrations declined to pre-impact levels post-1950, when changes in wastewater management reduced sewage loading to the lake. (Figure is redrawn from Tse et al. (2014))

OC), indicating strong sewage inputs (>10 μg/g has previously been reported as a signature of domestic sewage; Mudge and Bebianno 1997). The latter two studies described above particularly highlight the potential for fecal sterols as sewage tracers, since the sedimentary pattern of increases in coprostanol followed by declines after the installation of wastewater treatment facilities are not consistent with a diagenetic signal.

Antarctica presents a particularly interesting case study for fecal sterols because this continent does not have aboriginal inhabitants (and thus has a short history of human settlement), and the cold climate favors a higher degree of preservation of sterols until their incorporation into the sediment record (Ogura et al. 1990). High concentrations of coprostanol and the bacterium *Clostridium perfringens* have been reported near McMurdo Station and other research stations, with concentrations decreasing with distance from the outfall (Edwards et al. 1998; Hughes and Thompson 2004), and sediment cores showed increases in coprostanol corresponding to increased research activities (Venkatesan and Mirsadeghi 1992). Consequently, sediment cores can provide critical information that can be used to mitigate the impacts of human activities in sensitive Antarctic ecosystems, where sewage treatment options are limited. In future, similar paleolimnological studies utilizing fecal sterols can also be used to track the impact of sewage inputs to remote lakes in the

High Arctic, for example Meretta Lake in Resolute Bay (Douglas and Smol 2000), and the recovery of ecosystems following the removal of this stressor.

Conclusions

Lake and marine sediment cores are being utilized to successfully reconstruct deposition history for an increasingly diverse set of organic contaminants. We evaluated the reliability of sediment cores as archives of pollution for a variety of common legacy and emerging organic contaminants using multiple lines of evidence. This includes comparison of sedimentary profiles against known histories and/or modeled chemical profiles, comparison with profiles of inorganic contaminants that have a similar emission history, examinations of compositional changes over depth to assess degradation rates, and the chemical characteristics of the compound itself (log K_{ow}, half-life). Using this framework, we show that the polycyclic aromatic hydrocarbons and the chlorinated and brominated persistent organic pollutants (e.g. PCBs, PBDEs) are some of the most stable chemical compounds preserved in aquatic sediments, and the use of sediment cores as historical archives of these contaminants in the environment is well established. For fluorinated organic contaminants such as PFOS, their lipophobicity poses a unique challenge compared to PAHs, PCBs, and other persistent organic pollutants, and consequently their stability in sediment cores is less well established. Fecal sterols are highly prone to degradation in warm, oxic conditions before their burial in the sediments, with implications for their incorporation and preservation within sediment cores. Further study is required to assess the conditions that favor preservation and stability of both fecal sterols and perfluorinated substances in sediments, but early down-core studies described in this chapter suggest there is considerable potential for their widespread use in sediment core archives.

We covered only a small subset of the potential organic contaminants that can be measured in aquatic environments, and this field of research can only benefit from additional cross-disciplinary studies that assess the reliability of sediments as pollution archives. The framework we adopted here to evaluate the reliability of sediment cores as historical pollutant archives can be applied to any organic contaminant of interest. For example, the dioxins are another group of organic contaminants that are also commonly studied using a paleolimnological approach, similar to the other organochlorines and PAHs (Czuczwa et al. 1985; Baker and Hites 2000). The list of pharmaceuticals and personal care products that can be measured in water samples is growing (Loraine and Pettigrove 2006; Kolpin et al. 2002; Jones-Lepp 2006), although to the best of our knowledge, very little to no work has been done in sediment cores for most of these compounds. For all compounds, no matter how well studied, investigators must have a comprehensive understanding of the biases inherent in their chosen organic chemical proxy in order to provide meaningful interpretations of sediment core profiles. This line of inquiry would also be greatly enhanced by long-term experimental studies that test the stability of chemicals within sediments, as the integration of stability experiments with down-core profiles of organic contaminants is an approach that has been underutilized.

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Environmental Archives of Contaminant Particles

Neil L. Rose and Meri Ruppel

Abstract Particulates in the environment may be contaminants or pollutants. They may affect climate through: the absorption of energy in the atmosphere and by reducing the albedo of ice and snow surfaces; may enhance the transfer and distribution of pollutants such as trace metals and persistent organic pollutants via absorption and adsorption to their surfaces; may adversely impact the health of aquatic life and consequently other biota that depend upon it; in the atmosphere they may have direct effects on human health via respiratory disease and the transfer of substances deep into the respiratory system. Therefore, it is important to be able to determine temporal trends in particulate emissions and deposition. Natural archives such as ice, sediment and peat cores can provide well-resolved records, but research has mainly focussed on a few particle types, and predominantly black carbon. In this chapter we review the environmental records of black carbon and other industrially-derived particles, their analysis, interpretation and relative strengths and weaknesses. Finally we consider two emerging particle types: microplastics and nanoparticles. These latter groups have, so far, received little attention from palaeoecological perspectives but their direct impacts on aquatic biota and ability to transport pollutants within the atmosphere and aquatic ecosystems is becoming increasingly apparent in the literature and are predicted to further increase in coming decades.

Keywords Black carbon · Charcoal · Fly-ash · Ice cores · Microplastics · Nanoparticles · Sediments

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Introduction

The distinction drawn between a contaminant and a pollutant relates to the scale of its impact. A contaminant is a substance introduced into the environment, either directly or indirectly, such that levels that might naturally exist are exceeded (Frid and Dobson 2013) whereas a pollutant may be defined as a contaminant that causes harm or damage to an organism or ecosystem. In the atmosphere particles are often pollutants. Pope and Dockery's work in the 1990s (e.g., Pope et al. 1991, 1995; Pope and Dockery 1992; Dockery et al. 1993) highlighted the effects of fine airborne particulate matter, PM_{10} (defined as particles with an aerodynamic diameter ≤ 10 µm), on a range of human health issues including asthma, bronchitis and mortality, while more recently the emphasis has shifted to finer particulate fractions ($PM_{2.5}$; $PM_{1.0}$) and their role additionally in lung cancer and cardiopulmonary disease (e.g., Pope et al. 2002; Pope and Dockery 2006). The earlier health impact studies led to national assessments; for example, in the UK (COMEAP 1995; POST 1996; Pearce and Crowards 1996) and the Netherlands (Buringh and Oppenhuizen 2002), and also at the larger scale by the World Health Organisation (1999). These resulted in the instigation of regularly revised Air Quality Standards also at national and international levels (e.g., WHO guidelines: www.who.int/topics/air_pollution/en/). As an example, the current US EPA standards, revised in December 2012, lowered the annual mean $PM_{2.5}$ concentration from 15.0 to 12.0 µg m^{-3}, while maintaining the 24-h value of 35 µg m^{-3} (www.epa.gov/pm/2012/decfsstandards.pdf). Interestingly, PM_{10} are now referred to as the coarse particle fraction.

The standards for airborne particulates, and most of their defined impacts, relate to undifferentiated particulate mass, i.e. it is the total particle load that is considered. Hence despite there being considerable interest in the long-term exposure of particulates for health issues (e.g., Hodgson et al. 2009), palaeorecords have so far not been employed to generate useful data. However, where impacts from more specific particle types can be identified, such as black carbon (Anderson et al. 2001; Roemer and van Wijnen 2001; Janssen et al. 2012; Künzi et al. 2013) or oil fly-ash (Ghio et al. 2002) there may be a role to play. In this sense, black carbon is of particular importance because its impacts are not only directly related to human and environmental health, but it has a further indirect effect via its climate change impacts (Löndahl et al. 2010; Shindell et al. 2012). Consequently, knowledge of long-term changes in black carbon emissions would be a benefit to determining (i) health effects from aerosol exposure, (ii) climatic effects of aerosols and (iii) health effects of climate change. It should be no surprise, then, that the estimated economic value of damage from fossil-fuel combustion is enormous (Barbir et al. 1990) with the impacts to human health in the United States alone calculated at $ 361–886 billion (or 2.5–6 % GDP) annually (Machol and Rizk 2013) and for the UK £6–62 billion (0.4–3.5 % GDP) (Yim and Barrett 2012).

In aquatic and terrestrial environments, as well as the atmosphere and cryosphere, a further significant impact from particles derives from their ability to transport toxic pollutants attached to their surfaces. These adsorbed (also absorbed) substances are distinct from emissions of pollutants in particulate form (e.g., metal fume (Pires et al. 2006)) and include trace elements such as lead (Pb), cadmium (Cd) and arsenic (As), which are preferentially concentrated onto the respirable fraction of airborne particles emitted from coal-fired power plants (Natusch and Wallace 1974). Mercury (Hg), zinc (Zn) and polycyclic aromatic hydrocarbons (PAHs) are also transported in this way and the scale of PAH absorption can be related to the carbon content of the emitted fly-ash (Wey et al. 1998). Dioxins and furans (PCDD/Fs) have also been linked to 'soot black carbon' (Persson et al. 2002; Lohmann et al. 2005) as have acidifying ions (Guazzotti et al. 2001). Similarly, Ghosh et al. (2003) showed that carbonaceous particles extracted from harbour sediments preferentially accumulated both PAHs and polychlorinated biphenyls (PCBs), while Chen et al. (2009) demonstrated the affinity of oil-derived black carbon for perfluoroctane sulphonate (PFOS). PFOS is an emerging pollutant with known multiple toxicities including endocrine disruptive, reproductive and developmental effects.

Particles, and in particular the carbonaceous component, therefore have direct pollutant effects in a number of environments and, furthermore, may be used as indicators of contamination sources for other deposited substances (see examples later in this chapter). For these reasons, it is important to be able to ascertain the long-term records of particulates in the environment via the use of natural archives. These archives make it possible to distinguish between natural and anthropogenic sources in order to interpret environmental impacts appropriately.

There is a long record of natural particulate contamination. Black carbon has been reported in sediments since the Devonian (c. 415 M yr; Schmidt and Noack 2000) and Graseby et al. (2011) describe carbon-rich char particles with a passing resemblance to the morphologies of modern-day fossil-fuel derived particulates from Permian age rocks (c. 250 Myr BP) in the Canadian High Arctic. It is speculated that these were produced by combustion of Siberian coal and organic-rich sediments by basalts before being widely dispersed (see also Sanei 2015). Ancient carbonaceous particles have also been observed at the Cretaceous—Paleogene (K-P) (formerly Tertiary) boundary c. 65 Myr BP with suggested sources from both wildfires triggered by a bolide impact (Wolbach et al. 1985) but also from the impact itself into organic-rich geology (Harvey et al. 2008). Interestingly, these latter particles, while carbon-rich have a "bubble texture" and a light brown colour. Harvey et al. suggested that these features result from the particles "boiling" at low temperatures (300–800 °C) but not igniting. They are therefore distinguishable from modern industrially derived carbonaceous particulates, which ignite at higher temperatures and produce a black porous 'cenosphere' (e.g., Rose 2001). Morphologically and chemically, however, these K-P carbon cenospheres are remarkably similar to particles observed from a peat core taken from Misten in eastern Belgium (50°33'44.33"N; 6°9'50.70"E) and dated to c. AD 550 (Jérémie Beghin, Université de Liège; pers. comm.). The colouration, the bubble texture and the carbon-rich composition are the same (Fig. 1), but here it is suggested that the source is from some smelting-type activity. Further study is required to determine the formation processes for this intriguing particle type.

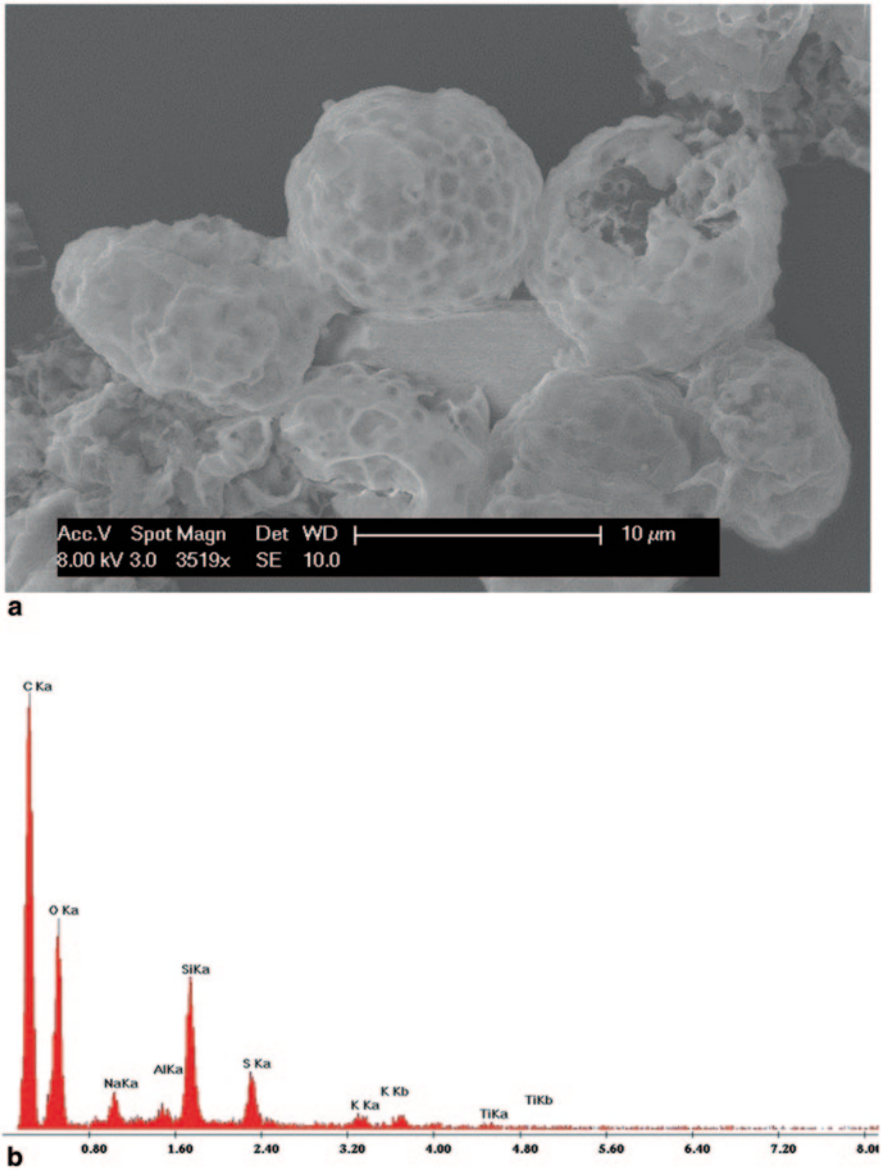


Fig. 1 **a** Scanning electron micrograph and **b** EDS-spectra of carbon-rich particles extracted from a peat core in Misten, eastern Belgium and dated to c. AD 550 (Both courtesy of Jérémie Beghin, Unité de Paléobiogéologie—Paléobotanique—Paléopalynologie (PPP), Département de Géologie, Université de Liège)

The record of charcoal particles in both palaeolimnological (Whitlock and Larsen 2001) and pedoanthracological (Nelle et al. 2013) natural archives extends over many millennia. In both lake sediments (e.g., Earle et al. 1996; Vannière et al. 2008;

Higuera et al. 2009) and peat archives (e.g., Breitenlechner et al. 2010; Bindler et al. 2011) these records represent the complex interactions between climate, vegetation-type, and human activity (Haberle 2001). Hence, charcoal as an indicator of fire frequency may be used to suggest where fires were natural or used as a land management tool. Natural fires may be less frequent (60–250 years) and irregularly spaced, while frequencies of 10–20 years are typical where controlled burning is used, for example, to maintain *Calluna vulgaris* dominated heathland (Birks 1997). Conversely where fire suppression is used as a management policy, a reduction in charcoal inputs may also result (Willis and Birks 2006).

Fire size, intensity and severity affect the production and also the transport of charcoal particles as they may be carried to great heights and over large distances in the process of dispersal (Whitlock and Larsen 2001). Aerial transport is affected by particle size with charcoal > 1000 μm in diameter being deposited close to the fire (Clark and Patterson 1997), while particles smaller than 200 μm are not expected to be deposited within approximately 6 km of a fire column (Whitlock and Larsen 2001). Taphonomic processes are an important consideration when interpreting charcoal records and include not only atmospheric dispersal and deposition but also transport from catchments via soil erosion (secondary charcoal) or via inflowing streams. These transfer processes may result in a considerable lag in the timing of a fire 'event' in a sediment record (Whitlock and Larsen 2001), and may also affect charcoal concentrations as sediments taken from near a stream inflow may be several times higher than those from deeper 'offshore' sediments (Patterson et al. 1987) as a result of movement from higher in a catchment (see also Rosen 2015).

Records of charcoal particles over tens of thousands of years have been used as an indicator of climatic change with warmer, drier climates leading to increased fire frequency (Vannière et al. 2008; Higuera et al. 2009). However, these changes also remain a key signature of human impacts through the Quaternary. For example, records over 40,000 years in Papua New Guinea have been interpreted as indicative of changes in human occupation (Hope 2009) while increased fire-frequency in the Mediterranean is equated with the development of human settlements, slash-and-burn agriculture, and mineral exploitation (Vannière et al. 2008). Distinguishing between climatic and anthropogenic charcoal signals is largely dependent on context. Supporting information most frequently pertains to pollen (e.g., Haberle et al. 2001; Whitlock and Larsen 2001; Vannière et al. 2008; Higuera et al. 2009; Breitenlechner et al. 2010) or macrofossil data (Willis and Birks 2006) to indicate vegetation changes, but also widely uses archaeological, dendrological and geochemical data to indicate, for example, metallurgical indicators of human expansion (Bindler et al. 2011; Pichler et al. 2013, see also Cooke and Bindler, this volume).

The need to distinguish between natural and anthropogenic sources of particles is not restricted to charcoal. Fossil-fuel combustion-derived inorganic ash spheres (IAS) (Rose 2001) appear morphologically similar to microspherules of volcanic (e.g., Lefèvre et al. 1986) or micrometeoritic origin (e.g., Handy and Davidson 1959; Hodge and Wright 1964). Natural sources of particles morphologically similar to IAS become less significant in more recent records as anthropogenic sources swamp those that are naturally produced. However, in areas where industrial particle inputs are low or infrequent, such confusions may still arise and as a result the records of unambiguously anthropogenic and/ or industrial particles, such as spheroidal carbonaceous particles (SCPs), become exceedingly useful as environmental change markers.

Carbonaceous particulates, often termed ‘black carbon’, are therefore very important in toxicological, pollutant transfer and environmental change studies especially in archives that include periods after the Industrial Revolution when emissions increased dramatically. The remainder of this chapter focusses on the particle record of the industrial period and in particular the environmental records of black carbon particles. Finally, we consider some of the environmental impacts and archives of two new and emerging particle types: microplastics and nanoparticles.

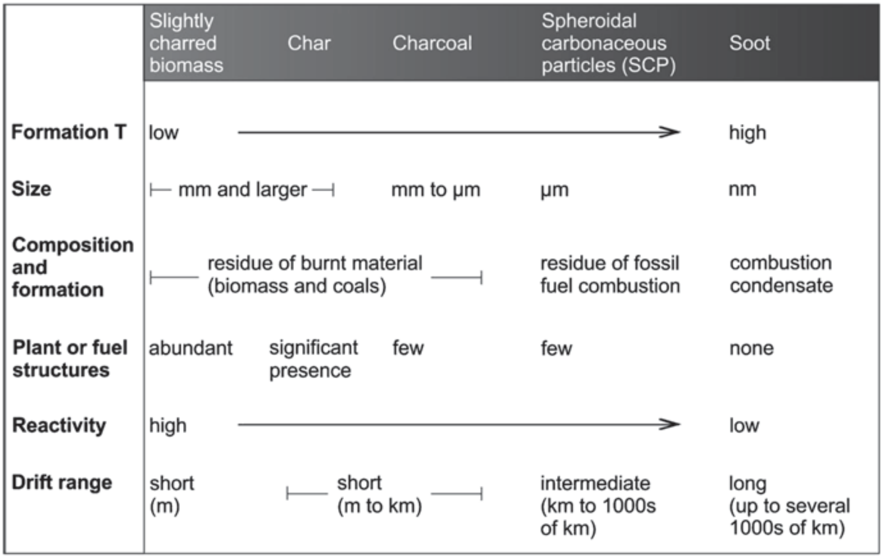
Black Carbon

What is Black Carbon?

The term ‘black carbon’ (BC) covers a range of particulates with a composition of > 60 % carbon and with accessory elements including hydrogen, oxygen, nitrogen and sulphur (Goldberg 1985). It is formed by the incomplete combustion of biomass such as grasslands or forest fires, anthropogenic industrial combustion of biomass or fossil fuels, diesel and gasoline engines, and small-scale domestic fires. Emissions from these sources are large. According to ‘bottom-up’ inventories, total global emissions of BC were estimated to be 7500 Gg for the year 2000 but with a large uncertainty range of 2000–29,000 Gg (Bond et al. 2013).

‘Black carbon’ therefore encompasses a wide spectrum of charred material and despite 30 years of research there is still no single accepted definition, especially between disciplines (Masiello 2004; Andreae and Gelencsér 2006). Terms such as black carbon, elemental carbon, soot, graphitic black carbon, pyrogenic carbon and refractory black carbon are often used interchangeably, and definitions for these are based on source processes, morphological characteristics, chemical composition and the optical properties of the material in question. Recently, for atmospheric sciences, Bond et al. (2013) defined black carbon very specifically as being a distinct type of carbonaceous material formed in flames and having a unique combination of physical properties. However, this definition does not cover all BC particles included in soil and sediment studies. In general, the term elemental carbon is used in atmospheric sciences while black carbon is used in soil and sedimentary disciplines (Hammes et al. 2007).

One way of understanding the myriad of particles under the BC umbrella is by considering the “black carbon combustion continuum model” first presented by Hedges et al. (2000). All components of the continuum (Fig. 2) are black particles that have formed as incomplete combustion products. These particles range from slightly charred biodegradable biomass, char and charcoal through to industrial particles formed at high temperatures, but there are no clear boundaries between these



	Slightly charred biomass	Char	Charcoal	Spheroidal carbonaceous particles (SCP)	Soot
Formation T	low				high
Size	mm and larger		mm to µm	µm	nm
Composition and formation	residue of burnt material (biomass and coals)			residue of fossil fuel combustion	combustion condensate
Plant or fuel structures	abundant	significant presence	few	few	none
Reactivity	high				low
Drift range	short (m)	short (m to km)		intermediate (km to 1000s of km)	long (up to several 1000s of km)

Fig. 2 Black carbon combustion continuum model. (Modified after Hedges et al. (2000) and Masiello (2004))

classes (Seiler and Crutzen 1980). Generally, they can be grouped into larger chars, which are residues reflecting the structure of the burned material, or the nature of the burning process, and smaller particles, such as soots, which are combustion condensates, i.e. formed from the vapour phase (Novakov 1984). Both types can form simultaneously from a single combustion source (Goldberg 1985).

Soot BC is slightly different from the rest of the BC continuum because it is produced from the vapour phase as a condensation product rather than as a combustion residue. These are the particles that are mostly considered by atmospheric scientists as BC (e.g., Bond et al. 2013), probably due to their small size and well-known optical (light absorbance) properties. Although soot BC may be produced in large natural fires if sufficient temperature is attained, it is common in industrial processes and during the combustion of natural gas, gasoline and diesel, which do not produce any other BC forms. It is generally recognized that soot forms through the production of polycyclic aromatic hydrocarbons (PAHs), which continue to form larger structures, eventually condensing into solid spheres (Kennedy 1997). The size of soot particles may vary from a single to hundreds of nanometres. Although incomplete combustion of organic material always produces PAHs in addition to BC particles, PAHs are not included in the BC continuum because they do not share other properties such as light absorbance.

The purest form of black or elemental carbon is graphite, which consists of sp^2–bonded carbon in planar layers. Graphite is formed over geological time-scales under conditions of high temperature and pressure. It is therefore not a combustion product and is not considered further here.

Black Carbon Effects on Climate

In addition to the toxicological impacts and pollutant transport properties of particles described at the start of this chapter, BC also has a strong warming effect on climate where its potency is based on its colour and surface characteristics (Ramanathan and Carmichael 2008). BC absorbs solar radiation and so warms the atmosphere prior to deposition (e.g., Bond and Bergstrom 2006; Bond et al. 2013) but also darkens surfaces once deposited (Warren and Wiscombe 1980), thereby significantly reducing the albedo of snow and ice (Clarke and Noone 1985) and hastening the melting process. The strong warming effect of small BC concentrations in snow results from the more rapid growth of snow grain size following BC deposition (Bond et al. 2013). Coarse-grained (old) snow has lower albedo than fine-grained (new) snow and this leads to a positive feedback process accelerating melting (Flanner et al. 2007). Due to its properties in the atmosphere and this feedback process, BC is considered to be the second most important component of global warming after carbon dioxide (e.g., Jacobson 2001; Ramanathan and Carmichael 2008; Bond et al. 2013). It has been suggested that up to 40 % of current net warming is attributable to BC as well as 30 % of Arctic melting (Baron et al. 2009), making it potentially a more important factor than greenhouse gases for climate warming in this region (e.g., Hansen and Nazarenko 2004; Bond et al. 2013 and references therein).

Climatic impacts of BC are not restricted to the Arctic. It has recently been suggested that increasing deposition of industrial BC forced the climatologically premature end of the Little Ice Age in the European Alps around 1850. Glaciers in the region started to retreat in the latter half of the nineteenth century when according to temperature and precipitation records they should have continued to grow until c. 1910 (Painter et al. 2013). In the Himalayas, the warming of the atmosphere by BC and the darkening of ice surfaces is thought to be a major contributor to the accelerating retreat of glaciers (e.g., Ramanathan and Carmichael 2008; Xu et al. 2009), while its contribution to “atmospheric brown clouds” across southern Asia (Ramanathan and Crutzen 2003; Lawrence 2011) affect evaporation and long-range moisture transport responsible for the monsoonal circulation. As a consequence precipitation trends over many regions of the tropics, particularly Africa, south Asia and northern China, have been negative over the last 50 years (Ramanathan and Carmichael 2008). Atmospheric heating by BC and ozone has also occurred at mid-latitudes resulting in a poleward shift of the tropospheric jet, thereby moving the main division between tropical and temperate air masses and expanding the tropical zone in the northern hemisphere (Allen et al. 2012).

Environmental Archives of Black Carbon

Methods most commonly used for the quantification of BC from environmental archives can be divided into five different categories: (i) optical; (ii) thermal (for both of these categories see references in Watson et al. 2005); (iii) microscopic (e.g., Stoffyn-Egli et al. 1997; Thevenon and Anselmetti 2007; Rose 1994, 2008); (iv) chemical (e.g., Masiello and Druffel 1998); and (v) indirect (e.g. molecular markers; Glaser et al. 1998). Additionally, some mixed methods have been employed such as the thermo-optical (e.g., Chow et al. 1993) or chemo-thermal (e.g., Gustafsson et al. 1997, 2001). Optical methods are usually used in atmospheric sciences for the quantification of elemental carbon and rely on its light-absorbing properties (see Watson et al. 2005 and references therein). By contrast, thermal methods developed for BC in sediments and soils rely on its resistance to degradation, in particular oxidation (Hammes et al. 2007). Many of these methods use a two-step approach in which the carbon oxidising below a certain temperature (≈350–550 °C) is termed organic carbon, while that at higher temperatures (≈650–1100 °C) is termed elemental carbon (Watson et al. 2005). Chemical methods determine BC as that which resists chemical extraction (e.g. removal of organic material and inorganic minerals with acid treatments) and this may be followed by microscopic techniques for specific particle types, such as charcoal and SCPs, which are counted after the chemical extraction has removed unwanted components of the surrounding matrix (Renberg and Wik 1984; Rose 1994).

Unfortunately there is no standard method for BC quantification for any environmental matrix. Watson et al. (2005) summarized over 50 inter-laboratory and inter-method comparisons for BC and elemental carbon determination. Analyses of identical samples showed typical differences by a factor of 2 between methods, but higher discrepancies (of a factor of up to 7) were measured in some cases and Schmidt et al. (2001) reported variability by a factor of 500 between measured concentrations of BC in an inter-comparison study of soil samples. For most methods it is not possible to precisely define which components of the BC continuum (Fig. 2) are being measured. No single method measures the whole range and it is likely that overlap between particle types within the continuum results in much of the discrepancy between analytical approaches. Such deficiency makes comparisons between studies using different analytical methods problematic and even inappropriate, as illustrated later in this chapter. Exceptions are where particle types can be more precisely defined by their morphology with specific identification criteria. In these cases, comparisons between measurements and analysts are more robust (e.g., Rose 2008).

There are numerous studies on the presence of BC in the environment, including the atmosphere (e.g., Ogren and Charlson 1983; Kaneyasu and Murayama 2000; Hitzenberger and Tohno 2001; Bae et al. 2004; Sharma et al. 2004), snow (e.g., Forsström et al. 2009; Hadley et al. 2010; Hegg et al. 2010; Doherty et al. 2010), ice (Cachier and Pertuisot 1994; Chylek et al. 1992a; 1992b), soils and lake sediments (e.g., Song et al. 2002; Cornelissen et al. 2005; Rumpel et al. 2006), fluvial sediments (e.g., Elmquist et al. 2008; Mitra et al. 2002) and marine sediments (e.g., Gustafsson and Gschwend 1998; Masiello and Druffel 1998; Middelburg et al. 1999). However, historical records are still relatively scarce. Models of concentrations and climatic effects of BC in the past have been mainly based on emission inventories and atmospheric circulation data (Shindell and Faluvegi 2009; Skeie et al. 2011). They are typically not directly constrained by measurements of BC

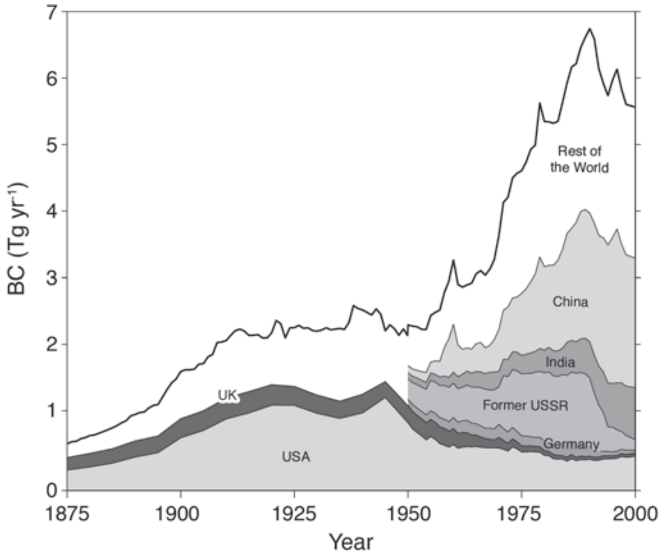


Fig. 3 Estimated historical fossil-fuel black carbon emissions. (Redrawn from Novakov et al. (2003))

deposition, which tend to be used only for validation of the model output. Published historical global BC emission inventories are based on estimates of different fuel consumption and changes in combustion technologies (e.g., Novakov et al. 2003; Bond et al. 2007). According to these inventories global BC emissions have increased 7-fold from pre-industrial levels (Bond et al. 2007), but these are, of course, not uniform around the world. Emissions from industrialized countries in Europe and North America have declined during the last few decades as a result of employing particle arrestor technology, increasing combustion efficiency and switching to cleaner fuels. Emissions from developing countries, especially China and India, have only started to increase rapidly during the last two or three decades (Novakov et al. 2003; Bond et al. 2007) (Fig. 3) resulting in a southward latitudinal shift in global BC emission sources since the last decades of the twentieth century (Skeie et al. 2011).

It may be expected that environmental archives should reflect these temporal trends, although local and regional transport and depositional processes may influence these records at the site-specific level (e.g., Ruppel et al. 2013). Past accumulation and fluxes of BC can be studied from sediments and soils as well as ice cores from continental ice sheets and glaciers. While ice sheets are invaluable archives of atmospheric pollutant deposition histories and may record inputs with seasonal resolution for thousands of years, their geographical distribution is limited and ironically it is the influence of BC on glacial melting that is now removing the record we would like them to preserve.

Black Carbon in Ice Cores

One of the first studies to show historical trends in BC was from an ice core in the European Alps (Lavanchy et al. 1999). Black carbon concentrations were found to increase by a factor of 3.7 from pre-industrial (1755–1890) to modern times (1950–1975) and by considering BC emissions from Germany, France, Switzerland and Italy these trends were found to mostly reflect particulate carbon emissions from Western Europe. A second ice core from an adjacent site (Jenk et al. 2006) but covering the period 1650–1940, showed a six-fold increase in BC concentration starting from around 1870. Radiocarbon analysis of graphitic carbon dioxide generated during thermal BC quantification also showed an increasingly anthropogenic origin after this time (Jenk et al. 2006).

In 2007, McConnell et al. published the records of BC deposition since 1788 derived from two ice cores taken on the Greenland Ice Sheet. They found a sevenfold increase in BC concentrations from 1850, peaking in the early decades of the twentieth century and followed by a decline to almost pre-industrial levels after 1950. Concentrations of BC prior to AD 1850 were found to closely match those of vanillic acid, used as an indicator for coniferous forest fires, but after 1850, BC concentrations reflected non-sea-salt sulphate indicating industrial emissions as the primary source (McConnell et al. 2007). North America was considered the most plausible source area for this contamination. However, McConnell et al. recognized that these high-altitude ice cores (2473 and 2713 m above sea level) were located in the free troposphere and hence BC deposition recorded there could not also be taken as representative of trends for lower altitude regions of the Arctic. Hirdman et al. (2010) confirmed that the source regions of BC for Summit on the Greenland ice sheet (3208 m above sea level) were representative only for this specific site and did not reflect the low-level atmospheric transport of pollution (Stohl 2006) from high latitude Eurasia that influences much of the rest of the Arctic (Quinn et al. 2011).

McConnell et al.'s (2007) highly influential paper was soon followed by other studies on the long-term records of BC in ice cores. Ming et al. (2008) reported elemental carbon concentrations in a Himalayan ice core while Xu et al. (2009) showed the records from five ice cores taken from glaciers on the Tibetan Plateau. Here, BC concentrations were relatively high in the 1950s–1960s but decreased during the 1970s–1980s, especially on glaciers influenced by long-range atmospheric transport from Europe (Xu et al. 2009). This pattern was seen to reflect decreasing emissions in Europe as a result of 'Clean Air' policies. However, during the 1980s–1990s and especially since the latter part of the 1990s, BC concentrations increased again, and this was thought to be due to industrialization in southern Asia. Ming et al. (2008) observed similar increases in BC concentrations after 1980–1990 in their core from the East Rongbuk Glacier near Mt. Qomolangma (Everest) (Fig. 4a).

These European (Lavanchy et al. 1999; Jenk et al. 2006; Legrand et al. 2007) and Himalayan (Ming et al. 2008; Xu et al. 2009) studies used a filter-based thermal-optical method, where comparably large amounts of ice are required in order to exceed the detection limit of the analysing instrument resulting in an annual to

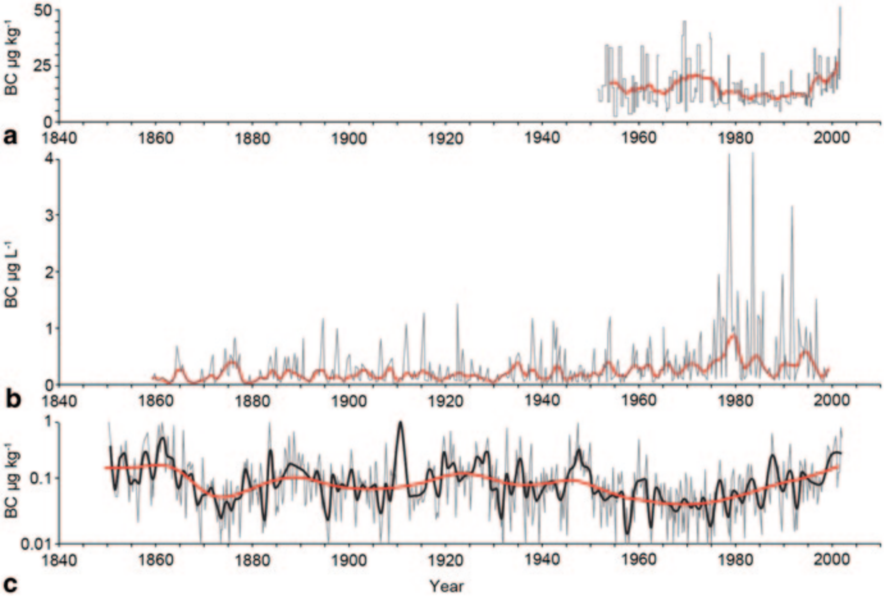


Fig. 4 **a** and **b** Black carbon concentration data from two adjacent ice cores taken from the East Rongbuk glacier on Mount Everest using two different analytical methods. **a** *Black line* is raw data; *red line* is smoothed (redrawn from Ming et al. (2008)); **b** *Black line* shows data re-sampled to 4 samples per year; *red line* is data smoothed with a robust spline (redrawn from Kaspari et al. (2011). Also for comparison, **c** the black carbon record for an ice core taken from Law Dome, Antarctica plotted on a monthly (*thin black line*) and annual (*thick black line*) resolution. *Red line* is 21 year smoothing (redrawn from Bisiaux et al. (2012b)). Note the difference in y-axis scales between the three figures

multi-year resolution. By contrast, McConnell et al. (2007) used a new method for BC analysis that had been developed for atmospheric samples (Stephens et al. 2003). In this method BC concentrations were determined with a single particle soot photometer or 'SP2'. This measures mass and size distribution of individual BC particles using laser-induced incandescence (Schwarz et al. 2006; McConnell et al. 2007) and thus only very small amounts of ice are required, thereby allowing a monthly resolution.

The SP2-method was also used for a study on BC deposition using an ice core retrieved from Mt Everest (Kaspari et al. 2011) close to the one collected by Ming et al. (2008) but the results of these two studies differed quite significantly. Firstly, the Kaspari et al. (2011) study did not observe the increase in BC concentrations after the 1990s evident in the Ming et al. (2008) core (Fig. 4a, b); and secondly the concentrations in the later core were much lower than in the earlier one. Given the close proximity of the coring locations, it is unlikely that this variance is due to depositional differences alone but—as presented earlier in this chapter—is more likely due to the different analytical methods employed (Kaspari et al. 2011). Ming et al. (2008) collected BC for analysis by filtering the melted ice through a 1 µm pore-size filter prior to thermal-optical analysis, so particles smaller than this were most likely not quantified. However, the SP2 method employed by Kaspari et al. (2011) detected only BC particles with an estimated size of ≈80–500 nm. Hence, it is likely that these studies were measuring two quite different parts of the BC continuum possibly with little or no overlap. It is important, when comparing BC data from different studies, to be clear which analytical techniques are being used and which BC fractions are being quantified in order to make the appropriate interpretation. The analysis of these potentially different size-fractions for this area of the Himalayas is interesting in itself, as it may imply that emissions of larger particles (Ming et al. 2008) have increased in the source area (South Asia) since the 1990s, whereas emissions of smaller ones (Kaspari et al. 2011) have not. This may point to an increase in low-efficiency industrial coal and oil combustion in the region over the last 20 years.

Results of BC deposition in the Antarctic are also of great interest, because the region is the most remote from human influence. Bisiaux et al. (2012a, b) retrieved six ice cores from Antarctica with a maximum distance of ≈3500 km between them. The BC records showed considerable temporal variability at annual to decadal scales, but common features included relatively low concentrations from 1890 to 1910, higher concentrations 1910–1930 but, in particular, an increasing concentration trend at the end of the twentieth century (1980–2000) (Fig. 4c). These depositional patterns, especially in the latter part of the twentieth century, were linked to changes in anthropogenic BC emission sources in the southern hemisphere and especially emissions from southern hemisphere grass fires and biofuel emissions, which were reduced over the 1950–1980 period (Bisiaux et al. 2012b).

In summary, ice cores are able to provide considerable insights into BC depositional history, variability between regions and in providing historical estimates for radiative forcing in both the atmosphere and when deposited on snow and ice (Ming et al. 2008; Kaspari et al. 2011). Although the distribution of appropriate sampling sites is quite limited globally, ice cores do indicate the scale of long-range atmospheric transport of anthropogenic emissions to the remotest regions, albeit that physical constraints (McConnell et al. 2007), climatic variables (Bisiaux et al. 2012b) and methodological considerations (Kaspari et al. 2011) may significantly affect results and interpretation. Black carbon distribution and deposition globally is rather heterogeneous and, because BC has a relatively short atmospheric residence time (days to weeks), mainly linked to regional sources. Consequently, in order to get a better insight into the distribution and effects of BC in the past, measurements are required from many locations more widely distributed than is possible to achieve with ice cores alone. Here, lake sediments can play an important role.

Black Carbon in Lake Sediments

As with ice cores, analytical methodology is a critical consideration for BC determination in sediments and will affect which fraction of the BC continuum is being quantified. An additional factor for sediments, when compared with ice and especially atmospheric samples, is that BC comprises a very minor component and needs to be separated from the inorganic minerals and thermally unaltered organic carbon (such as plant/animal material and humic substances) that comprise the bulk of the sediment. This is often achieved by different chemical and/or thermal pretreatments, which are based on the assumption that BC is more resistant to breakdown than other forms of organic carbon and some minerals (Hammes et al. 2007). These different methods may themselves result in the selection of differing fractions of the BC continuum, and analysis of the same samples with different methods can result in very different estimates for BC content (Hammes et al. 2007). However, where BC is quantified wholly or partly by visual methods, that is by identifying and counting particles using light (e.g., Goldberg et al. 1981; Odgaard 1993; Rose 1994, 2008) or scanning electron microscopy (e.g., Karls and Christensen 1998; Kralovec et al. 2002; Thevenon and Anselmetti 2007), then the fraction of the continuum is much more closely defined, albeit restricted to relatively large particles, >≈2 μm (e.g., Rose 1994; Thevenon and Anselmetti 2007).

The early work on BC quantification in sediments was mainly based on chemical extraction and visual identification approaches (e.g., Goldberg et al. 1981; Renberg and Wik 1984; Odgaard 1993; Rose 1990a; Stoffyn-Egli et al. 1997; Doubleday and Smol 2005), and while this work continues (e.g., Thevenon and Anselmetti 2007; Rose et al. 2012), there has been a recent escalation of interest in applying techniques developed for atmospheric research to sediment studies. These methods enable the quantification of smaller, high-refractory BC particles that cannot be assessed by visual methods (e.g., Gustafsson et al. 1997, 2001; Elmquist et al. 2007; Gelinas et al. 2001; Husain et al. 2008). The switch in focus towards smaller size fractions lies with the increasing interest in the climatic role of BC particles (longer atmospheric residence times and transport distances) and in advances in understanding the impacts of BC on human health (deeper penetration into respiratory tracts) (e.g., Hansen and Nazarenko 2004).

The chemo-thermal oxidation method (CTO-375) developed by Gustafsson et al. (1997; 2001) is one of the most widely used methods for this type of particle in sediments, but studies reporting the long-term accumulation trends of BC in sediments are still quite scarce. In Upper Mystic Lake in eastern North America (Gustafsson et al. 1997), the record for the period AD 1886–1989 showed low BC concentrations prior to industrialization, but increasing concentrations from c. 1940 to 1960 after which concentrations declined first slowly and later more rapidly. Combustion-derived PAH concentrations in the same core showed similar trends, as did records of sedimentary charcoal and spheroidal carbonaceous particles in Lake Michigan (Goldberg et al. 1981).

In Europe, Muri et al. (2006) also demonstrated a good agreement in the temporal records of BC, SCPs and PAHs in the sediments of three mountain lakes in the Slovenian Alps over the industrial period, peaking in the mid-twentieth century and declining through the following decades to 2000. A longer, 700-year record from Lake Aspvreten in Sweden (Elmquist et al. 2007) also compared BC and PAH fluxes. Pre-industrial fluxes of both contaminants varied little over the medieval period (Fig. 5), but BC increased ahead of ΣPAH starting in the period prior to the

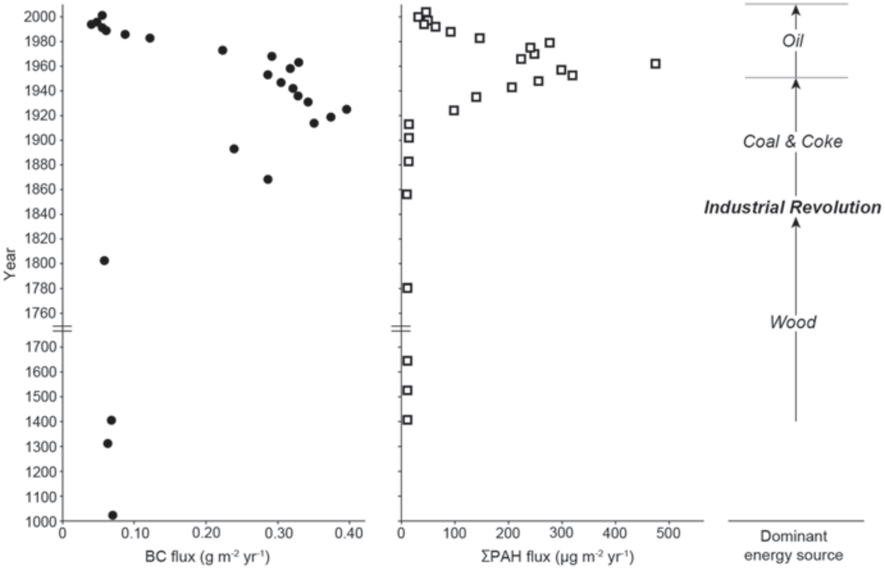


Fig. 5 Historical fluxes of BC and ΣPAH over 700 years from Lake Aspvreten, Sweden. The dominant combustion-based energy sources (i.e., wood, coal, and coke, or oil) are also displayed. (Redrawn from Elmquist et al. (2007))

industrial revolution and this was thought to be due to increased wood combustion (Fig. 5). This trend continued with BC fluxes peaking in 1920 and ΣPAH peaking in 1960 at 50 times the pre-industrial flux value. Both then declined to pre-industrial rates in the most recent sediment levels. Elmquist et al. (2007) suggested that the driver for these changes was fuel-use patterns with the early record influenced by a lower BC/PAH emission factor for coal than for wood combustion. Recent declines could be linked to decreasing reliance on petroleum fuels and legislative control.

These studies not only highlight the need to specify the fraction of BC that is being analysed to interpret the resulting records accordingly but illustrate that a knowledge of the changing roles of various fuel-types, their efficiencies and the impact that legislative approaches will have upon them may also be required. For example, in New York City, the historical BC inputs to two lakes as observed from their sediment records were seen to differ markedly from published historical reconstructions based on fuel consumption and estimated emission factors (Louchouarn et al. 2007). Only when the changing role of oil as a combustion fuel and the increased vehicular emissions resulting from diesel usage were considered could the sediment records and emissions data be resolved.

A recent significant step forward has been the use of sedimentary elemental carbon to reconstruct atmospheric concentrations (Husain et al. 2008). Atmospheric elemental carbon concentrations measured at Whiteface Mountain, New York, from 1978 to 2005 were calibrated against those from a lake sediment record retrieved from nearby West Pine Pond. Both sample types were analysed using the thermal

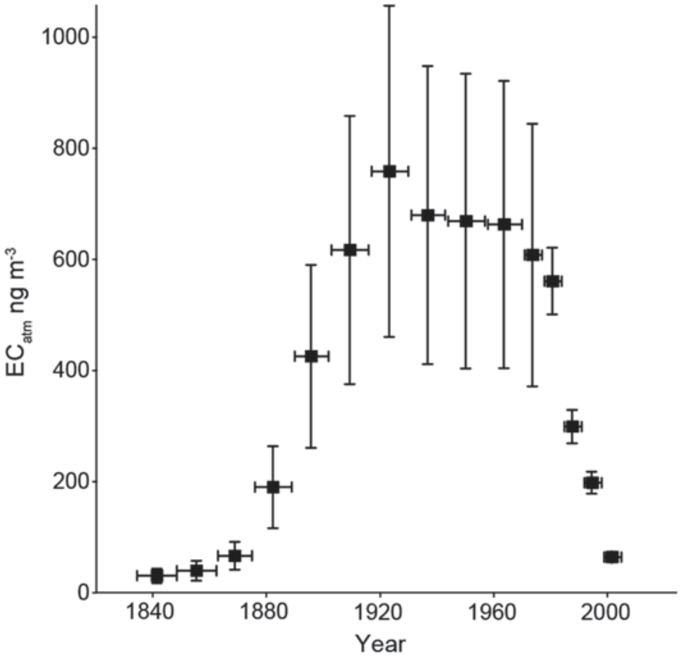


Fig. 6 Atmospheric elemental carbon concentrations 1835–2005 reconstructed from a lake sediment core taken from West Pine Pond, New York. (Redrawn from Husain et al. (2008))

optical method commonly used for atmospheric samples and more recently ice core samples (e.g., Lavanchy et al. 1999; Ming et al. 2008; Xu et al. 2009). The results showed a good temporal agreement over the calibration period. This calibration was then used to reconstruct atmospheric elemental carbon concentrations from 1835 to 1978 using the sediment record (Fig. 6), which showed good agreement with regional BC emissions. Such an approach emphasises the value of environmental archives and how they may be used to extend records where monitoring data are absent. These may become more important as historical records of BC are required to inform climate models.

Spheroidal Carbonaceous Particles (SCPs) in Lake Sediments

Spheroidal carbonaceous particles (SCPs) are the carbon-rich component of fly-ash, the particulate product of the incomplete combustion of coal-series fuels and fuel-oil at industrial temperatures. As such, SCPs form a discrete and well-defined fraction of the BC continuum (Fig. 2). Although the historical records of SCPs have been used in peat and ice cores as indicators of atmospheric contamination (e.g., Isaksson et al. 2003; Hicks and Isaksson 2006; Barnekow et al. 2007) and additionally in peat cores as means of core dating (Yang et al. 2001; Kuoppamaa et al. 2009) they have most widely been used in lake sediments where they have been estimated to comprise up to 3 % of BC, although this value is highly variable in space and time (Ruppel et al. 2013). A detailed introduction to the extraction and uses of SCPs in lake sediments has been included in previous volumes of this DPER series (Rose 2001; Rose and Yang 2007) and we will not replicate these here. However, as they have been so widely employed in sediment studies, for completeness, we will briefly outline their main uses with some examples.

The characteristic morphology of SCPs and their well-defined industrial source makes them useful and unambiguous indicators of atmospherically deposited contamination. They were first identified in marine sediments (Griffin and Goldberg 1979) and later in a freshwater sediment core (Lake Michigan; Griffin and Goldberg 1981) where their morphology was used to indicate changes in fuel use (wood to coal) while historical changes in concentration were used as an indication of intensity of fossil-fuel combustion. Their use in this regard became more important in the following decade when historical sediment records of SCP concentrations and fluxes in acidified lakes were used as supporting evidence for the acid deposition hypothesis in the surface water acidification debate (e.g., Battarbee 1990). Here, the SCP concentration record was found to mirror diatom-inferred pH reconstructions at many acidified lakes in the UK, Sweden and Norway and hence indicated a likely fossil-fuel combustion source for acidifying substances. They were used in a similar way in acidification studies in North America (e.g., Charles et al. 1990).

SCPs have also been widely used in lake sediment studies, both as a measure of atmospheric contamination from specific sources, and as a means to provide chronologies to recent sediments either instead of, or to provide independent corroboration for, radiometric dating. The dating of sediments using SCPs was first developed by Renberg and Wik (1984, 1985) in Sweden. The approach relies on the robust and repeatable historical concentration profiles for SCPs across broad regions (e.g., Rose et al. 1999b) but requires the profile to be calibrated to other chronologies (e.g., varves, ^{210}Pb or emission statistics) in the first instance. Initially, three dates were identified; the start of the record in the mid-nineteenth century; a rapid increase in concentration c. 1950, and a concentration peak, for which an ascribed date is more regionally variable but tends to occur in the 1960s—1980s in Europe (Rose 2001). More recently, the use of SCP cumulative inventory profiles has allowed more dates to be ascribed to the lake sediment SCP record (Rose and Appleby 2005) although the mid-nineteenth century remains the earliest dating horizon as this is when coal was first burned at the temperatures required for SCP formation. To date, there appears to be no evidence for the degradation of SCPs within natural archives and as a result they may continue to provide a useful means of providing chronologies to industrial-age records for centuries to come. As the limits of ^{210}Pb chronologies move forward in time (i.e. always the most recent c. 150 years) and are progressively unable to date the full industrial period, a combination of the two approaches should become a powerful and reliable technique for dating recent sediments.

Rose (2001) summarised the regions of the world (mainly Europe, and some areas of North America, China and north Africa) where historical SCP records had been produced, but in the time since that review, these have further expanded to include sites in south-eastern Europe, such as Bulgaria (Ognjanova-Rumenova et al. 2009) and Romania (Rose et al. 2009); the Ural Mountains of Russia (Solovieva et al. 2005, 2008); North Africa (Rose et al. 2003; Flower et al. 2009); western Greenland (Bindler et al. 2001); mountain lakes of the western United States (Landers et al. 2010); Chile (Chirinos et al. 2006; von Gunten et al. 2009); Japan (Yoshikawa et al. 2000; Tsukuda et al. 2006; Nagafuchi et al. 2009) and the Falkland Islands and Antarctica (Martins et al. 2010; Rose et al. 2012). Their presence has now, therefore, been recorded in most regions of the world. In almost all areas, the mid-twentieth century increase in SCP concentration is observable while the start of the record tends to depend on regional fossil-fuel combustion as well as site specific sediment accumulation rates. In regions of low SCP deposition, the start of the record may begin in the mid-twentieth century when the rapid increase in concentration surpasses the analytical limit of detection for the first time, rather than being the date of first SCP production. Post-1950, the SCP record is more variable in different regions of the world and this is dependent upon a number of factors including national and regional industrial development and decline, the introduction of policies leading to emission controls of industrial sources, and changing fuel-types such as the increase in the use of natural gas and renewable energy sources for power generation. Further development of regional SCP chronologies, such as that proposed for the UK (Rose and Appleby 2005), may therefore need work at a greater spatial resolution than might once have been required.

SCP sediment records have also been employed as proxies for other depositing contaminants. Fernández et al. (2002) considered the relationship between SCPs and PAHs in mountain lakes finding both gave consistent histories of pyrolytic emissions across Europe, but only when differing particle size fractions (PAH: <1 µm; SCP>5 µm) and hence source regions were considered. Rose and Juggins (1994) used the SCP record in surface sediments to determine non-marine sulphate deposition across a broad geographical region. This was developed further by Rose and Monteith (2005) who used annual sediment trap SCP fluxes over a 12-year period from Round Loch of Glenhead in Galloway, Scotland, and measured non-marine sulphate deposition from an adjacent atmospheric deposition monitoring site at Loch Dee, to calibrate the SCP flux record. They then used this to reconstruct site-specific non-marine sulphate deposition for the lake over a 154-year period (1848–2002) providing a much improved record compared with previous modelled estimates (Fig. 7). This relationship with other pollutants highlights the role of SCPs (and other BC) as a vector by which polluting substances such as trace metals and persistent organic pollutants can be transported (Wey et al. 1998; Chen et al. 2009). This property was also the foundation by which SCPs have been used in chemical source apportionment studies. Griffin and Goldberg (1979) used SCP morphology and surface texture to distinguish between coal, oil and wood derived particles, and this was developed further by Rose et al. (1996) in a chemical apportionment technique using the trace elements on SCP surfaces to distinguish between the main fuel types in the UK, and later continental Europe (Rose et al. 1999a). Although this was applied to regional surface sediments to determine geographical distribution of contaminants from fuel sources (e.g., Rose and Harlock, 1998; Fott et al. 1998)

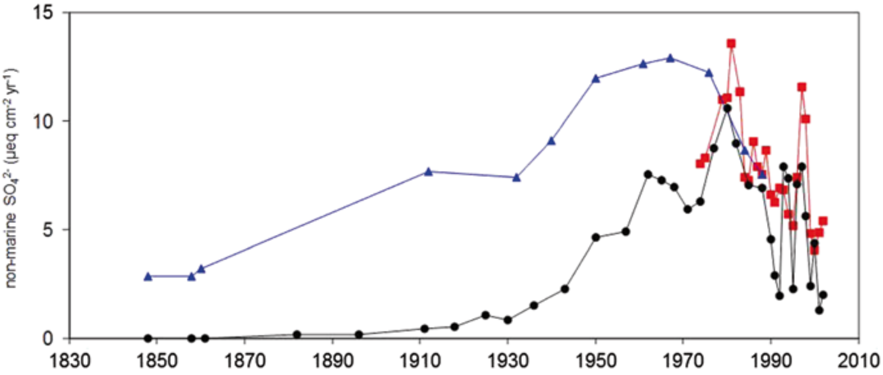


Fig. 7 SCP reconstruction of non-marine sulphate deposition at Round Loch of Glenhead, Galloway (1848–2002). Non-marine sulphate reconstructed from SCPs (●) and measured non-marine sulphate deposition for Loch Dee (🟥) compared with the estimated record based on a modelled historical national trend (▲) scaled to fit the geographically nearest available 1988 deposition figure and used in recovery models. (Redrawn from Rose and Monteith (2005))

and historically down a sediment core (Rose et al. 1996), to our knowledge this approach has not been developed or applied further.

Other Industrial Particles: Inorganic Fly-Ash Particles

While SCPs are produced from the incomplete combustion of the organic fraction of coals and fuel oil, the other component of fly-ash, inorganic ash spheres (IASs), are produced from the fusing of non-combustible components present within the fuel (Rose 2001). As a consequence IASs are almost solely derived from coal-series fuels as a result of mineral inclusions within coal seams and other non-combustible material from the seam edge. Because IASs derive from the melting of minerals, unlike SCPs, they are true spheres while their chemical composition is dependent upon the original mineral. This means that they are predominantly aluminosilicates, and this leads to additional difficulties in their extraction from sedimentary material (Rose 1990b), although iron-rich fly-ash particles in lake sediments may be identified and extracted by means of their magnetic susceptibility (Querol et al. 1993). Because IASs are also similar morphologically to some natural particulates (e.g., volcanic and meteoritic microspherules) and some chrysophyte cysts, they appear to have a background concentration in sediment records that is considerably higher in areas of volcanism (Nagafuchi et al. 2009). They have therefore been less widely used than SCPs in palaeolimnological studies.

As IASs are almost solely derived from the combustion of coal-series fuels and SCPs are from both coals and oil, the ratio of the concentrations of these two particle types (IAS:SCP) has been used as a means to distinguish fuel sources. IAS:SCP ratios exceeding 1.0 are usually ascribed a predominantly coal origin (Rose 1996).

This has been used to indicate contaminant particle sources in remote regions (Nagafuchi et al. 2009; Rose et al. 2012) and as a comparison with results from SCP fuel-type characterisation (Rose 1996).

Recent and Future Developments

A number of studies indicate that total BC emissions in North America and Europe have already been declining for some time as a result of the successful implementation of clean air policies, such as the introduction of particle arrestor technology, more efficient combustion and a switch to cleaner energy sources (e.g., Novakov et al. 2003). SCP depositional fluxes are already at levels not seen since the 1930s in some regions (e.g., Rose and Monteith 2005). While total BC emissions from developed countries are expected to continue to decrease, BC emissions in Asia increased by 30 % between 2000 and 2005 (Bond et al. 2013) and emissions are projected to increase further or stay the same over the next 20 years in China and India (Streets et al. 2004). Furthermore, emissions of finer fractions, too small to be removed by particle arrestor technology, and with longer atmospheric residence times, are not necessarily declining even in industrialized countries (e.g., Elmquist et al. 2007) and may increase further during the twenty-first century as a result of increasing energy consumption and vehicular emissions (Streets et al. 2004). Hence, fine BC may well continue to reach sensitive Arctic and Himalayan areas and continue to perturb the monsoonal cycle in southern Asia despite changing source regions (Koch and Hansen 2005).

Significant choices can already be made to reduce climate impacts of BC and these issues represent an opportunity to involve both developed and developing countries in a common air quality improvement effort. Choosing biomass rather than fossil fuels would reduce BC impacts, because BC particles resulting from fossil fuel combustion are thought to warm the atmosphere twice as much as those from biomass burning (Ramana et al. 2010). By bringing BC into climate negotiations the objective of developed countries to mitigate global warming could also meet the goals of developing countries for cleaner air (Grieshop et al. 2009) while additionally having significant health (Löndahl et al. 2010; Shindell et al. 2012) and economic benefits (Barbir et al. 1990; Machol and Rizk 2013).

New and Emerging Particle Types

Although BC will continue to be a significant particulate pollutant for many decades to come, other new and emerging particle types may also have increasing environmental impacts.

Microplastics

Of the 230 million t of plastics produced annually, more than 10% ends up in the oceans (Cole et al. 2011). Plastic can enter the environment by being intentionally or unintentionally discarded and also by being wind-blown from land-fill sites. Since the 1950s an estimated 1 billion tons of plastic have been discarded which may persist for hundreds of years (O'Brine and Thompson 2010; Bergmann and Klages 2012). Plastic resin pellets, the raw material for much manufacturing, may also be unintentionally released during manufacturing and transport. These are granules with a diameter of a few millimetres and may be carried by surface runoff and rivers to the ocean or to the ocean directly (Mato et al. 2001; Holmes et al. 2011). While "macro-litter" (Bergmann and Klages 2012) causes entanglement, suffocation and disrupts ingestion in many marine fauna (Derraik 2002), it may be broken down mechanically by UV radiation or by biological degradation (Imhof et al. 2012) into secondary particles, or microplastics, generally defined as being less than 1 mm in size (Imhof et al. 2012) or between 67–500 µm (Andrady 2011). Microplastics may also be derived from abrasives in personal care products or from shedding during laundry and may pass through standard wastewater treatment facilities unchanged (Engler 2012). As with BC described above, these particles can adsorb pollutants onto their surfaces including trace metals (Holmes et al. 2011), PAHs, PCBs, organochlorine pesticides (Mato et al. 2001; Cole et al. 2011) and brominated flame retardants (Zarfl and Matthies 2010; Engler 2012). Via ingestion, these can then enter the marine food web.

Research on these particle-types has mainly been focussed on their association with potentially toxic compounds, and the scale of contamination from the particles themselves, while seemingly ubiquitous, has not been wholly addressed. Microplastics were found in all samples taken from 18 beaches across six continents (Browne et al. 2011) with concentrations ranging from 8 L^{-1} in Australia to 124 L^{-1} in Portugal. These particles were mainly found to be polyester (56%) but also acrylic, polypropylene, polyethylene and polyamide fibres. Other studies have shown evidence for microplastics in all samples taken from Belgian (Claessens et al. 2011), UK (Holmes et al. 2011) and Singaporean (Ng and Obbard 2005) marine sediments and in Arctic surface waters (Zarfl and Matthies 2010).

In terms of temporal trends and environmental archives, very little data exist to date, although such data would be very useful in terms of assessing rates and even directions of change, which are currently largely uncertain (Cole et al. 2011). Concentrations of plastic marine debris in the North Atlantic subtropical gyre showed very little trend over a 22-year period despite a strong increase in discarded material (Law et al. 2010), but the total number of microparticles (fibres, granules and films) taken from sediment layers of a Belgian beach section (Claessens et al. 2011) showed an increasing temporal pattern (Fig. 8). However, continued degradation and weathering of microplastics results in the production of nanoscale particles and these may have a more significant future environmental impact.

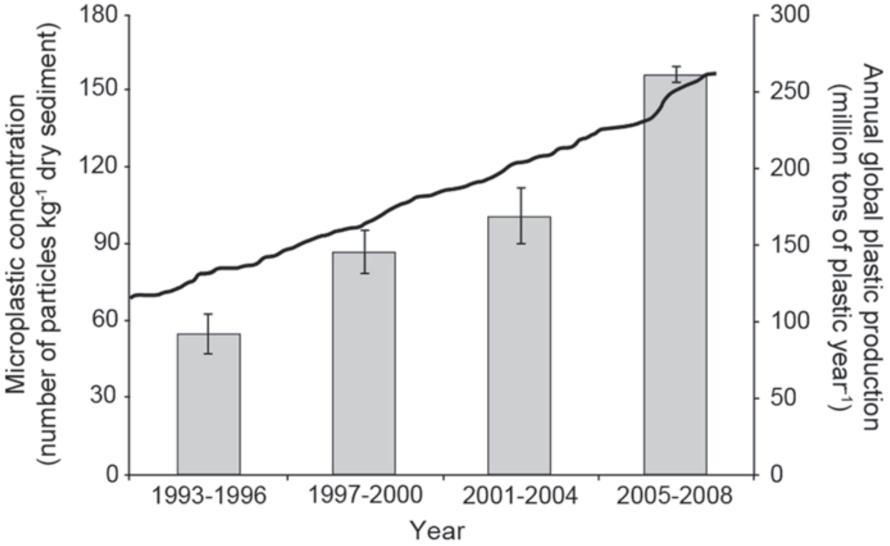


Fig. 8 The total number of microplastic fibres, granules and plastic films found in different sediment layers at the high water mark of a beach section at Groenendijk, Belgium. The *line* indicates estimated annual global plastic production (*right axis*). (Redrawn from Claessens et al. 2011)

Nanoparticles

A nanoparticle is defined as a substance having at least one dimension between 1 and 100 nm. It is particle size that gives these materials their unique properties, which are often quite different from larger versions of the same material (Klaine 2009). For example, carbon nanotubes have a higher strength-to-weight ratio than steel, are better thermal conductors than diamond and better electrical conductors than copper (Meo and Andrews 2001). The products of nanotechnologies are expected to increase exponentially and the environmental risks associated with their use are currently uncertain (Griffitt et al. 2008). The characteristics of these particles that play a role in their bioavailability, absorption, distribution, toxicity (Klaine 2009) and solubility (Misra et al. 2012) are also uncertain, although a recommended list of physical and chemical characteristics for toxicology studies on nanomaterials has been produced and includes size/shape/agglomeration; composition and structure; surface area, reactivity and charge; stability and solubility (MINChar 2008).

Although natural processes such as volcanic eruptions, forest fires, physical and chemical weathering of rocks may produce nanoparticles (Murr et al. 2004), these emissions are low compared with those produced by combustion processes (e.g., vehicular and stationary sources; hydrocarbon flames) (Utsunomiya et al. 2002; Sanchís et al. 2012). Current generation clean technology in coal-fired power plants has led to an unanticipated increase in emissions of particles 1–10 nm in diameter

(Junkermann et al. 2011) resulting in higher concentrations of nanoparticles (e.g., C_{70} fullerene, Sanchís et al. 2012) in areas of industrial activity. Particles of this size are effective precursors of cloud condensation nuclei, which may cause a shift in precipitation patterns (Junkermann et al. 2011), while carbonaceous nanoparticles such as nanotubes, BC and soot from natural gas combustion have been found to be cytotoxic and may pose a variety of respiratory health problems (Murr and Garza 2009; Scown et al. 2010). Further, the ability of nanomaterials to efficiently adsorb gases (SO_2, NO_x), trace elements (e.g., As, Mn, trace metals) and organic pollutants as well as viruses, bacteria and antibiotics (Khin et al. 2012; Yang et al. 2013), means they offer great potential for environmental remediation but also pose a more significant threat as carriers of toxic substances including PAHs (Hu et al. 2008), perfluorinated alkylated substances (e.g., PFOS) (Kwadijk et al. 2013) and other POPs such as PCBs (Andrady 2011) into the environment as noted above for BC and SCPs.

In addition to respiratory effects and their potential role as chemical ‘carriers’, a number of studies have now begun to explore the toxicological effects of nanoparticles on aquatic organisms and Scown et al. (2010) provide an excellent critical review. A number of different carbon-nanoparticles such as C_{60} fullerene and carbon nanotubes have been shown to exhibit antibacterial or antimicrobial activity with direct contact of the nanotube with the membrane being the likely cause of cell death, while the antibacterial properties of metal oxide nanoparticles (e.g., TiO_2, ZnO, CeO_2 and Al_2O_3) are well established (Scown et al. 2010). TiO_2 nanoparticles act as ‘photocatalysts’ and in the presence of UV light they react with oxygen and water to form highly reactive oxygen species (ROS) which damage cell membranes of bacteria. Hence, TiO_2 acts as an effective sewage disinfectant (Miller et al. 2012). However, ROS also inhibit growth of aquatic algae and clump on the surface of algal cells attacking membranes and limiting photosynthesis. The toxicity of metal oxides to algae shows a clear size relationship with larger particles exhibiting lesser effects (Navarro et al. 2008). However, Griffitt et al. (2008) found no toxic effects from TiO_2 on algae, daphniids (*Daphnia pulex*) or zebrafish (*Danio rerio*) although silver and copper nanoparticles were lethal to daphniids at concentrations of 40 and 60 $\mu g\ L^{-1}$ respectively. However, there is an apparent inconsistency in results between studies as TiO_2 has also been found to result in immobilisation and mortality to daphniids (Scown et al. 2010).

Daphniids were used in the majority of nanoparticle aquatic toxicity studies reviewed by Baun et al. (2008) and, as filter feeders, they may be more susceptible than other aquatic fauna (Scown et al. 2010) with exposure concentrations of 2.5–5 ppm fullerenes resulting in delayed daphniid moulting and reduced number of offspring. However, uptake, depuration and bioaccumulation of carbon nanotubes by daphniids is not straightforward and may depend on many factors including organic matter content of the water (Petersen et al. 2009). In sediment-dwelling invertebrates including amphipods (*Hyalella azteca*) and chironomids (*Chironomus dilutus*) carbon nanotubes added to water (1.00 $g\ L^{-1}$) were found to significantly reduce survival and growth over a 14-day period (Mwangi et al. 2012). These nanoparticles have also been found to be respiratory and neurotoxicants in rainbow trout (*Oncorhynchus mykiss*) (Smith et al. 2007), but while carbon-based nanoparticles are generally considered to have the capacity to induce toxicity in aquatic vertebrates, effects have (so far) usually been seen at concentrations unlikely to be found in many natural aquatic environments. By contrast, both carbon-based and metallic nanoparticles have been shown to exhibit developmental abnormalities in fish embryos (Scown et al. 2010). However, in all studies of ‘natural’ exposure, factors such as solubility, presence of other compounds and environmental parameters (e.g., pH, surface coatings, organic matter) are key considerations in confounding or exacerbating toxic effects to aquatic biota (Scown et al. 2010; Misra et al. 2012).

Nanoparticles therefore have the capacity to be significant and increasing environmental contaminants into the future, but to our knowledge there have, to date, been no studies considering long-term trends in engineered nanoparticles (ENPs; cf naturally produced nanoparticles) or attempts to extract these from environmental archives. Although Esquivel and Murr (2004) demonstrated the possibility of extracting nanoparticles from a 10,000-year-old ice core sample from Greenland and found a range of carbon nanotubes and fullerene-type particles, no historical record was attempted, possibly because the method was described as “tedious”. Standardised approaches, particle characterisations and an advancement of tools and techniques in order to assess and quantify these particles are urgently needed (Scown et al. 2010) as this particle type will undoubtedly become significantly more important in the coming decades.

Summary

Particulate contaminants may have a range of environmental impacts. In the atmosphere they can adversely affect human health via respiratory intake while those that are carbonaceous can additionally contribute to atmospheric warming, glacial and ice-cap melting and the transport of pollutants via absorption or adsorption to their surfaces. These pollutants include trace metals, PAHs and persistent organic pollutants such as PCBs, PCDD/Fs and brominated flame retardants. Determining temporal and spatial trends for particulates through the analysis of environmental archives can therefore provide useful information on a diverse range of issues.

The most common particle-type analysed from environmental archives is ‘black carbon’. This term covers a myriad of particles forming a combustion continuum from charred biomass through to high temperature refractory soots. There is a long record of black carbon in the environment, from natural Devonian and Permian sedimentary deposits, to charcoal records spanning tens of thousands of years and frequently used as an indicator of human influence. However natural and early human black carbon emissions are very much lower than those from industrial sources.

Black carbon records in ice, peats, soils, marine and lake sediments have been used to assess the scale, extent, onset and sources of contamination and also for providing chronological control for these sequences. There is no single quantitative analysis for black carbon and different methods assess different parts of the black carbon continuum. Care is therefore required when comparing temporal records and scales of contamination between studies that have used different approaches. While industrial black carbon emissions in Europe and North America have been declining for some years and are predicted to continue to do so over coming decades, emissions from vehicular sources, and industrial emissions from countries such as China and India are predicted to increase. As a consequence, while source regions may have altered, global black carbon emissions may continue to increase. Environmental archives will continue to play an important role in tracking the distribution and temporal trends from site-specific to international scales and in validating transport and deposition models.

Other emerging particle-types of concern include microplastics (< 1 mm) particularly in the marine environment and also nanoparticles (defined as possessing at least one dimension 1–100 nm). Both these particle-types have large capacities for pollutant adsorption to their surfaces, while nanoparticles maybe directly toxic to organisms in a number of environments. Currently, there are very few historical records published for these particle types and techniques for their extraction and analysis are urgently needed.

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Tracking Long-range Atmospheric Transport of Contaminants in Arctic Regions Using Lake Sediments

Jane Kirk and Amber Gleason

Abstract Due to the nature of global atmospheric circulation patterns, numerous contaminants of concern, including mercury (Hg) and persistent organic pollutants (POPs), undergo long-range transport to the Arctic where they can be deposited to landscapes and water bodies. As a result, both mercury and POPs have recently reached levels in Arctic mammals and fishes that are high enough to pose health risks to Northern peoples consuming these animals as traditional country foods. Dated lake sediment cores provide a valuable tool for examining temporal trends in atmospheric contaminant deposition. In addition, the recent application of novel multi-proxy approaches is allowing atmospheric contaminant deposition to be examined within the context of numerous climate-induced alterations to contaminant cycling, such as increased catchment contaminant inputs driven by climate-induced erosion. Here, we review current information on the use of dated sediment cores to examine post-industrial (post-~1850) changes to atmospheric mercury and POPs deposition, including atmospheric contaminant transport and deposition processes, the impacts of climate-induced changes on these processes, and the application of novel lake sediment core analyses to untangle trends in contaminant deposition due to multiple sources and environmental stressors. Hg and POPs are compared and contrasted throughout the chapter, as, although these contaminants are both of great concern in the Arctic, their differing physical-chemical properties and emission sources result in differing transport and deposition pathways. Finally, we make suggestions for future research that will allow dated lake sediment cores to continue to provide valuable information on contaminant deposition in the face of a changing Arctic climate.

Keywords Contaminants · Sediment cores · Arctic · Persistent organic pollutants · Heavy metals · Mercury · Atmospheric deposition · Long range transport · Environmental reconstruction

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Introduction

Due to the nature of global atmospheric circulation patterns, many contaminants of concern, including numerous heavy metals and persistent organic pollutants (POPs), undergo long-range transport to remote Arctic regions where they can be deposited to landscapes and water bodies. As a result, numerous heavy metals and POPs have recently reached levels in terrestrial and marine mammals and fishes that are high enough to pose health risks to Northern peoples consuming these animals as traditional foods, often referred to as country foods (AMAP 2011). Of the heavy metals, mercury (Hg), a potent neurotoxin, is currently of highest concern. For example, $>50\,\%$ of mothers and women of child bearing age in numerous Northern populations exceed the US Environmental Protection Agency's recommended blood Hg levels of 5.8 mg L^{-1} (AMAP 2011), which is high compared to the 50th percentile of American females of 0.72 mg L^{-1} (Department of Health and Human Services 2012). A recent meta-analysis of studies that have used analysis of archived and modern teeth, hair, and feathers to examine changes in Hg levels over the past ~800 years suggests that there has been a10-fold increase in Hg levels in upper trophic level Arctic marine animals (beluga, ringed seal, polar bear, birds of prey) over the past ~150 years, with an average rate of increase of 1–4 % per year (Dietz et al. 2009 and references therein). Numerous legacy POPs, such as PCBs, DDT, chlordane, and toxaphene, as well as emerging and currently used POPs, such as brominated flame retardants, polychlorinated naphthalenes and fluorinated compounds, are also of major concern (AMAP 2009). In Greenland communities, $>50\,\%$ of mothers and women of child bearing age still exceeded the blood Level of Concern of 5 μg L^{-1} for PCBs in 2002–2006 surveys (AMAP 2009).

Determination of temporal trends in contaminant deposition in the Arctic is obviously important from an environmental and human health perspective, as well as from a socioeconomic standpoint. Therefore, in the absence of long-term environmental monitoring data in many Northern remote regions, dated lake sediment cores have been invaluable in answering questions such as "has deposition increased?", "when?" and "by how much?". Information gained from dated lake sediment cores on increased contaminant loadings over the last ~150 years has been important for implementation of international agreements to decrease or phase out certain contaminants, including the United Nations Economic Commission for Europe's Convention on Long-range Transboundary Air Pollution POPs Protocol and Stockholm Convention on POPs (Muir and Wit 2010). Although data interpretation is slightly more difficult for metals such as Hg, where there are both natural and anthropogenic sources (as opposed to most POPs), the use of lake sediment cores to demonstrate post-industrialization increases in atmospheric deposition has been important in demonstrating that elevated metals concentrations in Arctic biota are not due to natural emissions or underlying geology. Information acquired from Arctic lake sediment cores, especially in light of the good agreement that has been demonstrated between deposition estimates obtained from dated lake sediment cores and the global mercury model GRAHM (Global/Regional Atmospheric Heavy Metals Model), is being used to inform the current United Nations Global

Hg Partnership. Numerous noteworthy strides have recently been made that allow dated lake sediment cores to continue providing new and useful information on contaminant deposition in the face of a changing climate. For example, recent application of multi-proxy paleolimnological approaches has allowed examination of the impacts of climate-induced increases in lake primary production and catchment erosion on contaminant deposition to lake sediments (Kirk et al. 2012). Understanding climate-induced changes to contaminant cycling is particularly important in the Arctic, where climate change is accelerating relative to the rest of the globe, with increases in average annual temperatures currently ~double those of the global average (UC 2011). Here we review current knowledge on the use of dated lake sediment cores to examine the post-industrial (post ~ 1850) deposition of contaminants that have undergone long-range atmospheric transport to the Arctic. We focus on Hg and POPs, which although both contaminate the Arctic and are expected to undergo climate-induced changes, have differing emission sources and physical-chemical properties which allows comparison and contrast of their transport and deposition pathways.

Long-range Atmospheric Contaminant Transport and Deposition

Atmospheric circulation patterns, contaminant source regions, and physical-chemical properties together impact a contaminant's journey to the Arctic via long-range atmospheric transport. Once contaminants are delivered to the Arctic, air-surface exchange rates, and the factors that drive these rates, determine their deposition to landscapes and water bodies. Contaminant transport and deposition to the Arctic and the potential impacts of climate-induced changes on these processes are discussed in the next two sections, whereas the post-depositional processing that occurs within freshwater ecosystems to produce sediment core records is discussed further below. Throughout this chapter, we focus on the use of lake sediment cores to examine long-range atmospheric transport of contaminants. However, due to the dynamic nature of many of the contaminants discussed and the unavoidable linkage of all the different environmental compartments, it is important to keep in mind that a fraction of the Hg and POPs recorded in lake sediment cores may have entered the Arctic via river discharge and ocean currents before entering the Arctic atmospheric pool and being deposited to landscapes and water bodies.

Wind transport can be highly efficient and can thus deliver contaminants from southern industrial regions to the Arctic within a few days (Bailey et al. 2000; Barrie et al. 1998; Halsall et al. 1998; Hung et al. 2001; Stern et al. 1997) (Fig. 1). The major atmospheric circulation pattern that governs delivery of contaminants to the Arctic is called the Arctic Polar Vortex (Macdonald et al. 2005 and references therein). This system produces high pressure areas over Siberia, the Yukon, and Baffin Island, and low pressure areas over the Aleutian Islands and the North Atlantic. In winter, these pressure systems force air in different directions producing three major

Fig. 1 Map of the Arctic including major pathways for atmospheric contaminant transport from source regions (*green* arrows), as well as median sea ice extent between 1979–2000 (*blue* line), and minimum sea ice extent in 2010 (*shaded* area) (redrawn from Kirk et al. 2012)

wind patterns, which together account for ~80 % of the annual south to north air, and thus the majority of the annual contaminant transport: air from the southerlies in the Norwegian Sea (40 %), eastern Europe and Siberia (15 %), and the Bering Sea (25 %) (Iversen 1996) (Fig. 1). Conversely, in summer the pressure cells weaken or disappear altogether and thus only ~20 % of annual south to north air movement occurs during this season. (Fig. 2 and 3)

The Arctic Oscillation (AO) index is commonly used to describe the strength of the Arctic Polar Vortex, with a positive AO reflecting lower pressure in the Arctic and higher pressure in the North Atlantic. Many studies have found correlations between atmospheric contaminant transport and the mode of the AO, as well as other circulation patterns (Wang et al. 2009; Becker et al. 2008; Ma et al. 2004; Macdonald et al. 2005; Macleod et al. 2005). For example, a positive AO is generally associated with increased contaminant transport to the Arctic (Becker et al.

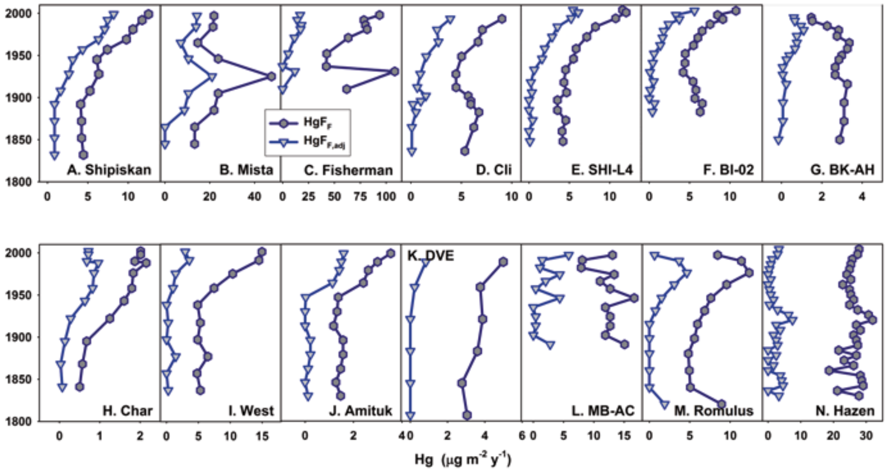

Fig. 2 Hg fluxes adjusted for sediment particle focusing (HgF$_{F)}$ compared to Hg fluxes adjusted for sediment particle focusing and post-industrialization increases in sedimentation rate (HgF, $_{adj}$) (µg m^{-2} y^{-1}) in 14 high and sub-Arctic study lakes (redrawn from Kirk et al. 2011)

2008; Ma et al. 2004). More specifically, stronger than normal southerly winds at high latitudes result in long-range transport of POPs with Eurasian emission sources north of 40 °N (Breivik et al. 2007). Transport of POPs with emission sources south of 40 °N, however, are actually decreased by the strong northerly winds associated with positive AOs. Thus source regions also play a key role in contaminant delivery, with both new emissions and re-emission of previously deposited contaminants contributing. For example, GRAHM source attribution modeling which combines information on atmospheric circulation patterns, emissions data, and environmental concentrations and chemical properties suggests that ~2/3 of the Hg deposited to the Arctic is natural and re-emitted whereas 20–28 % is from new anthropogenic sources with largest contributions coming from East Asia (10–15 %), Europe (2–3 %), North America (2–2.5 %), and South Asia (1.5–2 %) (Durnford et al. 2010; AMAP 2011) (Fig. 1).

Most contaminants that undergo atmospheric long-range transport have semi-volatile characteristics and relatively high Henry's Law constants and thus sufficient stability in the atmosphere to allow widespread dispersion by wind currents. Distinctions have typically been made among metals and POPs with regards to transport/deposition mechanisms. Hg is somewhat unique as it undergoes long-range atmospheric transport as elemental Hg(0), which has an atmospheric residence time of 6–12 months (Holmes et al. 2010; Slemr et al. 2011), but is deposited mainly as inorganic Hg(II) species which have relatively high deposition velocities. Thus, the atmospheric chemistry governing the oxidation of Hg(0) to Hg(II) plays a role in Hg deposition rates. In Arctic marine environments, Hg(0) oxidation and the subsequent deposition of Hg(II) is enhanced after polar sunrise during a series of photochemical reactions called "atmospheric Hg depletion events" (AMDEs)

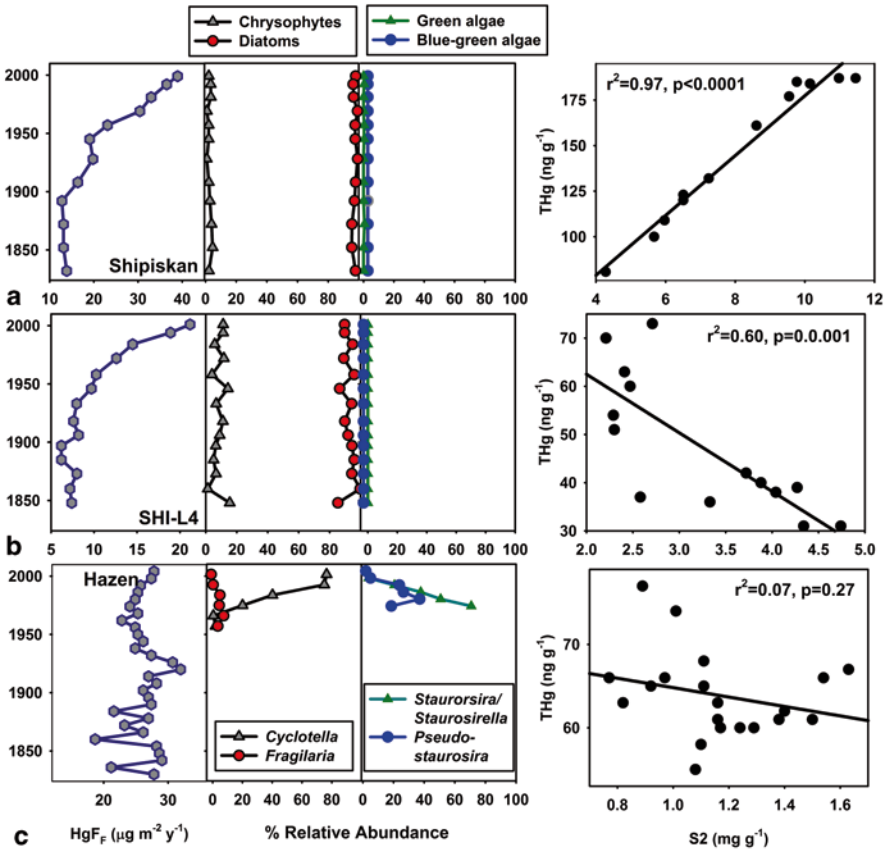

Fig. 3 Examples of Hg and algal profiles in dated lake sediment cores from 3 Canadian Arctic lakes (Shipiskan, SHI-L4, and Hazen). Hg profiles are presented as fluxes (HgF_F) corrected for particle focusing while algal profiles are presented as relative abundance (%) of microfossil diatom species. Finally, the third panel demonstrates the relationship between Hg and S2 carbon concentration (ng g^{-1}) (redrawn from Amyot et al. 2012)

(Steffen et al. 2008). There is now strong evidence that during AMDEs, Hg(0) is oxidized by bromine atoms, which are produced during “bromine explosions” following the debromination of sea salt in sea ice and aerosols (Mao et al. 2011; Steffen et al. 2008). It is hypothesized that Br atoms are the dominant global Hg(0) oxidant and are not only produced from sea salt but from a variety of biogenic and anthropogenic sources (Driscoll et al. 2013; Holmes et al. 2006). Hg(II) deposited to landscapes and water bodies during AMDEs and other atmospheric oxidation reactions can, however, be photo-reduced to Hg(0) then remitted, thereby re-entering the atmospheric Hg pool (Durnford and Dastoor 2011; Poulain et al. 2004; Lalonde et al. 2002). In fact, Hg(II) photo-reduction is an important removal mechanism of Hg from the surface of lakes and ponds (Amyot et al. 2000; Poulain et al. 2007).

In contrast, POPs delivery is typically described in terms of “global distillation” or “cold condensation” and the “grasshopper effect”. This effect refers to the tendency of POPs to volatilize from landscape surfaces in warm regions, migrate in the atmosphere, rest, then migrate again, eventually becoming trapped in cold Arctic regions (Wania and Mackay 1996). Recent work, however, suggests that several highly stable compounds, such as some highly brominated compounds (decabromodiphenyl ether or deca-BDE, for example) and fluorinated chemicals such as perfluorinated carboxylates (PFCAs) and perfluorinated alkyl sulfonates (PFSAs), reach the Arctic either by atmospheric transport on particles or degradation of volatile precursors (in the case of deca-BDE) (Muir and Wit 2010). Thus, the transport of some POPs may be similar to metals such as Pb, which travels as aerosol particles. Once in the Arctic atmosphere, POPs are deposited to landscapes and water bodies by both wet and dry deposition with precipitation rates playing a role in scavenging efficiency.

Impacts of Climate Change on Contaminant Transport and Deposition

Although there are major uncertainties regarding the impacts of climate change on delivery of contaminants to the Arctic on both inter-annual and long-term time scales, numerous predictions can be made (Ma and Hung 2013; AMAP 2011). Firstly, projections suggest that future climate change will produce conditions similar to a strongly positive AO which is hypothesized to result in an overall increase in contaminant transport to the Arctic. Additional changes to atmospheric circulation that may affect contaminant delivery to the Arctic are predicted, such as re-positioning of the zonal jet stream, which moves across the Northern hemisphere. For both Hg and POPs, increased occurrence of forest fires are also expected to increase episodic long-range transport to the Arctic, with several instances of increased air concentrations of POPs already linked to fires in the Yukon, Alaska, eastern Europe, and California in recent years (Eckhardt et al. 2007; Hung et al. 2010; Sofowote et al. 2011).

Climate-induced changes may alter many aspects of the redox chemistry that drives atmospheric Hg deposition. Firstly, warmer air temperatures will alter net Hg(0) oxidation rates, with calculations suggesting an overall decrease in Hg(II) production in the atmosphere (AMAP 2011). However, these calculations do not take into account the impact of climate-induced alterations on the presence of strong atmospheric oxidants, such as atomic Br radicals. A significant shift from multi-year to annual sea ice could alter the timing, spatial extent, and intensity of the “bromine explosions” and thus the quantity of Hg(II) deposited to marine and coastal environments during AMDEs. Shifts in post-deposition Hg(II) photo-reduction rates may also occur. For example, changes in snow chemistry may alter the stability of deposited Hg(II) during spring, with certain chemicals, such as chloride, known to stabilize Hg(II), while other chemicals such as humic acids, are known to favor Hg(II) reduction (Kirk et al. (2012) and Durnford and Dastoor (2011) and references therein).

For POPs, deposition rates are expected to be altered by climate-induced warming and altered precipitation patterns, which will alter volatilization and scavenging efficiency. Melting of sea and glacial ice and permafrost may result in volatilization of previously stored POPs from land and ocean surfaces, thus driving up atmospheric concentrations and deposition of both new and legacy POPs, which have decreased in recent years. Increases in atmospheric concentrations of the chlorinated pesticide and legacy POP γ-hexachlorocyclohexane (γ-HCH) at Zeppelin Mountain, Svalbard, Norway and Alert on Ellesmere Island, Nunavut between 1993–2007 correspond well with increases in average air temperatures and decreases in sea ice concentrations (Ma and Hung 2013). Furthermore, results from a recent perturbation modeling exercise suggest that, under a warming scenario of 10 °C over the next 100 years, air-surface exchange from soil, water and snow/ice could increase atmospheric PCB-52 and -153 concentrations by 8 and 3 %, respectively (Ma and Cao 2010). To further complicate matters, warmer air temperatures could increase atmospheric residence times of persistent semi-volatile chemicals. For example, estimates suggest that, between 1993–1999, the atmospheric half-life of γ-HCH was ~ 3.5 years but increased to ~ 9.5 years between 2000–2007 when temperatures warmed and ice extent decreased (Ma and Hung 2013). Finally, projected alterations to precipitation patterns could alter scavenging ratios and thus POPs deposition rates. Although snow is a much more efficient atmospheric scrubber than rain, projected increases of 20 % in annual precipitation by the end of the twenty-first century, mostly in the form of rain (ACIA 2004), will still have an overall effect of increasing POPs deposition. Meyer and Wania (2007) have estimated that a 10 % change in rain would alter γ-HCH deposition by 5 %.

Climate-induced changes can also alter inputs of Hg and POPs to freshwater water bodies via runoff. Climate-induced permafrost degradation, catchment erosion, and glacial melt can release previously stored contaminants to downstream water bodies. Permafrost thawing and catchment erosion may have particularly striking effects on lake inputs of Hg, which can be stored in catchment soils (Deison et al. 2012; Blais 2010). Due to the strong affinity of Hg to dissolved organic matter (DOM), the transport of Hg to freshwater ecosystems is also often controlled by DOM (Driscoll et al. 2013; Dittman et al. 2010; Brigham et al. 2009; Driscoll et al. 1994); which, initially, is predicted to be released from thawing permafrost (ACIA 2005). However, once the soil active layer deepens, DOM release may actually decrease over the long-term (Prowse et al. 2006; Kokelj et al. 2005). As discussed above, increased glacial melt may have more dramatic impacts on the release of POPs to downstream water bodies.

Once delivered to water bodies via either atmospheric deposition or runoff, Hg and POPs can both be emitted back to the atmosphere. Climate-induced increases in water column mixing and duration of the ice-free season may increase rates of Hg(II) photo-reduction and subsequent emission of Hg(0); whereas alterations to lake water chemistry, such as increased turbidity and primary productivity, may decrease UV penetration and thus photo-reduction rates. The impact of increased water column DOM on photo-reduction rates is complex and dependent on both DOM quantity and quality (Vost et al. 2012; Si and Ariya 2011; O'Driscoll et al. 2006; Garcia et al. 2005). Lengthening of the ice-free season, increased water temperatures and altered stratification regimes, such as increased water column mixing, may result in higher rates of POPs volatilization from lake surfaces.

Use of Sediment Cores to Examine Contaminant Deposition

The use of lake sediment cores as natural archives of post-industrial (post ~ 1850) contaminant deposition and Pb-210 dating methods have been discussed in detail previously (Muir and Rose 2004 and references therein; Oldfield and Appleby 1984; Blais et al. 1995) and are reviewed throughout several chapters in this book. Briefly, contaminant sedimentary records are produced by the annual sinking of particulate-bound contaminants to lake bottoms. Generally, Pb-210 derived sedimentation rates (g m^{-2} $year^{-1}$) are multiplied by contaminant concentration data (μg g^{-1}) for each core slice to obtain fluxes (F; μg m^{-2} $year^{-1}$) which reflect contaminant deposition over time. A variety of indices can then be used to look at temporal changes in contaminant deposition, including changes in fluxes over different time periods (ΔF), ratios of fluxes over different time periods or flux ratios (FR), and % increases (Muir et al. 2009). However, it is important to keep in mind that contaminant fluxes reflect post-depositional processing of contaminants that enter lakes both directly via atmospheric deposition and from catchment contributions and thus capture *net* contaminant deposition to aquatic ecosystems.

Firstly, sediment focussing, which is the process by which water turbulence moves sediments from shallower to deeper zones of a lake (Blais et al. 1995), can affect contaminant profiles. Thus, it is common to correct contaminant fluxes using sediment particulate focussing factors (FF) which can be calculated for individual lakes using a comparison of catchment soil and lake sediment core Pb-210 values (Blais et al. 1995). More recently, FFs in Arctic lakes have been estimated by dividing observed Pb-210 fluxes (Bq m^{-2} $year^{-1}$) by the flux predicted for the same latitude based on a collection of soil Pb-210 measurements (Kirk et al. 2011; Muir et al. 2009; Muir et al. 1996; Omelchenko et al. 1995). Diagenesis or the post-depositional alteration of contaminant profiles may also occur; although this may be more of a concern for some POPs than for Hg (Muir and Rose 2004). The stability of Hg in lake sediments has been demonstrated by re-coring a well characterized lake with varved sediments over long time scales (Rydberg et al. 2008) and by comparing temporal trends in sediment Hg flux rates with industrial Hg emission rates in lakes downwind of point sources (Lockhart 2000). Unlike Hg, some POPs can undergo degradation in sediments, including the dechlorination of chlorinated compounds, such as DDT and toxaphene in anoxic sediments (Rawn et al. 2001; Oliver et al. 1989). POPs with higher water solubility will also be more prone to diffusion at the sediment water interface (Muir and Rose 2004). However, a basic understanding of a lake's biogeochemistry, good dating results, and comparison of profiles of contaminants and basic parameters such as organic carbon and multi-elements can often avoid misinterpretation of diagenesis for changes in contaminant deposition.

Working with Arctic sediment cores also presents unique logistical and analytical challenges, (Muir and Rose 2004). In addition to the financial support and careful planning required for work in remote locations, most noteworthy of these analytical challenges are those presented by low rates of sedimentation and Pb-210 deposition. Low sedimentation rates may result in more limited temporal resolution than is achieved in more productive lower latitude lakes where the annual flux of material to the lake bottom is higher. Low Pb-210 deposition rates result from the natural tendency of Pb-210 fall out to decline exponentially with latitude (Preiss et al. 1996) and for permafrost to prevent radon gas (the parent of Pb-210) from escaping from high latitude soils (Hermanson 1990). In addition, prolonged annual ice-cover limits atmospheric deposition of Pb-210 to Arctic lakes. Therefore, longer gamma counting times and a combination of Pb-210 and Cs-137 dating methods are often applied.

Perhaps more importantly, Pb-210 has a half-life of 22.3 years and therefore can only be used to obtain dates and sedimentation rates for the last 100–150 years, or to the ~1860s (Appleby 2001). Thus, as time goes on, it becomes increasingly difficult to obtain "pre-industrial" (often defined as pre~1850) contaminant fluxes. This is not currently an issue for examining POPs, which were not released into the environment until well into the 1900's. However, for Hg, extrapolation of Pb-210 chronologies is required to obtain "pre-anthropogenic" fluxes. A recent study of 4 lakes (2 Arctic and 2 high elevation mountain lakes) used a combination of Pb-210 and radiocarbon (C-14) dating methods to demonstrate that extrapolation of Pb-210 sedimentation rates resulted in an overestimation compared to models that include C-14 dates (Cooke et al. 2010). The authors suggested that improper extrapolation of Pb-210 dates may result in a systematic over-estimation of pre-industrial Hg fluxes and thus an underestimation of anthropogenic atmospheric Hg deposition to the Arctic (Cooke et al. 2010). Applying novel dating methods may become necessary for determining baseline contaminant deposition in newly cored lakes.

Due to recent climate-induced changes across the Arctic, those using dated sediment cores to examine trends in atmospheric deposition have sometimes also inadvertently captured climate-induced changes to contaminant cycling, such as increased catchment erosion (Kirk et al. 2011; Muir et al. 2009; Fitzgerald et al. 2005). The analysis of geological or crustal tracer elements, such as magnesium or aluminum, in lake sediments and catchment soils has allowed correction factors for changes in sediment rates and catchment contaminant contributions to be applied (Kirk et al. 2011; Muir et al 2009; Fitzgerald et al. 2005; Perry et al. 2005). It has also been suggested that climate-induced increases to primary productivity and thus to organic carbon (OC) in lake water columns may have a dramatic effect on the deposition of Hg and POPs to lake sediments and thus on their use as archives of atmospheric deposition (Carrie et al. 2010; Stern et al. 2009; Outridge et al. 2007). Several studies have recently examined the "algal scavenging" hypothesis using multi-proxy paleolimnological approaches, including analysis of sediment Hg and POPs, carbon fractions, and diatom assemblages (Kirk et al. 2011; Carrie et al. 2010; Stern et al. 2009; Outridge et al. 2007; Stern et al. 2005). Given the complex environmental stressors in Arctic ecosystems, using multi-proxy approaches to compare the timing of different regime shifts may be the only way to understand current changes in contaminant deposition within a historical context.

Despite the numerous processes involved in the transport and deposition of contaminants to Arctic sediments, dated lake sediment cores have proven quite robust in determining trends in atmospheric deposition over the last ~150 years, with commonalities observed in the overall timing and magnitude of major depositional shifts among different studies. Due to the continued post-industrial emissions of Hg and combination of natural and anthropogenic sources, Hg studies have generally focussed on calculation of anthropogenic fluxes. There is a smaller body of work on POPs in dated lake sediment cores than on Hg, with POPs studies often focussed on comparing the timing of altered deposition patterns with increased usage and implementation of emissions controls.

In the next two sections, we review current studies on Hg and POPs in dated lake sediment cores with emphasis on spatial and temporal trends and the use of novel approaches to examine climate-induced changes in contaminant deposition in the Arctic.

Hg in Arctic Lake Sediment Cores

Hg fluxes have been reported in ~100 circumpolar Arctic lakes, with recent (post-1990s) flux measurements concentrated in Alaska, Canada, Greenland, and Sweden, and recently reviewed in detail (Amyot et al. 2012; Goodsite et al. 2013; AMAP 2011; Landers et al. 1998; Lockhart et al. 1998). Hg concentrations have also been reported in a number of undated lake sediment cores from northern Norway, Sweden, and Russia (Rognerud et al. 1998; Bindler et al. 2001; Blais et al. 1998) as well as a dated core from Lake Ellasjøen in the Norwegian Arctic which has bird guano contaminant sources (Evenset et al. 2007). Here, we will focus on high and sub-Arctic dated lake sediment cores that reflect regional trends in contaminant deposition.

Hg concentrations generally range from <10 ng g^{-1} to >400 ng g^{-1} in high and sub-Arctic lake sediments, with concentrations generally higher in surface sediments than in pre-industrial horizons (Cooke et al. 2010; Muir et al. 2009; Lindeberg et al. 2006; Fitzgerald et al. 2005; Bindler et al. 2001; Lockhart et al. 1998). Calculation of fluxes indicate that Hg deposition has increased between ~1.5- and 12-fold since the industrial revolution (~1850) with methods of correcting fluxes varying among studies (Landers et al. 1998; Lockhart et al. 1998; Bindler et al. 2001; Fitzgerald et al. 2005; Lindeberg et al. 2006; Outridge et al. 2007; Muir et al. 2009; Stern et al. 2009; Carrie et al. 2010; Cooke et al. 2010). Both pre- and post-industrial (from ~1960 to the 1990s) Hg fluxes have been reported for several high and sub-Arctic North American lakes north of 53°N, many of which have been corrected for particle focussing (see Goodsite et al. 2013 and references therein). In a total of 57 lakes, pre-industrial Hg fluxes ranged from 0.7 to 54 µg m^{-2} year^{-1} (geometric mean 7 µg m^{-2} year^{-1}), while post-industrial fluxes ranged from 2 to 52 µg m^{-2} year^{-1} (geometric mean 14 µg m^{-2} year^{-1}). Hg fluxes increased post-industrialization in 53 of these lakes and decreased in 4 resulting in anthropogenic fluxes ranging from -14 to 35 µg m^{-2} year^{-1} (geometric mean 7 µg m^{-2} year^{-1}).

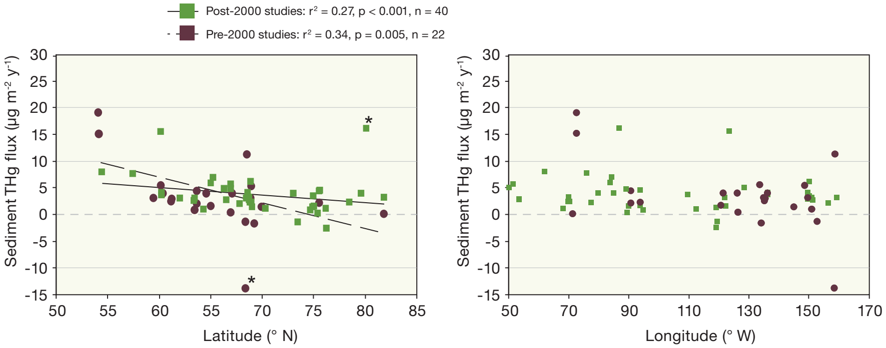

Fig. 4 Latitudinal trends in anthropogenic Hg fluxes obtained from dated sediment cores from Arctic and sub-Arctic lakes in Canada, Alaska and Greenland. Results from cores obtained pre- and post-2000 are compared, and outliers (marked with asterisks) were omitted from the regression analysis (pre-2000 cores are from Lockhart et al. 1998 and Landers et al. 1998; post-2000 cores are from Carrie et al. 2010; Muir et al. 2009; Fitzgerald et al. 2005; Figure is from Amyot et al. (2012), used with permission)

Latitudinal trends in rates of Hg deposition obtained from dated lake sediment cores have been examined in several studies (Goodsite et al. 2013; AMAP 2011; Muir et al. 2009; Landers et al. 1998; Lockhart et al. 1998). Most recently, latitudinal trends in ΔHgF fluxes corrected for focussing and erosional inputs/changing sedimentation rates from 3 post-2000 studies ($n = 40$) were compared to trends from earlier studies where ΔHgF fluxes had been corrected only for focussing ($n = 23$; Fig. 4) (Amyot et al. 2012). Both the slopes of the linear regressions and the magnitude of the ΔHgF fluxes were similar in all 63 lakes (ΔHgF = −2.6–16 and −14–19 μg m^{-2} year^{-1}; $r^2 = 0.27$ and 0.34, in post and pre-2000 studies respectively, $p < 0.001$) suggesting that deposition to Arctic lake sediments has not dramatically changed over the last ~20 years. In urban areas of the Northern hemisphere, fluxes from lake sediment cores are decreasing by 30–50 %, reflecting decreases in local Hg emissions (Lindeberg et al. 2007). However, in the Arctic, information gained from lake sediment records and source attribution and deposition modelling together reflects the continued importance of Asian emissions to Hg deposition rates (Durnford and Dastoor 2011).

Many current studies have noted increases in sedimentation rates, particularly in the more recent sediment horizons (Cooke et al. 2010; Carrie et al. 2010; Muir et al. 2009; Fitzgerald et al. 2005). For example, in 30 Canadian Arctic lakes, average sedimentation rates ranged between 10 and 1000 g m^{-2} year^{-1}, with post-industrial increases of 10 % observed in 15 of these lakes (Muir et al. 2009). In keeping with numerous climate-induced changes that many Arctic lakes have recently experienced, such as shifts in algal communities (Smol et al. 2005), and increased summer evaporation (Smol and Douglas 2007a), primary production (Michelutti et al. 2005), and inorganic sedimentation (Hughen et al. 2000; Thomas and Briner 2009), several studies have concluded that widespread increases to lake sedimentation rates are due to increased catchment erosion (Cooke et al. 2010; Muir et al. 2009; Fitzgerald et al. 2005; see also discussion above). Thus, to tease apart Hg inputs from catchment erosion and from other sources (which includes anthropogenic atmospheric sources), correction factors based on either analysis of geological tracer/crustal elements or changes in sedimentation rates have been applied to Hg flux data. Based on the assumption that elements such as magnesium, titanium and aluminum in lake sediments originate largely from clastic catchment minerals, Fitzgerald et al. (2005) used the ratio of magnesium in catchment soils:lake sediments to calculate the catchment contribution of Hg. They concluded that 11–64 % of Hg in recent sediment horizons is derived from soil erosion. Alternatively, Muir et al. (2009) first confirmed a strong relationship between aluminum flux ratios and ratios of pre- and post-industrialization sedimentation rates ($r^2 = 0.92$, $p < 0.001$), which is indicative that increased post-industrialization sedimentation rates originate from catchment sources. Hg fluxes were then corrected for changing sedimentation rates using the equation of Perry et al. (2005). Similar approaches have been applied in numerous lower latitude lakes (Landers et al. 2008; Perry et al. 2005). Adjusted anthropogenic Hg fluxes have been calculated for 39 of the 57 lakes described above and are generally much lower than unadjusted fluxes (range −2.6–27 µg m^{-2} $year^{-1}$; geometric mean 4.5 µg m^{-2} $year^{-1}$) (Goodsite et al. 2013). Figure 2 illustrates the difference between adjusted and unadjusted Hg fluxes in a subset of high and sub-Arctic lakes ($n = 14$; Kirk et al. 2011; Muir et al. 2009) and thus demonstrates the impact these corrections can have on calculations of anthropogenic Hg fluxes and on conclusions regarding atmospheric Hg deposition in the Arctic.

Climate-induced increases to lake primary productivity have also been hypothesized to have a large impact on deposition rates of Hg to Arctic lake sediments (Carrie et al. 2010; Stern et al. 2009; Outridge et al. 2007) in a process similar to the "biological pump", which governs the vertical movement of Hg through the ocean water column (Sunderland et al. 2009; Cossa et al. 2009). Increased primary production and altered algal assemblages have been well documented across the circumpolar Arctic, with shifts from small, benthic diatom taxa associated with cold conditions and extended ice-cover to diatom taxa characteristic of littoral habitats and mossy substrates most commonly observed; in deeper lakes, an increase in the relative abundance of planktonic taxa indicating decreased ice-cover and/or enhanced thermal stratification has also been observed (Michelutti et al. 2007; Smol et al. 2005; Douglas et al. 1994; Rühland et al. 2003; Smol and Douglas 2007a, b). The "scavenging hypothesis" suggests that increased deposition of detritus resulting from increased primary production can scavenge Hg from the water column to lake sediments. To examine the "scavenging hypothesis", a multi-proxy approach which allows the timing and magnitude of shifts in climate indicators and Hg accumulation rates to be compared is therefore required.

Recently, Rock-Eval analysis (Lafargue et al. 1998; Sanei et al. 2005) of dated lake sediment cores has been applied to examine changes in S2 carbon, which is a high molecular weight, kerogen derived aliphatic hydrocarbon fraction of OC which is thought to correspond to the biomacromolecular structure of algal cell walls (Carrie et al. 2010; Stern et al. 2009; Outridge et al. 2007). In 4 studies, significant relationships ($r^2 > 0.75$) between concentrations of Hg and S2 carbon were observed in the 5 high and sub-Arctic cores examined (Jiang et al. 2011; Carrie et al. 2010; Stern et al. 2009; Outridge et al. 2007). Diatom abundance or concentration was also measured in a subset of these lakes and was found to correlate with S2 carbon (Jiang et al. 2011; Outridge et al. 2007). Based on these results, ~70–96% of increased post-industrialization Hg deposition in Arctic lakes was attributed to increased algal scavenging (Jiang et al. 2011; Stern et al. 2009; Outridge et al. 2007). In another study, Hg profiles were compared to profiles of climate-indicators in cores from 14 Canadian high and sub-Arctic lakes (Kirk et al. 2011). Several of these lakes also showed post-industrial shifts in algal assemblages consistent with climate-induced changes. However, in six of the 14 study lakes, no Hg:S2 relationship was observed, and in one lake a significant negative Hg:S2 relationship was observed due to increased Hg and decreased S2 C deposition during the post-industrialization period. In six of the seven lakes where a significant positive Hg:S2 relationship was observed, algal assemblages either did not change through time or the timing of the shifts did not correspond to changes in Hg deposition. The authors concluded that, although Arctic lakes are experiencing a myriad of changes, including increased Hg and S2 deposition, or changing algal assemblages, increased lake primary production is not driving changes in Hg fluxes to sediments. Most recently, Cooke et al. (2012) examined profiles of total organic matter, spectrally inferred chlorophyll *a* concentrations, diatom abundance, and carbon stable isotopic signatures throughout the early Holocene. During the early Holocene, summer temperatures were higher than present and autochthonous primary production was consequently elevated. Despite the climate-induced increases in lake primary production observed during the early Holocene, Hg deposition to the lake sediments did not increase during this period and no strong, significant relationships between any of the climate proxies examined and sediment Hg concentrations were observed ($r^2 < 0.19$). The authors concluded that post-industrial increases in Hg accumulation observed in their study lake reflect both increased atmospheric deposition of anthropogenic Hg and increased sedimentation rates.

Some of the disagreement among studies described above may in part stem from the differences in methods used, as well a lack of “calibration” of different proxies. For example, spectrally inferred chlorophyll *a* reconstructions in dated lake sediment cores have been compared to long-term measurements of chlorophyll *a* in lake water in a series of systems (Michelutti et al. 2010; Wolfe et al. 2006). Similar “calibration” of Rock Eval S2 carbon as well as comparison of spectrally inferred chlorophyll *a* and S2 carbon lake sediment profiles would aid in the future use of these proxies as indicators of changing lake primary productivity. The use of relative abundance measures to examine changes in algal assemblages have also been “calibrated” with training sets that establish quantitative relationships between present-day limnological properties and diatom relative abundances using multivariate gradient analysis (e.g., Antoniades 2004; Ryves et al. 2002; Lim et al. 2001; Joynt and Wolfe 2001; Laing and Smol 2000; Korhola et al. 1999; Weckstrom et al. 1997; Pienitz et al. 1995). Unfortunately, no such “calibration sets” exist for diatom absolute abundance or concentration data, partly because there are inherent problems in using concentration data with these proxies (Smol 2008); thus work examining the best way to use this metric would be informative.

Another way to corroborate the use of dated lake sediment cores to examine changes in atmospheric Hg deposition is to compare Hg fluxes obtained from dated lake sediments to other measures of atmospheric deposition. For the Canadian high and sub-Arctic, both measured and modeled estimates of net atmospheric Hg deposition are available. The GRAHM model estimates depositional fluxes of 4.5 µg m^{-2} for the high Arctic and 9 and 12 µg m^{-2} for the western and eastern subarctic, respectively (Steffen et al. 2012). Estimates obtained with the GEOS-Chem model range between 3.0 µg m^{-2} (Holmes et al. 2010) and 3.7 µg m^{-2} (Fisher et al. 2012) for the area north of 66.5 and 70 °N, respectively. These values compare well to average high and sub-Arctic fluxes obtained from 32 dated lake sediment cores from across the Canadian Arctic after correction for particle focussing and increasing sedimentation (average 2.8 and 7.5 µg m^{-2}, respectively), and showed a similar negative relationship between latitude and Hg deposition (Muir et al. 2009). However, both fluxes from models and dated lake sediment cores are higher than direct measurements of Hg loads from high Arctic snowpacks (0.5–3.5 µg m^{-2}, St. Louis et al. 2007), as well as meltwater (0.04–0.4 µg m^{-2}, Kirk et al. 2006) and wet deposition (0.5–2.0 µg m^{-2}, Sanei et al. 2010) for Churchill, Manitoba in the Canadian sub-Arctic. Field measurements differ from model simulations because snowpack and meltwater loads, which incorporate both wet and dry net deposition, do not reflect deposition over a full 12-month cycle while wet-only deposition fluxes do not include the contribution of dry deposited Hg species. Thus future work to improve our understanding of the processes driving atmospheric deposition and to compare modelled and sediment core derived flux values to measured wet-and dry depositional fluxes at a variety of locations is warranted.

POPs in Dated Lake Sediment Cores

Below we provide an overview of the use of dated lake sediment cores to examine trends in the atmospheric deposition of numerous legacy POPs, including organochlorines: polychlorinated biphenyls (PCBs), hexachlorocyclohexane (HCH), hexachlorobenzene (HCB), dichlorodiphenyltrichloroethane (DDT), toxaphene or chlorobornanes (CHB), ACHB, chlordane (CHL), dieldrin, aldrin, and endrin, all of which have been removed from use or heavily restricted prior to the year 2000. Almost all of these (with the exception of HCH, which was added later), were listed in the original “dirty dozen” under the Stockholm Convention on Persistent Organic Pollutants, which was signed in 2001. In addition, we discuss PAHs as well as new POPs, including endosulfan, brominated flame retardants BFRs, polychlorinated naphthalenes (PCNs), and perfluorinated chemicals (PFCs). Most POP lake sediment profiles typically follow historical patterns of use, with a range of lag times observed and attributed predominantly to varying transport times to different parts of the Arctic (Muir and Rose 2004). In addition, climate-induced changes, such as increased lake primary productivity and glacial melt, may be driving up sediment fluxes of legacy POPs in recent sediment horizons, which, as for Hg, complicates interpretation of atmospheric deposition patterns. In general, there are fewer data on POPs in dated lake sediment cores than on Hg, with limited application of correction factors or multi-proxy approaches to examine the effects of climate change on deposition of POPs to lake sediments. This is in part due to the expense and time consuming nature of POPs analysis relative to Hg. In addition, unlike Hg, local sources, such as small Northern communities or bird colonies can have a dramatic effect on POPs profiles (see Kallenborn, this volume, for a complete discussion on tracking contaminants from biovectors). For example, elevated depositional fluxes of insecticides and pesticides, such as toxaphene and DDT, in several lakes of the Yukon, Canada, reflect the application of these chemicals in this region. In addition, HCB and DDT fluxes in high Arctic pond sediments with bird colonies were ~10 and 60 times greater than in nearby ponds without colonies present (Blais et al. 2005). Thus, to discuss the long-range transport and subsequent deposition of POPs, we focus the below discussion on remote locations with no significant local influence.

Legacy POPs

PCBs

Of the POPs, PCBs have been of most interest and concern in the Arctic (AMAP 2004). PCBs are industrial organochlorines widely used as transformer, hydraulic and heat-exchange fluids. Cumulative global PCB production between 1930 and 1993 was ~1.3 Mt of which the US Monsanto Corporation production comprised ~48% between 1930 and 1977 (Breivik et al. 2006; de Voogt and Brinkman 1989). Like many legacy POPs, global PCB production was largely discontinued in 1993 and thus secondary emissions or re-emissions are of growing significance (Breivik et al. 2006). PCBs are comprised of many related chemicals or congeners, with ∑PCB referring to the sum of all the different forms. The different PCB congeners are identified by the number and position of the chlorine atoms around the biphenyl rings.

PCB and legacy organochlorine fluxes corrected for particle focussing have been measured in ~25 high and sub-Arctic sediment cores (Breivik et al. 2006; Stern et al. 2005; Muir and Rose 2004; Stern and Evans 2003; Gubala et al. 1995; Muir et al. 1995, 1996, 2002; Cleverly et al. 1996; Evans et al. 1996; Lockhart 1997; Rawn et al. 2001). Profiles typically following trends in historical use patterns (Muir et al. 2013; MacDonald et al. 2008) and have thus been detected in Arctic sediments since the 1940s (Eisenreich et al. 1989). However, due to the lag in transport of PCBs released at mid-latitudes to the North, significant inputs were not detected until the 1960s (Muir and Rose 2004). ∑PCB concentrations and fluxes in high and sub-Arctic lake sediments generally range from ~3–90 ng g^{-1} and ~100–3000 ng m^{-2} $year^{-1}$ respectively, with peaks observed anywhere between the 1960s and late 1990s (Muir et al. 2013; Stern et al. 2005; Muir and Rose 2004; Stern and Evans 2003) (Table 1). Higher fluxes (up to ~4000 ng m^{-2} $year^{-1}$) have also been observed in the western basin of Great Slave Lake in Northern Canada,

Table 1 Summary of surface and/or average depositional fluxes (ng m^{-2} $year^{-1}$) obtained from dated lake sediment cores from across the high and sub-Arctic for a variety of "legacy" and new POPs

POP	Flux (ng m^{-2} $year^{-1}$ (dw))			Lake Names	Latitude (°N)	Region	Reference
	Maximum (year)	*Surface*	*Average*				
∑PCB							
	n/a	2410	n/a	Lindeman	59	N. British Columbia	Rawn et al. 2001
	n/a	1660	n/a	Kusawa	60	Yukon	Rawn et al. 2001
	n/a	n/a	1450[a]	Kusawa	60	Yukon	Muir et al. 1996
	n/a	n/a	850[a]	Hawk	63	NW. Hudson Bay	Muir et al. 1996
	n/a	n/a	520[a]	Far	63	NW. Hudson Bay	Muir et al. 1996
	n/a	1350	n/a	Hanson	64	Yukon	Rawn et al. 2001
	n/a	220	n/a	G	67	W. Greenland	Malmquist et al. 2003
	n/a	30–90	n/a	B; C; D; E; F; H	67	W. Greenland	Malmquist et al. 2003
	n/a	112	n/a	Char	74	Cornwallis Island	Breivik et al. 2006
	n/a	n/a	500[a]	Amituk	75	Cornwallis Island	Muir et al. 1996
	n/a	n/a	110	Sophia	75	Cornwallis Island	Muir et al. 1996
	370 (1997)	370	n/a	DV09	75	Devon Island	Stern et al. 2005
	n/a	1152	n/a	Romulus	79	Ellesmere Island	Breivik et al. 2006
	n/a	292	n/a	AX-AJ	80	Axel Heiberg Island	Breivik et al. 2006

Table 1 (continued)

POP	Flux (ng m^{-2} year^{-1} (dw))			Lake Names	Latitude (°N)	Region	Reference
	Maximum (year)	*Surface*	*Average*				
∑HCH							
	n/a	n/a	135	Lindeman	59	N. British Columbia	Rawn et al. 2001
	n/a	n/a	79	Kusawa	60	Yukon	Rawn et al. 2001
	n/a	n/a	85	Hanson	64	Yukon	Rawn et al. 2001
	37.9 (1993)	31	n/a	DV09	75	Devon Island	Stern et al. 2005
	n/a	90	n/a	Lindeman	59	N. British Columbia	Rawn et al. 2001
	n/a	82	n/a	Kusawa	60°N	Yukon	Rawn et al. 2001
	n/a	33	n/a	Hawk; Far	63	NW Hudson Bay	Muir et al. 1995
	n/a	33	n/a	Hanson	64	Yukon	Rawn et al. 2001
	n/a	38	n/a	Amituk; Sophia	75	Cornwallis Island	Muir et al. 1995
	24.2 (1997)	24	n/a	DV09	75	Devon Island	Stern et al. 2005
	n/a	3.4	n/a	Hazen	82	Axel Heiberg Island	Muir et al. 1995
∑CHL							
	n/a	90	n/a	Lindeman	59	N. British Columbia	Rawn et al. 2001
	n/a	82	n/a	Kusawa	60	Yukon	Rawn et al. 2001
	n/a	33	n/a	Hawk; Far	63	NW. Hudson Bay	Muir et al. 1995
	n/a	33	n/a	Hanson	64	Yukon	Rawn et al. 2001
	n/a	10–40	n/a	B; C; D; E; F; G; H	67	W. Greenland	Malmquist et al. 2003

Table 1 (continued)

POP	Flux (ng m^{-2} year^{-1} (dw))			Lake Names	Latitude (°N)	Region	Reference
	Maximum (year)	*Surface*	*Average*				
	n/a	38	n/a	Amituk; Sophia	75	Cornwallis Island	Muir et al. 1995
	24.2 (1997)	24	n/a	DV09	75	Devon Island	Stern et al. 2005
	n/a	3.4	n/a	Hazen	82	Axel Heiberg Island	Muir et al. 1995
∑CBz							
	n/a	52	n/a	Lindeman	59	N. British Columbia	Rawn et al. 2001
	n/a	301	n/a	Kusawa	60	Yukon	Rawn et al. 2001
	n/a	42	n/a	Hanson	64	Yukon	Rawn et al. 2001
	n/a	10–20	n/a	B; C; D; E; F; G; H	67	W. Greenland	Malmquist et al. 2003
Toxaphene							
	n/a	410	n/a	Hawk; Far	63	NW. Hudson Bay	Muir et al. 1995
	n/a	95	n/a	Amituk; Sophia	75	Cornwallis Island	Muir et al. 1995
	166 (1980)	103	n/a	DV09	75	Devon Island	Stern et al. 2005
	n/a	120	n/a	Hazen	82	Axel Heiberg Island	Muir et al. 1995
∑DDT							
	n/a	n/a	172	Lindeman	59	N. British Columbia	Rawn et al. 2001
	n/a	n/a	66	Kusawa	60	Yukon	Rawn et al. 2001
	n/a	110	n/a	Hawk; Far	63	NW. Hudson Bay	Muir et al. 1995
	n/a	n/a	358	Hanson	64	Yukon Territory	Rawn et al. 2001

Table 1 (continued)

POP	Flux (ng m^{-2} $year^{-1}$ (dw))			Lake Names	Latitude (°N)	Region	Reference
	Maximum (year)	*Surface*	*Average*				
	n/a	61	n/a	Amituk; Sophia	75	Cornwallis Island	Muir et al. 1995
	15.5 (1957)	7	n/a	DV09	75	Devon Islandy	Stern et al. 2005
	n/a	5	n/a	Hazen	82	Axel Heiberg Island	Muir et al. 1995
Dieldrin							
	n/a	47	n/a	Hawk; Far	63	NW. Hudson Bay	Muir et al. 1995
	n/a	43	n/a	Amituk; Sophia	75	Cornwallis Island	Muir et al. 1995
	46.1 (1971)	41	n/a	DV09	75	Devon Island	Stern et al. 2005
	n/a	7	n/a	Hazen	82	Axel Heiberg Island	Muir et al. 1995
∑PAH							
	n/a	9100	n/a	Kusawa	60	Yukon Territory	Lockhart et al. 1997
	170,000 (1926–1932)	n/a	n/a	Øvre Neådalsvatn	62	Norway	Fernandez et al. 2000
	14,000 (1954)	6000	n/a	Hawk	63	NW. Hudson Bay	Lockhart et al. 1994
	n/a	6800	n/a	Ste. Therese	64	Mackenzie River basin	Lockhart et al. 1997
	n/a	140,000	n/a	Yaya	69	Mackenzie River basin	Lockhart et al. 1997
	7000 (1978–1993)	n/a	n/a	ArresjØen	79	Norway	Fernandez et al. 2000

Table 1 (continued)

POP	Flux (ng m^{-2} year^{-1} (dw))			Lake Names	Latitude (°N)	Region	Reference
	Maximum (year)	*Surface*	*Average*				
Endosulfan							
	6.2 (1997)	6.2	n/a	DV09	75	Devon Island	Stern et al. 2005
∑*PBDE*							
	n/a	13	n/a	Mcleod	63 °N	Alaska	Landers et al. 2008
	n/a	7	n/a	Matcharak	67	Alaska	Landers et al. 2008
	28.5 (1997)	29	n/a	DV09	75	Devon Island	Stern et al. 2005
key PBDE congeners							
BDE-47	n/a	92	n/a	B2	57	N. Quebec	Breivik et al. 2006
BDE-47	1.3 (1997–2000)	1	n/a	G	67	W. Greenland	Malmquist et al. 2003
BDE-47	n/a	9	n/a	Char	74	Canada	Breivik et al. 2006
BDE-47	n/a	<16	n/a	Romulus	79	Ellesmere Island	Breivik et al. 2006
BDE-47	n/a	<4	n/a	AX-AJ	80	Axel Heiberg Island	Breivik et al. 2006
BDE-209	n/a	43	n/a	B2	57	N. Quebec	Breivik et al. 2006
BDE-209	n/a	9.4	n/a	Char	74	Canada	Breivik et al. 2006
BDE-209	n/a	<3	n/a	Romulus	79	Ellesmere Island	Breivik et al. 2006

Table 1 (continued)

POP	Flux (ng m^{-2} $year^{-1}$ (dw))			Lake Names	Latitude (°N)	Region	Reference
	Maximum (year)	*Surface*	*Average*				
BDE-209	n/a	8	n/a	AX-AJ	80	Axel Heiberg Island	Breivik et al. 2006

[a] focus corrected

due to inputs from rivers that drain more contaminated areas in the south. As with Hg, PCB fluxes are generally higher at sub-Arctic than high Arctic locations, with significant latitudinal gradients observed when mid-latitude lakes are included in trend analyses (see Muir et al. 1996 for example). Typically, there is also a gradient in PCB composition with latitude, with tri- and tetrachlorobinphenyl acconting for a higher proportion of ∑PCB in high Arctic sediments than at lower latitudes (Breivik et al. 2006; Muir et al. 1995).

Interestingly, maximum PCB fluxes are also sometimes observed in the most recent sediment horizons, highlighting the impact of transport lag time and climate related changes on PCB deposition in Arctic lakes. In an annually laminated high Arctic core from Lake DV09 on Devon Island, Nunavut, maximum fluxes of ∑PCB, as well other POPs, such as ∑HCH, toxaphene, and chlordane and short-chain polychlorinated n-alkanes (sPCAs; part of a group of organic contaminants previously referred to as chlorinated paraffins but not discussed further in this chapter) were measured in surface sediments (Stern et al. 2005). As with Hg, it has been hypothesized that algal scavenging due to climate-induced increases in lake primary production is driving elevated POPs deposition to surface sediments (Outridge and Stern 2009; Stern et al. 2005). In DV09, ∑PCB, ∑HCH, toxaphene, chlordane and ∑sPCA fluxes and diatom counts (cell gram^{-1}) increased simultaneously between the 1960s and 1990s (Muir et al. 2013; Stern et al. 2005). However, these relationships were not observed for ∑DDT or polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs; also not discussed further in this chapter). In Amituk Lake, S2 carbon was measured and was not found to correlate strongly with ∑PCB or DDT but did correlate with ∑HCHs, dieldrin, and chlordane (Muir et al. 2013; Outridge and Stern 2009). In Romulus, Char, and Hazen lakes, significant relationships were not observed between S2 carbon and ∑PCBs, DDT or HCH. Therefore, it has been suggested that snow and ice melt may be driving present-day increases in PCB and legacy POPs fluxes, especially in glacially-fed systems such as Lake Hazen on Ellesmere Island, Nunavut (Muir et al. 2013). To our knowledge, this is all the data that currently exists on the impacts of increased lake primary production on the deposition of POPs to Arctic lake sediments. Continued analysis of PCBs, other legacy POPs and climate proxies in post-2000 sediment cores would be of great interest as climate-induced changes are projected to increase.

HCH

HCH was used as an insecticide predominantly between the years 1948–1997 and is considered the most plentiful contaminant in the Arctic (Lohmann et al. 2007). Commercially, HCH exists as two mixtures: technical HCH (composed of 60–70 % α-HCH, 5–12 % β-HCH, 10–15 % ɣ-HCH and other isomers) and lindane (relatively pure ɣ-HCH) (Stern et al. 2005). Technical HCH was produced mainly between 1948–1997, with restrictions implemented in China, India, and the former Soviet Union in the 1980–1990s (Stern et al. 2005; Li 1999a). In contrast, lindane became commercially available in the 1970–80s and although its release has decreased in recent years, it is still used in Europe, North America, and Asia (Stern et al. 2005; Stern and Evans 2003). Overall, trends in ΣHCH are similar to those observed for PCBs, with concentrations and fluxes in high and sub-Arctic lake sediments generally ranging from ~0.1 to 3 ng g^{-1} and ~1 to 140 ng m^{-2} year^{-1}, respectively, and peak deposition observed in the 1960s and 1970s as well as in recent surface sediments (Muir et al. 2013; Stern et al. 2005; Muir and Rose 2004; Stern and Evans 2003) (Table 1).

Isomer compositions, such as enantiomer ratios (ERs), have been examined for several organic contaminants in a variety of environmental media to track contaminants sources and pathways; however they have only been examined in a few Arctic lake sediment cores. In two glacially-fed high Arctic lakes (Buchanan and Hazen), ɣ-HCH, comprised a large portion of the total HCH (23 and 37%, respectively). Alternatively, in two lower latitude Ontario lakes, ɣ-HCH contributed only 2% and 18% of ∑HCH (Muir et al. 1995). Furthermore, the proportion of α-HCH was elevated in Buchanan and Hazen lakes relative to more southern locations, which is consistent with the HCH signature in Arctic ice caps (Gregor 1990; Gregor and Dahl 1990) as well as with the tendency of α-HCH to volatize rapidly from land surface at lower latitudes. Alternatively, β-HCH comprised 45–65% of ∑HCH in four Ontario lakes but only l-2% in four high Arctic lakes (Muir et al. 1995), which is consistent with the significant contribution of β-HCH to ∑HCH in Lake Ontario sediments (Eisenreich et al. 1989). More recently, Stern et al. (2005) examined α- and ɣ-HCH levels in Lake DV09 and found similar ratios to those reported by Muir et al. (1995), but only in surface sediments. In deeper sediment horizons, the α/ɣ-HCH ratio decreased, which is in disagreement to the ratios expected based on historical usage patterns. The authors hypothesized that α-HCH is preferentially degraded in Arctic lake sediments and suggested that further research on the relative stability of these compounds is warranted (Stern et al. 2005).

HCB

Hexachlorobenzene (HCB) was used as a pesticide and fungicide beginning in the 1950s with peak global usage occurring between the 1970s and early 1980s (Barber et al. 2005; Bailey 2001). Although the use of HCB has been banned globally, it is a by-product of many industrial processes and is therefore still released to the environment today. Reporting methods vary for HCB, with some studies providing values for total chlorobenze (∑CBz), of which HCB is often a major component, while others report only on HCB. For example, in Hanson Lake, Yukon, which is located in the Canadian sub-Arctic, HCH constituted 65–100% of ∑CBz throughout the core. Overall, trends in HCB and ∑CBz deposition are similar to those described above for PCBs and HCH, with concentrations and fluxes generally ranging from ~0.3 to 2 ng g^{-1} and ~1 to 80 ng m^{-2} year^{-1}, respectively for HCB and ~0.1–2.9 ng g^{-1} and ~42–300 ng m^{-2} year^{-1} for ∑CBz (Malmquist et al. 2003; Muir et al. 2013; Rawn et al. 2001; Muir et al. 1995) (Table 1). The magnitude of HCH deposition appears to be similar among Canadian high and sub-Arctic lakes and remote lakes at more southern latitudes (Rawn et al. 2001; Muir et al. 1995;).

DDT

DDT was first used to control the spread of diseases such as malaria and typhus, then between 1946 and 1973 became the most widely used agricultural pesticide globally with the US and the former Soviet Union by far the largest consumers (Li and Bidleman 2003). Although DDT was banned in the US in 1972, it was used agriculturally in other countries until 1993 and is still used on smaller scales for controlling the spread of diseases (Li and Bidleman 2003). DDT can degrade to metabolites such as p, p'DDD and p, p'-DDE in the environment and thus measurement of degradation products is important when examining trends in atmospheric deposition using dated lake sediment cores (Stern et al. 2005; Muir et al. 1995). ∑DDT concentrations and fluxes generally range from ~0.01–11 ng g^{-1} and ~1–360 ng m^{-2} $year^{-1}$, respectively, in the high and sub-Arctic lakes (Stern et al. 2005; Muir and Rose 2004; Muir et al. 1995; Rawn et al. 2001). In DV09, p, p-DDE comprised the largest fraction of ∑DDT, with the ratio of p, p-DDE:∑DDT deceasing with core depth and the ratio of p, p′-DDD:∑DDT showing the opposite trend (Stern et al. 2005). Alternatively, in cores collected in the late 1980s, p, p′-DDD comprised the largest portion of ∑DDT in surface sediments, although the ratio of p, p′-DDD:∑DDT decreased with increasing latitude (Muir et al. 1995). Differences may be due to variations in total DDT inputs, microbial activity or anaerobic conversion rates among locations (Stern et al. 2005). Although trends in DDT deposition generally follow historical patterns of use, highest fluxes have recently been observed in surface sediments and, as discussed above, could be due to climate-induced changes as well as continued use of DDT despite widespread bans (Stern et al. 2005). Similar to PCBs, DDT fluxes are higher in sub-Arctic than in high Arctic cores, which is likely due to a combination of higher local and regional inputs (Muir and Rose 2004).

Toxaphene or CHB

After the banning of DDT (see above), toxaphene became one of the most heavily used pesticides in the world, with an estimated cumulative usage of 1.33 Mt and largest consumption in the US (Li and Bidleman 2003; Voldner and Li 1995). Toxaphene is a complex mixture of polychlorinated bornanes (CHBs) and camphenes and was first used in 1945 with production peaking in ~1975. Although production was banned in many countries in the 1980s, it was not severely restricted until as late as 1993 and may still be in use in some countries (Li and Bidleman 2003; Voldner and Li 1995). Toxaphene may be degraded in lake sediments through both dechlorination and dehydrochlorination pathways resulting in a shift in composition toward lower chlorinated homologs (Stern et al. 2005). Despite potential loss via degradation, toxaphene was one of the dominant organochlorine pesticides in Arctic lake sediments in the 1980s, with concentrations and fluxes ranging between ~0.1–17 ng g^{-1} and ~4–410 ng m^{-2} $year^{-1}$, respectively (Stern et al. 2005; Muir et al. 1995). To account for toxaphene degradation, Stern et al. (2005) measured both toxaphene and its metabolites or ∑CHB in Lake DV09. ∑CHB fluxes peaked (166 ng m^{-2} $year^{-1}$) in ~1980, just ~5–6 years after maximum global production, then decreased throughout the 1980s and 1990s (Stern et al. 2005).

CHL

CHL was predominantly produced for use as an agricultural insecticide and for urban termite control between 1945 and 1988. Despite being widely banned in the 1980s, CHL was still being produced and used in 1997 (Barrie et al. 1992). It is a complex mixture of >20 different components, including *cis*- and *trans*-chlordane isomers (CC and TC) and *cis*- and *trans*-nonachlor (CN and TN), each of which may degrade differently in the environment. ∑CHL concentrations and fluxes generally range from ~0.1–4 ng g^{-1} and ~3–90 ng m^{-2} $year^{-1,}$ respectively (Malmquist et al. 2003; Stern et al. 2005; Muir et al. 1995; Rawn et al. 2001). CHL ERs were examined in sediments of Lake DV09 on Devon Island and correlated well with those measured in air over similar periods, suggesting that lake sediments tracked atmospheric deposition patterns quite well (Stern et al. 2005). For example, the fraction of TC (FTC = TC/(TC + CC) observed in slices dated to the late 1950s was comparable to the technical mixture (0.58 vs 0.61) (Stern et al. 2005; Bidleman et al. 2001), but decreased through time reaching 0.27–0.33 in the most recent sediment horizons. FTC values in surface sediments are comparable to those recently observed in Arctic air and indicate that recent CHL inputs originate predominantly from secondary, weathered sources rather than newly emitted CHL (Stern and Evans 2003).

Dieldrin, Aldrin and Endrin

The so-called “drins” are related chemicals used mainly as crop insecticides between 1950 and 1992 (Barrie et al. 1992). Dieldrin and aldrin were synthesized from the famous Diels-Alder reaction, which is where their names originate, while endrin is a stereoisomer of dieldrin (Vorkamp et al. 2004). Although aldrin was heavily used, it is readily degraded to dieldrin in the environment, which is the form of major concern in the Arctic. Concentrations and fluxes of dieldrin in Arctic lake sediments generally range between ~0.1–3 ng g^{-1} and ~2–50 ng m^{-2} $year^{-1}$, respectively (Muir et al. 1995; Stern et al. 2005) (Table 1). Similar to HCH, deposition appears to be similar among Arctic lakes and remote lakes at more southern latitudes; although Arctic fluxes are much lower than in parts of Lake Ontario where fluxes of

900–3600 ng m^{-2} year^{-1} have been observed due to local sources (Muir et al. 1995; Eisenreich et al. 1988).

Polyaromatic Hydrocarbons (PAHs)

PAHs are one of the most widespread organic pollutants and are of major concern as several are carcinogenic. They are a large group of chemicals all consisting of two or more fused aromatic rings and range in size from relatively simple structures, such as naphthalene, to large complex molecules, such as hexacene (Savinov et al. 2000). They are present in fossil fuels and are formed by the incomplete combustion of carbon-containing fuels and are somewhat unique organic pollutants as they originate from both natural and anthropogenic sources. They are emitted from a number of industries, such as smelters and pulp and paper mills, as well as from natural forest fires, oil seeps, and organic matter degradation (Savinov et al. 2000; Yunker and MacDonald 1995) with anthropogenic sources greatly outweighing natural ones (Fernandez et al. 2000). Natural and anthropogenic PAHs may originate from both petrogenic and pyrogenic sources. Petrogenic PAHs are formed through slow processes at moderate temperatures and are associated with fossil fuels, such as petroleum and coal. Pyrogenic PAHs are formed during higher temperature combustion, such as in automobile motors, coal fired power plants, and in the processing of coals into coal tars. Different types of combustion yield unique combinations of PAH products, which allows sources to be fingerprinted by examination of different PAH ratios. For example, the degree of alkylation is generally inversely proportional to the formation temperature. However, only lighter compounds, such as fluorene, phenanthrene, pyrene, and chrysene, and fluoranthrene, can undergo long distance transport to the Arctic (Halsall et al.1997; Wania and Mackay 1996).

PAHs in Arctic lake sediment cores have been reviewed by Muir and Rose (2004). ∑PAH concentrations and fluxes generally range from 20–900 ng g^{-1} and 6–170 µg m^{-2} year^{-1}, respectively, with the timing of maximum PAH fluxes varying greatly among lakes (Fernandez et al. 1999; Fernandez 2000; Muir and Rose 2004; Lockhart 1994; Lockhart 1996; Lockhart 1997; Muir and Lockhart 1994; Lockhart et al. 1995; Lockhart et al. 1997). Peaks in ∑PAH fluxes prior to the 1950s often coincide with peaks in retene, which is associated with forest fires (Ramdahl 1983), or changes in the 1,7-dimethylphenanthrene/2,6-dimethylphenanthrene ratio, which is a marker for coniferous wood combustion (Benner et al. 1995). The most dramatic increases in PAH deposition attributable to anthropogenic sources are often observed post-~1960, with peaks sometimes observed in surface sediments. Latitudinal trends in the proportion of fluoranthrene:fluorene have been observed in lake sediments, with ratios decreasing exponentially (from 38 to 1) along a transect from Spain (42 °N) to Svalbard (79 °N) (Rose et al. 2004). This is consistent with the preferential long-range transport of lighter PAHs (fluorene) over larger ones (fluoranthrene); however this dataset was complicated by a large coal-fired power plant in Svalbard, which is a significant PAH source to local lakes (Rose et al. 2004).

Despite the wealth of information that can be obtained from PAH fingerprinting, this tool has not been utilized widely in Arctic lake sediment cores. The combination of PAH ratios with combustion indicators, such as black carbon, could provide valuable information on the impacts of changing energy consumption patterns on Arctic contaminant deposition. In addition, as climate-induced changes result in more widespread forest fires, examination of the relative changes of different PAH markers over time will provide valuable information on different PAH sources to Arctic lakes.

New POPs

Endosulfan

Endosulfan is an organochlorine pesticide that is sold as a mixture of two isomers, α-endosulfan(I) and β-endosulfan(II), in ratios from 2:1 to 7:3 (Weber et al. 2010). It is currently being phased out, as it was just added to the Stockholm Convention in 2011 with exemption for India and Uruguay (Li and Kurt-Karakus 2013). To our knowledge, profiles of α-endosulfan(I) and β-endosulfan(II) have only been measured in an Arctic sediment core from DV09 (Stern et al. 2005). As has been observed in Arctic air, only α-endosulfan(I) was detected, with concentrations and fluxes highest in surface sediments (0.04 ng g^{-1} and 6.2 ng m^{-2} $year^{-1}$, respectively) (Stern et al. 2005; Hung et al. 2002). α-Endosulfan(I) levels rapidly declined in sub-surface sediments and was undetectable in slices dated prior to 1988 despite the widespread use of this product throughout the 1980s. The inability to detect endosulfan in sediments prior to 1988 may be due to degradation to endosulfan sulfate, which is the major metabolite of endosulfan and the form most often found in sediments (Stern et al. 2005; Usenko et al. 2007).

BFRs

BFRs are a group of chemicals which are used globally to enhance the resistance of materials such as textiles, plastics, and building materials, to fire (de Wit et al. 2010). Of the BFRs, polybrominated diphenyl ethers (PBDEs) are some of the most widely used and of highest concentration in the Arctic (Alaee et al. 2003). PBDEs are chemically similar to PCBs and are sold as different chemical mixtures, each of which may contain a number of the 209 existing congeners (de Wit et al. 2010). In 2009, commercial mixtures penta- and octa-BDE were added to the Stockholm Convention for POPs, however deca-BDE is still in use. PBDEs have been examined in 12 high and sub-Arctic dated lake sediment cores, with the major constituents of penta-BDE (BDE-47, -99, and -100) and deca-BDE (BDE-209), most commonly measured (Breivik et al. 2006; Stern et al. 2005; Malmquist et al. 2003). Arctic ∑PBDE fluxes ranged from <20 to ~ 530 ng m^{-2} $year^{-1}$ with PBDEs generally first detectable in sediments dated to the ~1980s and highest fluxes observed in surface horizons. However, PBDEs were also sometimes detected in horizons preceding PBDE manufacturing, which illustrates the challenges of measuring these highly ubiquitous contaminants in remote lake systems (Breivik et al. 2006; Stern et al. 2005).

Surface fluxes of BDE-47 and -209 were found to decline with latitude, although the relationship was only significant for BDE-209 (Breivik et al. 2006). Based on the relationship between latitude and measured BDE-209 and PCB sediment fluxes, Breivik et al. (2006) was able to calculate empirical half distances (EHDs), which represent a chemical's mobility in the atmosphere. EHD values were then compared to metrics of atmospheric transport obtained from various dynamic and steady-state models. Values obtained from dated lake sediment cores suggested that atmospheric travel distances for BDE-209 and PCBs are comparable; however a steady-state model indicated that PCBs are much more mobile than BDE-209 whereas the dynamic COZMo-POP model predicted the opposite. The authors concluded that to understand long-range atmospheric transport of PDE-209, model predictions need to be ground-truthed with empirical data and that an improved understanding of the processes governing atmospheric transport, including rates of wet and dry deposition to different landscape surfaces and photolysis of BDEs sorbed to atmospheric particulates, is required (Breivik et al. 2006). This study highlights the utility of dated lake sediment cores, not only in examining temporal trends in contaminant deposition, but also in understanding the transport of different chemicals to the Arctic via the atmosphere. Finally, although many of the PBDEs of concern are currently being phased out, numerous new non-PBDE BFRs have been detected in Arctic air and measurements of these compounds in dated sediment cores would be valuable.

PCNs

PCNs were first patented as flame retardants and were most heavily produced during the 1920s-1930s for a variety of industrial applications, such as dye, textile and paper, and fungicide production (Falandysz 1998; Helm et al. 2006; World Health Organization 2001). Although PCN production decreased significantly in the 1970s, after 80 years of use and production of 0.15 Mt PCN residues are still widespread in the environment (Jakobsson and Asplund 2000). There are two main sources of PCNs to the environment, volatilization from contaminated surfaces and combustion, which includes both waste incarnation and industrial combustion (Helm and Bindleman 2003). Like PAHs, PCNs may also be released from wood and coal combustion and examination of various ratios of the 75 existing congeners can be used for source elucidation (Abad et al. 1999, 2008; Harner et al. 2006; Helm and Bidleman 2003; Helm et al. 2006; Iino et al. 2001; Jansson et al. 2008; Lee et al. 2007; Noma et al. 2006). Despite the widespread presence of PCNs in Arctic air (Harner et al. 1998; Bidleman et al. 2010), PCNs have not been examined in Arctic lake sediment cores and thus this is a significant knowledge gap.

PFCs

PFCs are organofluorine compounds where the hydrogen atoms have been replaced by fluorine atoms on a carbon chain. The carbon-fluorine bond is very strong, making PFCs recalcitrant to degradation and persistent in the environment, and imparts unique properties to these chemicals. For example, since the 1950s, many PFCs have been used as surfactants in a diverse array of applications, including making materials stain, oil, and water resistant. The most widely studied PFCs are perfluorooctanoic acid (PFOA), which is used in the production of Teflon, and perfluorooctane sulfonate (PFOS), which is used in firefighting foams, Scotchgard^{TM} (a stain and water repellent widely used to treat fabrics and furniture), and countless other applications (Key et al. 1997; Moody et al. 2000;). PFOS was added to the Stockholm Convention on POPs in 2009; however numerous other PFCs of concern, such as perfluoroalkyl carboxylates and sulfonates (PFCAs and PFSAs, respectively) have captured a great deal of attention over the last 10 years due to their widespread presence in the environment (Butt et al. 2010; Houde et al. 2006; Lau et al. 2007). Sources of PFCs to the Arctic are quite complex and not well understood, and have recently been thoroughly reviewed (Butt et al. 2010). Some PFCs may be discharged directly from local sources, such as airports, while others may originate from the degradation of precursor compounds or by ocean and atmospheric transport. Stock et al. (2007) recently quantified PFCs in Arctic lake sediment cores from Amituk, Char, and Resolute lakes on Cornwallis Island, Nunavut; although only concentrations and not depositional fluxes were reported. In all three lakes, concentrations of ∑PFCs were highest in the surface sediments, with those in in Amituk and Char lakes ranging from 5–7 ng g^{-1}. In Resolute Lake, however, concentrations were highly elevated (up to 100 ng g^{-1}) due to inputs from the local airport (Stock et al. 2007). Profiles of PFCAs, PFSAs, as well as their precursors and degradation products, differed among lakes, although some important commonalities were observed. For example, ratios of PFOA:PFNA and PFDA:PFUA in Amituk and Char lakes were consistent with those observed in glacial ice caps (Young et al. 2007) and precipitation from remote regions of North America (Scott et al. 2006), indicating that there is a common atmospheric source to remote regions. In addition, the presence of degradation products in Amituk and Char lake sediments, such as FTUCAs, suggests that degradation of FTOHs and FSAs occurs in Arctic environments. The resolution of the three Arctic sediment cores analyzed to date was somewhat coarse (i.e., 1–1.5 cm slices with the top 1.5 cm from Amituk Lake core representing ~ 30 years of deposition); thus analysis of high resolution cores for a variety of different PFCs, their degradation products, and chemical precursors would allow detailed examination of temporal trends in the transport and deposition of these chemicals to the Arctic.

Conclusions and Suggestions for Future Research

Atmospheric transport delivers a variety of contaminants to the Arctic from southern industrial regions (Fig. 1). Dated lake sediment cores provide a tool to examine changes in the atmospheric deposition of contaminants over time, with Hg and POPs of highest concern in the Arctic. Depositional Hg fluxes have been measured in dated sediment cores from a number of lakes (~ 100) across the circumpolar Arctic. Despite the various factors that can potentially confound interpretation of depositional trends, including a combination of natural and anthropogenic Hg sources, and climate-induced increases to catchment erosion and lake primary productivity, there is general consensus that trends in depositional fluxes obtained from dated lake sediment cores reflect changes in anthropogenic atmospheric deposition. In fact, agreement between modelled and sediment-derived depositional fluxes has recently been demonstrated and future work to compare these values to measured wet-and dry depositional fluxes at a variety of locations is warranted. The recent application of novel multi-proxy approaches has allowed changes in Hg deposition to be examined in the context of climate-induced environmental changes, while the application of correction factors has allowed confounding increases in sedimentation rates and catchment Hg contributions to be accounted for in the calculation of anthropogenic Hg fluxes. Recently, the analysis of natural abundance ratios of Hg isotopes in a variety of different environmental media has opened new avenues for investigating Hg sources, transport, and transformations. Hg stable isotope fractionation provides a new probe into the pathways and history of Hg in ecosystems, as well as the potential to fingerprint various Hg sources (Blum 2011). Although the applicability of this tool in Arctic lake sediments has not yet been tested, there is future potential for source elucidation.

Compared to Hg, fewer dated sediment cores have been analyzed for POPs, with a larger body of work on legacy POPs, especially PCB and DDT, than on new and emerging chemicals. Generally, sediment POPs profiles are in good agreement with emission and usage history; however flux maxima in most recent sediment horizons have been observed for several legacy POPs including PCBs, HCH, toxaphene, and chlordane despite maximum production and usage of these chemicals during much earlier time periods. Climate-induced increases in lake primary production, and the resulting algal scavenging, as well as release of previously stored POPs from melting snow and ice, have been suggested as possible sources of legacy POPs to surface sediments; however there is limited data to support either hypothesis. The projected acceleration of glacial and sea ice melt will continue releasing POPs deposited to the Arctic over the last 70 years to the atmosphere as well as directly to freshwater ecosystems; thus measurement of POPs in conjunction with climate proxies in dated lakes sediment cores from multiple Arctic locations would be valuable. Various congener and isomer ratios, including enantiomer ratios, have been used for chemicals such as PCBs, HCH, chlordane, PBDEs, and PFCs, to trace or fingerprint different POPs sources. Thus the field of source attribution is much more advanced and straightforward for many of the POPs than it is for Hg and additional fingerprinting in Arctic lake sediment cores would be beneficial, especially for PAHs and new and emerging contaminants that have not yet been heavily restricted. Furthermore, for legacy POPs, comparison of various congener and isomer compositions from melting snow and glaciers to those observed in dated lake sediment cores may be informative as climate-induced melting increases. For some POPs, measurement of degradation products (i.e., toxaphene and DDT) is also important for differentiating patterns produced from trends in atmospheric deposition trends versus those produced from diagenesis.

There are numerous additional proxies that have not yet been combined with contaminant analyses in Arctic lake sediment cores that could be potentially informative as climate-induced changes alter the cycling of contaminants and nutrients further. For example, chlorophyll *a* reconstructions and carbon and nitrogen isotope analyse may provide information on changing lake primary production, while carbon and nitrogen ratios may provide an understanding of changing nutrient inputs. In addition, calibration of different proxies in well characterized aquatic ecosystems where long-term lake water chemistry datasets are available would further the credibility of new tools. In fact, the continued analysis of dated sediment cores using a variety of novel approaches may aid us in untangling the individual impacts of numerous multiple stressors, including anthropogenic atmospheric contaminant deposition and climate-induced changes to lake primary production, snow and ice melting, permafrost degradation, and catchment erosion, on Arctic freshwater ecosystems.

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Tracking Long-Range Atmospheric Transport of Trace Metals, Polycyclic Aromatic Hydrocarbons, and Organohalogen Compounds Using Lake Sediments of Mountain Regions

Jordi Catalan

Abstract High mountain regions may be perceived as areas of high environmental quality, yet many contaminants are ubiquitous on the planet through long-range atmospheric transportation. Mountain lake sediments record and archive how this global contamination is proceeding and have developed throughout history, particularly since rapid industrialization in the 1950s. Action against diffuse atmospheric contamination transported far away from the sources requires the development of national and international protocols, which must be based on reliable scientific evidence. Research on mountain lake sediments aims to provide long-term references, models for interpretation of results, and sound understanding of the mechanisms that lie behind the observed patterns of contamination. Mountains offer an excellent setting for environmental research because short distances may provide marked physical gradients (e.g., air temperature), and ecosystems are relatively amenable to observation and modelling. The lake sediment contributions are important complements to other observational approaches used in global change research. This chapter focuses on trace metals, polycyclic aromatic hydrocarbons (PAHs) and organohalogen compounds (OHCs). After a short introduction regarding contaminants and the several operative ways to examine the sediment archive, the main features of contaminant distribution in mountain lake sediments are described, followed by a section on the understanding of the processes behind the patterns (e.g., atmospheric transport, catchment interactions, air-water exchange, water column dynamics and eventual sediment archiving), and finishes with a section on biological assessment.

Keywords Global change · Diffuse pollution · Contaminants cold-trapping · Legacy contaminants · Mining archaeology · Mercury · Persistent organic pollutants · Alpine lakes

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Introduction

Diffuse, Background Pollution

Long-range atmospheric transport (LRAT) of acidifying substances on lakes and forests was the first indication that human activity can change the state of ecosystems situated far away from the site where the contaminant originated (Beamish and Harvey 1972). While the atmospheric increase of carbon dioxide was still a matter of academic debate, evidence of acidic deposition impact in remote areas, due to the industrialization emissions, cut across societal sectors in the early 1970s. As a result, international agreements to control emissions and mitigate the effects of acidification were undertaken both at national and international levels. The archiving of acidification proxies by the mountain lake sediments will not be addressed here because there are recent reviews (e.g., Catalan et al. (2013) and references there in). Nonetheless, acidification merits mention in this introduction because it was the beginning of the international awareness that human atmospheric pollution was changing the nature of background atmospheric deposition across large parts of the planet with highly uncertain consequences for the biosphere and humankind (Rockstrom et al. 2009a).

Contaminants are substances of synthetic origin (or natural of origin but enriched by human activity) that persist sufficiently in the environment to cause health problems to humans or to other living beings and, eventually, interfering with natural ecosystem dynamics. Monitoring all kinds of contaminants at large scales using remote sensing or deploying instrumental stations in a sufficiently dense network across large and scarcely inhabited areas is not feasible; therefore, natural registers, such as lake sediments, provide an extremely valuable source of information to track long-range distribution of atmospheric contaminants (Camarero et al. 1995). Occasionally, these natural registers can also provide evidence of ecosystem responses to the contamination pressure.

Mountains offer an excellent setting for environmental research because short distances may provide marked physical gradients (e.g., air temperature). Mountain regions are distributed worldwide and many of them contain lakes whose sediments are archives of regional deposition of contaminants. Because of the mountain geomorphology, the ratio between the lake area and its watershed is low and hence favors sediment archives with atmospherically dominated variability. That is, direct atmospheric deposition and short distance transport by surface and subsurface flows dominate matter loads to the lakes, particularly in glacial cirques and former volcanos. In contrast, the sediment archive variability in lakes and reservoirs in the main valleys and at low altitude plains is highly influenced by the way the fluvial transport organize and fluctuate over large areas and time (Fan et al. 2010). Lakes without direct human influences in the catchment are usually more appropriate for studying atmospheric pollution. In some cases, however, the atmospheric origin of some contaminants can be determined comparing lakes without human occupations in the watershed with those with some impact (Datta et al. 1998; Schmid et al.

2007). The mountain regions represent topographic barriers to air transport and, as a consequence, provide a more regionalized view of the background planetary pollution compared to remote high-latitude areas (e.g., Arctic), which may be closer to a hemispheric average. Several high mountain ranges are imbedded within regions of high emissions.

In this chapter, I will examine: (i) LRAT of contaminants tracked using lake sediments in mountain regions; (ii) the main patterns of current and past contaminant distributions; (iii) the processes to consider in the interpretations of the sediment records; and (iv) the extent to which toxic impacts can be inferred from the same sediment sequences. Advantages, shortcomings and complementarities of sediments with respect to other observational matrices such as direct air sampling, deposition, snowpack, soils and vegetation will be also addressed.

The Contaminants

Three groups of contaminants that differ in their origin, transport characteristics, bioaccumulation features and potential toxicity will be considered (Table 1): trace metals, polycyclic aromatic hydrocarbons (PAHs) and organohalogen compounds (OHCs).

Trace Metals

The term trace metal is increasingly used to include heavy metals, metalloids and organometals (e.g., Pb, As, MeHg) that fall along a continuum of biogeochemical behaviors and share the potential to be toxic to biota; thus the term has more of an environmental connotation rather than chemical (Luoma and Rainbow 2008). The term "trace" refers to the usual concentrations observed within organisms. The concentration in a specific medium, particularly in the sediments, can be far beyond what is considered analytically a "trace concentration".

Some trace metals are required by living organisms in small doses; they are referred as essential metals. The affinity of essential metals for sulfur and nitrogen has been evolutionary exploited in metabolic pathways, which are common to most living forms. Non-essential trace metals are not necessarily more toxic than essential ones, and the thresholds at which trace metal availability become toxic may be lower for some essential metals than for non-essential ones. An approximate order of toxicity for trace metal inorganic forms is Hg > Ag > Cu > Cd > Zn > Ni > Pb > Cr > Sn, although toxic effects vary between organisms (Luoma and Rainbow 2008).

Mountain lake sediments are naturally rich in trace metals because of the weathering of fresh rocks in their catchments. Therefore, it becomes mandatory to take into account these natural metal loads for assessing current atmospheric contamination and also that soil characteristics may modify the transport towards the lake (Navas and Lindhorfer 2005). Comparing the concentration in the sediment upper levels with concentrations in older sediment sequences corresponding to pre-industrial

Table 1 Lake sediment contaminant concentrations at mountain sites of low, moderate or high contamination. The values are only indicative, actual fluxes depend on sediment accumulation rates, which may vary significantly among mountain lakes

Contaminant	Concentration range		
	Low	Moderate	High
Trace metals (μg g^{-1} DW)			
Mercury (Hg)	0.01–0.03	0.1–0.3	2–4
Lead (Pb)	2–25	50–300	500–2000
Zinc (Zn)	10–50	100–400	5000–18,000
Copper (Cu)	1–10	20–150	500–2000
Arsenic (As)	1	5–15	2000–3500
Cadmium (Cd)	0.1	0.5–2	20–50
Polycyclic aromatic hydrocarbons (ng g^{-1} DW)			
Sum PAHs	< 500	1000–2000	5000–20,000
Phenanthrene	1–10	20–60	400–600
Fluoranthene	10–50	100–300	1400–2000
Benz[a]anthracene	5	20–50	200–500
Chrysene (+ triphenylene)	1–50	100–300	1000–2000
Benzo[b + j]fluoranthenes	1–50	80–300	800–2700
Benzo[k]fluoranthene	1–40	100–300	700–1500
Benz[e]pyrene	5–20	50–300	900–1500
Benz[a]pyrene	3–5	20–70	400–800
Indeno[1,2,3,-cd]pyrene	1–60	100–300	1000–2000
Benzo[ghi]perylene	1–30	70–150	700–1400
Retene	1	2–4	10–1000
Perylene	0–2	10–150	1000–6000
Organohalogen compounds (ng g^{-1} DW)			
Sum PCBs	1.0	2–10	30–100
PBC-28 + 31	0.1–0.2	0.3–0.4	0.5–1
PCB-52	0.02–0.05	0.3–0.5	1–3
PCB-101 + 90	0.08–0.4	0.6–0.8	1–5
PCB-118	0.1–0.2	0.4–0.7	0.9–1.3
PCB-153	0.2–0.4	0.7–0.9	2–4
Sum DDTs	0.2–1	2–10	20–40
Sum toxaphenes	< 1	2–10	20–40
HCHs	< 0.1	0.5–1	7–12
α-HCH	< 0.1	0.5–1	6–9
γ-HCH	< 0.1	0.5	0.8–1.5
HCB	0.1–0.2	0.5–0.7	1–2
Sum PBDEs	< 1		10–25

Table 1 (continued)

Contaminant	Concentration range		
	Low	Moderate	High
BDE-209	0.1		10–25
BDE-190/173	0.05		0.2–1
BDE-99	0.01–0.02		0.2
BDE-100	0.02–0.04		0.5–2
BDE-47	0.03–0.06		1–2
BDE-28	0.001–0.002		0.01–0.03

periods is a simple approximation. For some trace metals, the distinction between on-site and atmospheric sources can be made using stable isotope ratios, which usually differ between the two sources (Fig. 1). For instance, lead isotope ratios (i.e., $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$, or $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$) have been used to distinguish between alternative potential pollution sources related to mining (Camarero et al. 1998) and ore smelting areas (Reynolds et al. 2010). The Pb isotope ratios are useful also for investigating the different pathways (e.g., organic matter association, horizon distribution) of endogenous and exogenous sources in the catchment soils and the eventual implication for transport to lakes (Semlali et al. 2001).

Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs), also discussed elsewhere in this book (e.g. Korosi et al. this volume, Rose and Ruppel this volume), are organic compounds with two or more fused aromatic rings. PAHs have received increased attention in air pollution studies because some are highly carcinogenic or mutagenic (Srogi 2007). PAHs are widespread contaminants resulting from incomplete combustion of organic materials. In the atmosphere, they can undergo photodecomposition when exposed to UV light from solar radiation and react with oxides yielding diones, nitro- and dinitro-PAHs, and sulfonic acids. They are highly lipophilic, thus they easily attach to organic particles in water. In the water column of lakes, differential algal scavenging can change the PAHs profile between atmospheric deposition and sediment deposition (Wang et al. 2011). In soils and lake sediments, PAHs may be degraded by microorganisms (Haritash and Kaushik 2009). All these processes increase the complexity of the interpretation of the PAH sediment archive. In addition, air-soil PAH exchanges vary seasonally because of the volatilization features of these compounds; this variation adds to the seasonality of the emissions (Wang et al. 2011). Therefore, measurements integrated over several years are more environmentally meaningful than point assessments. In that sense, the sediment record is of some advantage.

There are many PAH compounds of natural and artificial origin. Environmental studies usually report 16 priority PAHs initially established by the US

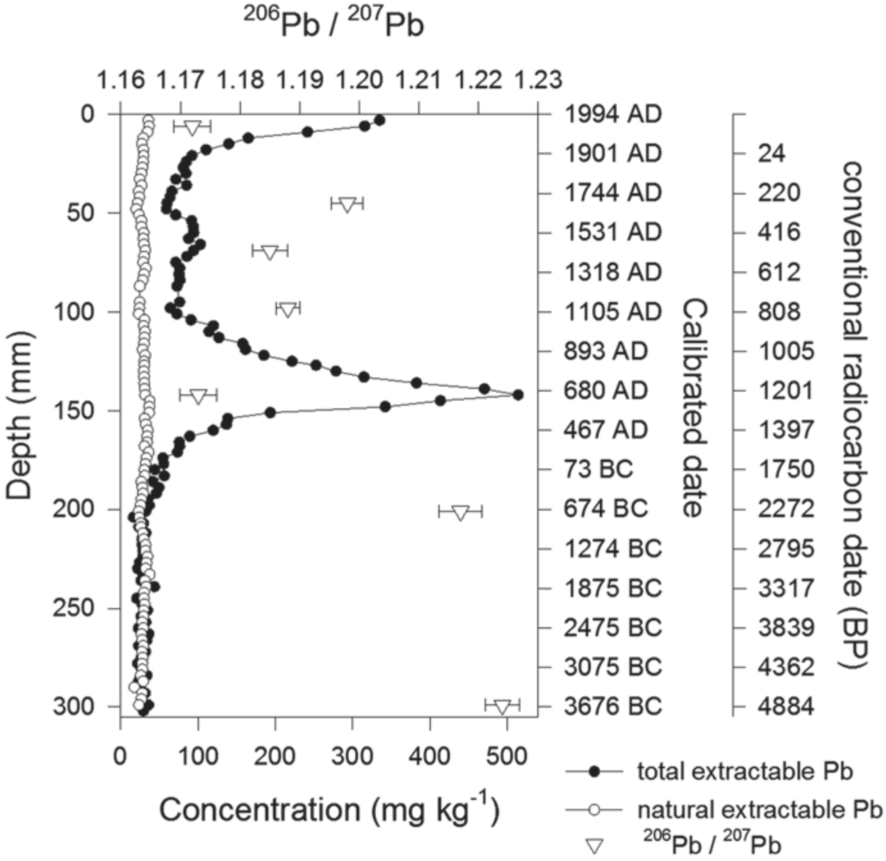

Fig. 1 Lead profiles in the sediments of Lake Redòn (Pyrenees). *Solid circles*, total Pb; *empty circles,* Pb from watershed sources as estimated using Al concentrations; *inverse triangles*, ^{206}Pb/^{207}Pb isotopic ratio. Atmospheric Pb deposition started to be significant during the Roman period and has been present since there, with a maximum at 680 AD and a second large input during post-1950s period. The Pb isotopic ratio varied according to the flux changes and indicates mining sources even at recent times. From Camarero et al. (1998) with kind permission from Springer Science and Business Media

Environmental Protection Agency. In palaeolimnological studies, the number analyzed is usually lower and changes from one study to another. Any comparison of total PAHs should be aware of this variability in the analytical practice, yet there are usually a few compounds that account for much of the PAH total at each site. In some cases, instead of total PAHs, sums of certain compounds are reported; for instance, parent PAHs, excluding derived and diagenetic forms, or pyrolytic PAHs, focusing on compounds produced at high temperature combustion. The PAH profile differs according to the combustion source, therefore the composition at remote sites has been used to try to infer the relative contribution of different sources, mainly for distinguishing between low temperature combustions of biogenic fuels (wood, biofuels, dung cakes, etc.), coal and fossil fuel. PAHs can also be compared with other proxies indicative of combustion, such as black carbon (Gustafsson et al. 2001) and spheroidal carbonaceous particles (SCP) (Rose and Rippey 2002, Rose and Ruppel, this volume), for instance. The latter is produced solely by high temperature combustion of coal and oil, whereas PAHs and black carbon are produced in any combustion of organic matter. There are still a limited number of studies comparing these proxies in mountain lakes (Muri et al. 2006).

Organohalogen Compounds

Many synthetic OHCs, with cyclic or aromatic structure, have been produced for agricultural, urban, and industrial applications. Some of them, due to their persistence and volatility, are spreading globally and have been jointly named as persistent organic pollutants (POPs). The Stockholm Convention on Persistent Organic Pollutants (2001) is a global treaty to protect human health and the environment from these kinds of chemicals, and maintains an official list of compounds included in this category that is periodically revised (http://chm.pops.int/). The chemical stability of POPs is due to the halogen substituents: primarily chlorine, but also bromine and fluorine. Many OHCs have been used as insecticides (e.g., dichlorodiphenyltrichloroethane (DDT), hexachlorocyclohexanes (HCHs), aldrin, toxaphenes, chlordane, mirex, endosulfan, etc.) during different periods since the first half of the twentieth century. Hexachlorobenzene (HCB) was used as a fungicide, and today is a by-product in the manufacturing of various chlorinated organic solvents. Polychlorobiphenyls (PCBs) were synthesized for use as dielectrics in transformers, fire retardants, high thermal stability oils and other applications. The production was stopped in the 1970s, but there is still a large stock in some countries to be disposed of; due to their scarce reactivity and resistance they are found worldwide. Whilst some of these compounds were synthesized as pure products, they were often produced and used as mixtures, as in the case of PCBs, HCHs, and toxaphenes. Hence, numerous compounds were introduced into the environment. In some cases, the initial product is transformed into other contaminants (e.g., DDT transforms into DDE and DDD). Dioxins and dibenzofurans are not manufactured; rather, they are generated through processes such as the combustion of organic materials that contain chlorine atoms.

In the 1970s polybrominated diphenyl ethers (PBDEs) were introduced, designed as flame retardants. Similar to PCBs, they were initially produced as mixtures, which have been increasing in the number of brominated sites (tetra-, penta-, octo-) until the fully brominated form BDE-209 was produced. The volatility of this latter compound is extremely low, and its hydrophobicity high, even compared to other organohalogens. Hence, it was expected that it will not diffuse away through the atmosphere or water. Surprisingly, it has been found in remote areas as other PBDEs (Bartrons et al. 2011; Breivik et al. 2006). The extremely high production and fast increase of background levels of PBDEs in a few years caused concern and progressive substitution for other flame retardants (Law et al. 2006).

Recently, the surfactants perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) are receiving attention due to their ubiquitous presence in humans and the environment, and their potential for bioaccumulation (Houde et al. 2011). The stability of PFOS and perfluorinated carboxylic acids (PFCAs) limits their degradation. High water solubility and low Henry's Law constant render them susceptible to wet deposition, making LRAT in the vapor phase unlikely. However, these perfluorinated compounds have been recorded in water of mountain lakes (Loewen et al. 2008). It seems that volatile precursors (fluorotelomer alcohols, FTHOs), intermediates in the production of polymers primary used in water resistant coatings, are atmospherically transported to remote areas where their degradation becomes the source for PFCAs. Identifying sources and pathways involved in transporting PFCAs to remote locations may help to follow how environmental stocks respond to recent changes in fluorochemical production practices and phase-out initiatives.

Many OHCs are toxic to humans and are now banned or heavily restricted, but others are still produced or in use across the planet or at least in some parts (e.g., DDT against mosquitoes carrying malaria). Recent studies have indicated that dicofol may be a potential source of fresh DDT for high mountain regions worldwide (Meire et al. 2012b); the o, p'-DDT/p, p'-DDT ratio have been used as an indication of new *vs.* old DDT (Li et al. 2006). DDT impurities of up to 0.1 % can be found in technical dicofol formulations, but can reach up to 20 % with some poor production techniques. Stocks in use and awaiting destruction (e.g. PCBs) may still be large even decades after production stopped. In Brazilian mountains, PCB levels in the air are proportional to the surrounding human population (Meire et al. 2012a). Therefore, existing POPs will be a matter of environmental surveillance and research for many years. The environmental consequences of the addition of new products to this legacy of contaminants, forming "pollution cocktails" of increasing complexity, are uncertain.

Different Ways to Study the Sediment Archive

Alpine mountain lakes (i.e., those located above tree line) are usually relatively small, morphologically simple and relatively deep compared to their surface areas, and located in catchments of relatively low sediment export. Therefore, the sedimentation patterns across the lake, excluding most littoral zones and inflows, are relatively constant, and one can assume that the sediment sequence corresponds to a temporal series without hiatus or temporal discordances. For comparisons, it is generally correct that within-lake variation is lower than among lakes. In contrast, lakes in the main valley of large watersheds and located below tree line tend to show complex sedimentation patterns and, therefore, a single core may not be representative of the overall accumulation rate. On the other hand, lakes located at high elevation plateaus (e.g., Andes, Himalayas), particularly if they are situated in dry areas, differ from the conventional paradigm of mountain lakes. In this chapter, I will make only occasional reference to plateau lakes. In any case, there are alternative ways to study and evaluate the sediment record of contaminants. The appropriate methodology depends on the question being addressed and the trade-off between the accuracy required and the operational cost (time, logistics, and analytical capacity).

Time Series

The canonical approach is to interpret sediment archive as a historical sequence. Therefore, the core must be dated to obtain a chronological sequence. Lakes with varved sediments, i.e. with distinguishable annual layers of sediment deposition (couplets or varves), are valuable because of the chronological accuracy (Brännvall et al. 1999), but are rarely found. In most cases, one has to rely on indirect dating methods. For the most recent period (<200 years), dating using ^{210}Pb, complemented with ^{137}Cs and other radioisotopes, may provide excellent age-depth models if the sediment is finely sliced (Appleby et al. 1986). When interest goes beyond the last two centuries (for instance, looking for metallurgy pollution of ancient cultures; see Cooke and Bindler, this volume), dating relies on ^{14}CAMS techniques and age-depth modelling (Blaauw and Heegaard 2012). Although this technique has improved enormously over the last few decades, it performs better at ages older than 500 years. Therefore, the age period from 200 to 500 years sometimes is covered with extrapolations of ^{210}Pb and ^{14}C age models (Camarero et al. 1998).

Obviously, dating becomes critical when the main target is not 'how much' but 'exactly when'. For instance, the deposition of spheroidal carbonaceous particles (SPC), which are produced in high temperature combustion, vary many orders of magnitude throughout the European mountains. However, the timing for an exponential increase in the 1950s is coherent all over the European continent indicating a synchrony in industrialization despite the marked differences in intensity among countries (Rose et al. 1999).

Mountain lakes exhibit sediment focusing. Therefore, contaminant concentrations have to be converted into atmospheric deposition fluxes with caution (Van Metre and Fuller 2009). Knowledge of ^{210}Pb deposition in the catchment may help to correct for focusing (Appleby 2008, see also Kuzyk et al. this volume) or some lithogenic elements may be used to standardize the measurements through time and across the lake (see below). The question investigated determines how much uncertainty in the estimation of the deposition fluxes the study can tolerate, and sampling has to be tailored accordingly. It is not uncommon to be examining changes in a range of more than one order of magnitude. In any case, knowledge about the local sedimentation process is always useful.

Total Inventories

Occasionally, the main interest of a study is the total inventory of the contaminant during a certain period. For instance, for synthetic organic contaminants, the target could be comparison among sites of the accumulation since the substance was first produced. It would not be efficient to measure many samples in great detail along each core. The key point is just to assure that the core section measured covers the entire temporal period of use of that contaminant. As a general guide, for mountain lakes above tree line and without permanent significant streams, the first 15 cm of sediment usually reach more than 50 years ago (Battarbee et al. 2002). This core length is sufficient to evaluate the total inventory of synthetic substances made during the last few decades (e.g., OHCs). Again, if the lakes being compared differ in the degree of sediment focusing, the relative difference in total inventory may not reflect the actual differences in atmospheric flux. A way to standardize the comparison, within an area of similar atmospheric deposition characteristics, is to use the total amount of ^{210}Pb. Correction for focusing may notably reduce apparent differences in atmospheric contaminant deposition among nearby lakes (Fernandez et al. 2000).

Top-Bottom Approach and Enrichment Factors

For contaminants that exist naturally, one may choose to compare current changes with a reference in the past over large areas. For instance, one may need to assess the impacts of the last industrialization burst in a region compared to the historical background levels. In these cases, a so-called "top-bottom" palaeolimnological approach may be instructive (Smol 1995). This method involves comparing contaminant levels of an upper (top) sediment section, assumed representative of the present, with those at some sediment depth representing an arbitrary past (e.g., top and 15 cm depth sections in mountain lakes (Camarero et al. 2009)). This approach can be criticized in many ways as there is a poor substitution of well-dated sequences (e.g., see chapter by Boyle et al., this volume). However, the advantage relies in the cost efficiency. Therefore, it is appropriate for studies considering a large number of sites, in which the synoptic evaluation is more valuable than each individual case. The differences between the two sediment levels measured are expressed as enrichment factors (EF). There is a high risk to obtain misleading results as changes in erosion rates or sediment focusing patterns between the two periods may have occurred at each site. Therefore, it is highly preferred to normalize the values using some lithogenic tracer that may account for these processes. The selection of the tracer may depend on the nature of the catchment bedrock, and the analytical capability. Different elements have been used (e.g., Ti, Zr, Al, and Rb) (Boes et al. 2011). Comparisons with EF calculated from Pb isotopes indicate variability between 10–30% depending on the element; therefore, it is advisable to try multiple reference elements and critically evaluated the differences when possible (Boes et al. 2011). Even when using several elements as reference, EF methods are not completely free of misinterpretation (see chapter by Boyle et al., this volume); therefore, scientific pros and cons in the evaluation of a particular environmental problem have to be considered before application. The top-bottom approach should not be used for compounds that undergo significant diagenetic transformation within the sediments (see Outridge and Wang, this volume).

Whole-Lake Budgets

The deepest central lake area may not accurately represent the whole-lake basin (Yang et al. 2002c). For certain studies (e.g., whole-watershed contaminant mass balance), a precise and accurate estimation of the whole-lake accumulation rate is required. Cores from several sites are necessary to take into account current and past lake focusing heterogeneity. The number of sites may vary according to the sedimentary characteristics of the lake. Progressing deltas in the inflows, high rugosity of the shoreline and other geomorphologic complexities will demand coring a large number of sites, but 5–10 sites, distributed to proportionally cover the main zones (axes) of variability, are sufficient in many small to medium size lakes (Rippey et al. 2008). In order to minimize cost, contaminants can be measured in one central site, and the spatial variability on accumulation rates taken into account by extrapolating these measurements based on some indicative, but easy to analyze, variable (e.g., organic matter content). Sometimes, the depositional correlation between cores is quite low and then analyzing multiple cores becomes prescriptive. This is the case, for instance, when the contaminant transport towards the lake is bound to large and heterogeneous particles, such as plants debris (Yang et al. 2002a).

Altitudinal and Other Geographical Variability

Under current dynamic environmental conditions, assessments over large areas and comparison between different regions are of primary interest. The temporal perspective that a single sediment archive can provide is always valuable, but the interpretation may benefit from contextualization within a geographical framework. Environmental conditions in mountains change with altitude, and this variability has to be considered when planning for sampling and in comparisons among sites. In fact, altitude is a factor that is a local surrogate for many variables, yet the relationship with some of these variables changes with latitude (Körner 2007). When comparing regions across continents, altitude is not a correct normalizing factor and other variables (e.g., air temperature) have to be considered according to the features of the contaminant. There are factors that change smoothly with altitude, such as temperature, but others distribute in belts. Vegetation is the best example for the latter. Particularly noteworthy is the distinction between truly alpine lakes (those above threeline) and lakes located in forested areas. The form and quantity of carbon (dissolved and particulate) cycling through these two types of lakes can markedly differ, with strong implications for the transport and retention of some of the contaminants. High mountains are also topographic barriers, the depositional contrast among nearby sites at the same altitude may be astonishing, depending on the range morphology and its orientation respect to the air mass circulation. Finally, when dealing with LRAT, it is necessary to consider that geographical distance to sources is not equivalent to the likelihood for transport from them. The air mass trajectories can effectively shorten (or lengthen) the geographical distances so that the meaning of local and background sources is diffuse without a study of the airshed of each lake.

It is worthwhile to consider altitudinal and geographical issues beforehand, when planning the sampling surveys, not only as factors in the posterior data analysis. Most environmental sciences face the issue of how to deal with geographical, physical, ecological and socio-economical co-variability. One can try to block geographical differences in emissions, for instance, by sampling within relatively small areas, but then it becomes difficult to find a large gradient of the factor under study (e.g. air temperature, organic matter, etc.), yet there are exceptional locations (Landers et al. 2010). This is a methodological problem that environmental chemistry has not fully addressed compared to other environmental sciences that face similar problems (e.g., geochemistry, ecology, etc.). Whereas dynamic models are relatively easily accepted as a methodological tool, despite the uncertainties that the parameterization may carry, relatively complex statistical analysis of data are also necessary. At the end, there is no way to disassociate entirely the influence of geography, history and dynamical processes using sampling designs; therefore, there is a need to include in the study of patterns more sophisticated statistical methods, just as other earth and environmental science have done (Legendre et al. 2002; Peres-Neto et al. 2006).

Contaminant Distribution

The nineteenth century Industrial Revolution increased the atmospheric emissions of contaminants, yet the tipping point of long-distance pollution occurred when massive use of fossil fuel reserves started in the 1950s. Combustions were a primary source of contaminants, but the availability of low cost energy triggered the development of massive production of new products that revolutionized agriculture and industry. Some of the processes for fertilizer and pesticide production were known before that time, but had not been fully exploited because they were energetically too costly. Since then, industrialization and environmental safety measures have not developed at the same pace worldwide. Historical, socio-economic and political factors lie behind geographical and temporal variation in the production and emissions of contaminants. Tracking LRAT of contaminants using mountain lake sediments can contribute not only to the assessment of current contamination levels but also to the development of the environmental history, particularly for regions where scarce documentary information exists.

Release of contaminants is coincident with technological progress. Although the 1950s were a tipping point, particularly in the variety of contaminants produced, trace metal atmospheric pollution started with early metallurgy and contaminant transport to real long-distance is evident at least since the Roman Empire in Europe (Renberg et al. 2001). In central China, the concentrations of Cu, Ni, Pb, and Zn increased gradually from about 3000 BC; enormous inputs of these metals corresponded to China's Warring States Period (475–221 BC) and the early Han Dynasty (206 BC–220 AD) (Lee et al. 2008). Many ores are located in mountain areas or nearby. In addition to background contamination, mountain lake sediments also may document unexpected high emissions from these locations, and contribute to an environmental history of mining (Cooke et al. 2011; Cooke and Bindler, this volume).

Many mountain ranges around the world have lakes with similar ecosystem features. Therefore, comparisons among mountain regions worldwide may resolve basic questions about LRAT of contaminants. Existing information is highly biased towards North America and Europe, yet the information is notably increasing for Asia and South America in recent years. Since our planet is immersed in an ongoing global change, further studies will be necessary on broad geographic scales, including areas that have been previously studied as many relevant investigations were performed more than a decade ago. The situation is continuously changing because the new production and use of compounds and the shifting long-range atmospheric trajectories due to climate change. We should expect that increasing awareness of the long-range transport of pollution (Rockstrom et al. 2009b) will foster investigations of the mountain lake sediments throughout the planet. In this section, I summarize the main worldwide patterns of contaminants, as revealed through mountain lake sediments. It does not aim to be a comprehensive review but to illustrate the range of variation, and the geographical and historical main features found up to present.

Trace Metals

Trace metal contamination is the oldest airborne atmospheric pollution recognized. In Europe about half of the cumulative burden of atmospheric Pb contamination was deposited before industrialization (Bindler et al. 2008). While some Scandinavian and Greenland records provide evidence of long-range atmospheric pollution (Renberg et al. 2001) the mountain sediment archive probably has a stronger contribution of nearby ore exploitations, as indicated by Pb isotopes in the case of the Pyrenees (Camarero et al. 1998). In that sense, mountain lake sediment archives have much potential for regional mining and metallurgy history, complementing other archives, such as peat bogs (Bindler et al. 2011). In Sweden, the first traces of atmospheric lead pollution recorded in lake sediments date to about 3500 years ago (Bindler et al. 2008). Signals in the sediments reflecting Roman metallurgy are found from Scandinavia boreal forest lakes (Brännvall et al. 1999) to Southern Europe mountain lakes (Camarero et al. 1998). Lead pollution comparable to levels found since the Industrial Revolution (~1800 A.D.) were found during Medieval times (1200–1600 A.D.) in the Austrian Alps (Schmidt et al. 2008) and even earlier, during post-Roman times (~600 A.D) in the Pyrenees (Camarero et al. 1998) (Fig. 1). Archaeological studies are indicating early occupation of the mountains in the Neolithic, and soon after the mid-Holocene (5000 year B.P.), fire was used to increase pasture lands and early mining and metallurgy impacts occurred in mountain valleys, either to use mineral resources or wood as fuel for metallurgy (Bal et al. 2011). Signatures from Bronze Age may also be recorded in other parts of the world as there is evidence from lakes in alluvial planes in China (Lee et al. 2008). In fact, there is a broad scope of historical circumstances for investigation: the high mountain impacts of Medieval times in Europe (Camarero et al. 1998; Schmidt et al. 2008); China's Warring States period (Lee et al. 2008); Andean cultures and colonial period mining (Strosnider et al. 2011; Cooke et al. 2011; Cooke et al. 2009); and west colonial occupation in North America and settlement of smelters (Baron et al. 1986; Mast et al. 2010), among many others. At each region, this historical background becomes the reference for assessing the trace metal pollution during the last two centuries of industrialization, and particularly the last five decades of intensive use of fossil fuels.

The decades after the surge in industrialization following the 1940s and 1950s are usually the target of current environmental concern. Studies covering large territories are particularly valuable to provide a general assessment. This was the case of a pan-European study of trace metals (Pb, Cd, Zn, Cu, As, Hg and Se) in mountain lake sediments that was performed in the year 2000 AD across the most important mountain ranges in Europe including the Pyrenees, Alps, the Rila Mountains, Retezat, Julian Alps, the Tatras and, Scottish mountains (Camarero et al. 2009). A top-bottom palaeolimnological approach was applied to compare current levels with pre-industrial concentrations. The concentrations of trace metals in many locations were comparable to those reported in aquatic sediments receiving high direct contamination loads. This is largely the consequence of high natural loads due to rock weathering in these low vegetated catchments, in which fresh exposed rock surface is produced continuously by geomorphic processes related to freezing of water. Therefore, Ti was used to normalize for lithogenic inputs and focus on atmospheric loads. The EFs for most elements were well above 1.5 in many lakes, indicating post 1950s atmospheric contamination. Pb was the element that showed the highest contamination level at the European scale (median EF of 2.3), followed by Hg and As. Zn, Cd, Cu and Se contamination was detectable to a lower degree. An indication of the generalized increase of diffuse atmospheric contamination is the exceptional increase of correlation among the current concentration of the different trace metals respect to the correlation in the pre-industrialization reference (Fig. 2). The only exception was As, indicating that the increase of this element has been due to other causes.

The Tatra Mountains and Scotland have been the most affected by trace metal pollution (Camarero et al. 2009). Natural mechanisms leading to the formation of highly organic, metal-binding sediments may be the cause of the high levels in Scotland (Yang et al. 2002a), whereas those in the Tatra Mountains are due to elevated deposition (Kopáček et al. 2006), which may be a general feature in Eastern Central Europe in the early post-industrialization decades. Metal enrichments in the Rila Mountains in Bulgaria are comparable to those in the Tatras, but concentrations are much lower. In the Alps, enrichments in Pb, Hg and Zn are higher in southern than in central areas suggesting a flux of these pollutants from the south, the highly industrialized area of Northern Italy. In the Pyrenees, the conspicuous feature is the high natural levels of As (Camarero 2003). The Retezat in the Carpathian Mountains of Romania is among the least contaminated regions in Europe (Camarero

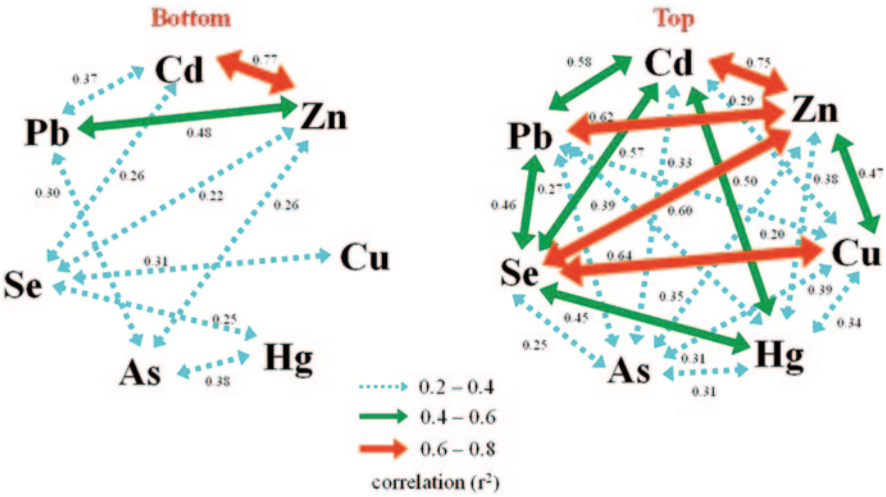

Fig. 2 Correlation between trace metals in *top* (0–2 cm) and *bottom* (15–17 cm) sediment samples from 75 mountain lakes of the Pyrenees [data from Camarero (2003)]. Note the increase in the correlations in recent times due to increase atmospheric contamination. It was assumed that the bottom layers corresponded to pre-1950s periods

et al. 2009). Although high resolution sediment studies in Lacul Negru (Rose et al. 2009) provided indications of Zn and Cd contamination from as early as the sixteenth century and from the eighteenth century for lead Pb, Cd and Hg. The level of contamination in the sediments of Lacul Negru is typically higher than in mountain lakes of Scandinavia but lower than that found in the Tatra Mountains, the Central Alps and the UK.

Top-bottom palaeolimnological approaches make sense when studying a large number of lakes over large areas; thus they are rather exceptional. Most existing studies evaluate contaminant time series from a single or a few sites. This approach is highly informative but is lengthy for the evaluation of contamination over large territories (e.g., continents); it depends on the progressive accumulation of studies across the territory. This is the case for the Asian continent, for which there is still insufficient data for a general assessment as has been done in Europe, but there are some valuable studies offering an initial view. In the Khamar Daban Mountain Range (Siberian Central Asia), the lake sediments of Lake Kholodnoye (1760 m a.s.l.) provided evidence of Pb and Zn pollution from the 1920s (Flower et al. 1997), the contamination tendency stepped up in the early 1970s and at the time of the study had not declined. According to the SCP levels, contamination was estimated to be about 100 times lower than in acidified UK sites. However, whether the recent contamination in the Khabar Daban Mountains (Siberia) is derived mainly from background atmospheric contamination of the Northern Hemisphere or from regional emissions was not determined. At Southern latitudes, in Daihailake (Inner Mongolia, China), there is no clear evidence of the current increase of trace metal atmospheric pollution (Han et al. 2007). Air-deposited Cu and Pb were evaluated using Ga as a normalizing element of fluvial transport and lithogenic origin. The Cu and Pb pollution was related to monsoon variability. Further south, the record of Lake Shudu (Yunnan province, China) also indicated scarce trace metal pollution during the last decades (Jones et al. 2012). Therefore, despite the scarce number of studies in north-central Asia, it seems that current background trace metal pollution is low compared with Europe. Nonetheless, the number of studies is still low in relation to the vast (mountain) territory of the continent. Cd atmospheric contamination has been found in soils of the Gongga Mountain in the eastern edge of the Tibetan Plateau (Wu et al. 2011); and recent studies from lake sediments in the Tibetan Plateau (Yang et al. 2010a) has shown that the first indication of Hg pollution is much earlier than the onset of the Industrial Revolution in Europe, but the most significant pollution increase is from the 1970s, followed by a further marked and continuous increase from the 1990s synchronous with the recent economic development in Asia (especially China and India). As most of the sites are exceptionally remote and situated above the atmospheric boundary layer, these results underline the need to understand the local Hg cycle in both regional and global context.

For some time, it was believed that preindustrial gold/silver mining in the Americas dominated the inventory of Hg global emissions. Recently, the evaluation of Hg deposition history over the last millennium, from a suite of lake-sediment cores collected from remote regions of the globe, indicates that atmospheric Hg emissions from early mining in America were modest as compared to recent industrial emissions (Engstrom et al. 2014). Most of the large quantities of Hg employed in the gold and silver mines was not volatilized, but rather was immobilized in mining waste. In North America, the Baron et al. (1986) early work in subalpine lakes of the Rocky Mountains indicated that Pb atmospheric pollution started in the second half of the nineteenth century, probably related to mining activities in Colorado. There was no clear evidence of increased deposition related to recent industrialization. Mining in the past ~150 years was also the main source of trace metal pollution (Ag, As, Cd, Cu, In, Pb, Bi, Sb, Sn, Te, Zn and S) arriving to Uinta Mountains (Utah) (Reynolds et al. 2010). Lead concentrations declined in sediment deposited since about the mid-1970s, probably because of the cessation of smelting, temporary halt to mining for establishing better emission control systems, and the phase-out of leaded gasoline. In the Western US National Parks, Pb, Cd, SCP in lake sediment indicate deposition due to high-temperature combustion of fossil fuels (Landers et al. 2010). SCP increased in lake sediments in the conterminous 48 states during the twentieth century, peaking around the 1960s. However, in recent decades, sediment Pb, Cd, and SCP have declined substantially, reflecting source reductions due to regulations. Atmospheric deposition of Hg began to increase around 1900 in the Rocky Mountains, reaching a peak sometime after 1980 (Mast et al. 2010). The average ratio of modern to preindustrial fluxes was 3.2, which is similar to remote lakes elsewhere in North America. Current-day measurements of wet deposition are lower than the modern sediment-based estimates, perhaps owing to inputs of dry-deposited Hg to the lakes, although catchment processes may play also a role. In the Western US National Parks, deposition of anthropogenic Hg, indicated by temporal patterns in sediment cores, increased in nearly all parks during the twentieth century (Landers et al. 2010), starting between 1975 and ~1990 depending on the area. Currently, Hg sediment flux appears to be generally increasing or showing no change in some lakes and decreasing in others. This finding reflects a complex array of factors consistent with decreasing regional contaminant sources, increasing global contributions, and influences of individual watersheds on sediment Hg loading (Landers et al. 2008).

Tropical and southern hemisphere mountain lakes have been less studied for trace metal contamination than those in the Northern Hemisphere. Recent studies in the Rwenzori Mountains of Uganda show that the lakes have been contaminated by Hg from atmospheric deposition starting at least by the late nineteenth century (Yang et al. 2010b). The Hg accumulation increased by about 3-fold since the mid-nineteenth century, similarly to other remote regions worldwide. High Hg levels in the pristine lacustrine ecosystems of the Nahuel Huapi National Park, a protected zone situated in the Andes of Northern Patagonia (Argentina) have been related to local volcanic activity since many-fold concentrations above the background values were observed underlying some tephra layers in the sediment cores (Guevara et al. 2010). Extended fires might be another potential atmospheric source because the earlier Hg peaks coincide with reported charcoal peaks, whereas the upper Hg peaks coincided with evidence of extended forest fires from tree-ring data and historical records.

Trace metal emission controls started several decades ago in North America and Europe. It was expected to find a quick trace metal decline in the remote lake sediment records, as was found in precipitation (Pacyna et al. 2009). There were examples of that decline (Muir et al. 2009), but there were exceptions due to the ‘legacy contamination’ stored in the lake’s catchments. In fact, soils have been accumulating trace metals for decades and these contaminants are now slowly being released. In Scotland, Pb fluxes to the lakes have been steady despite emission reductions (Yang et al. 2002b). In the Pyrenees, a net export of Pb and As from the catchments to the lakes was found, whereas Zn atmospheric contamination was largely retained in the catchment (Bacardit and Camarero 2010c). Nearly all Pb entering the lakes was retained in the sediments, whereas 5–38 % of As and Zn was lost through the outflow.

Polycyclic Aromatic Hydrocarbons

The PAHs are probably the clearest indicators of the Industrial Revolution based on fossil fuels and the environmental carelessness (ignorance) of the first decades of their massive use. PAHs also exemplify the success of emission controls, as declines in the sediment records have closely followed these actions. Differences in concentrations and loads were extremely high among regions (Fig. 3), mostly depending on the distance from fuel burning areas (Fernandez et al. 2000). Fluxes between 50 and 150 $\mu g\ m^{-2}\ yr^{-1}$ were common throughout remote mountain lakes of Europe during the last decades of the twentieth century (e.g., Alps, Pyrenees), even in scarcely industrialized areas. PAH fluxes ranged from up to 1000–2000 $\mu g\ m^{-2}\ y^{-1}$

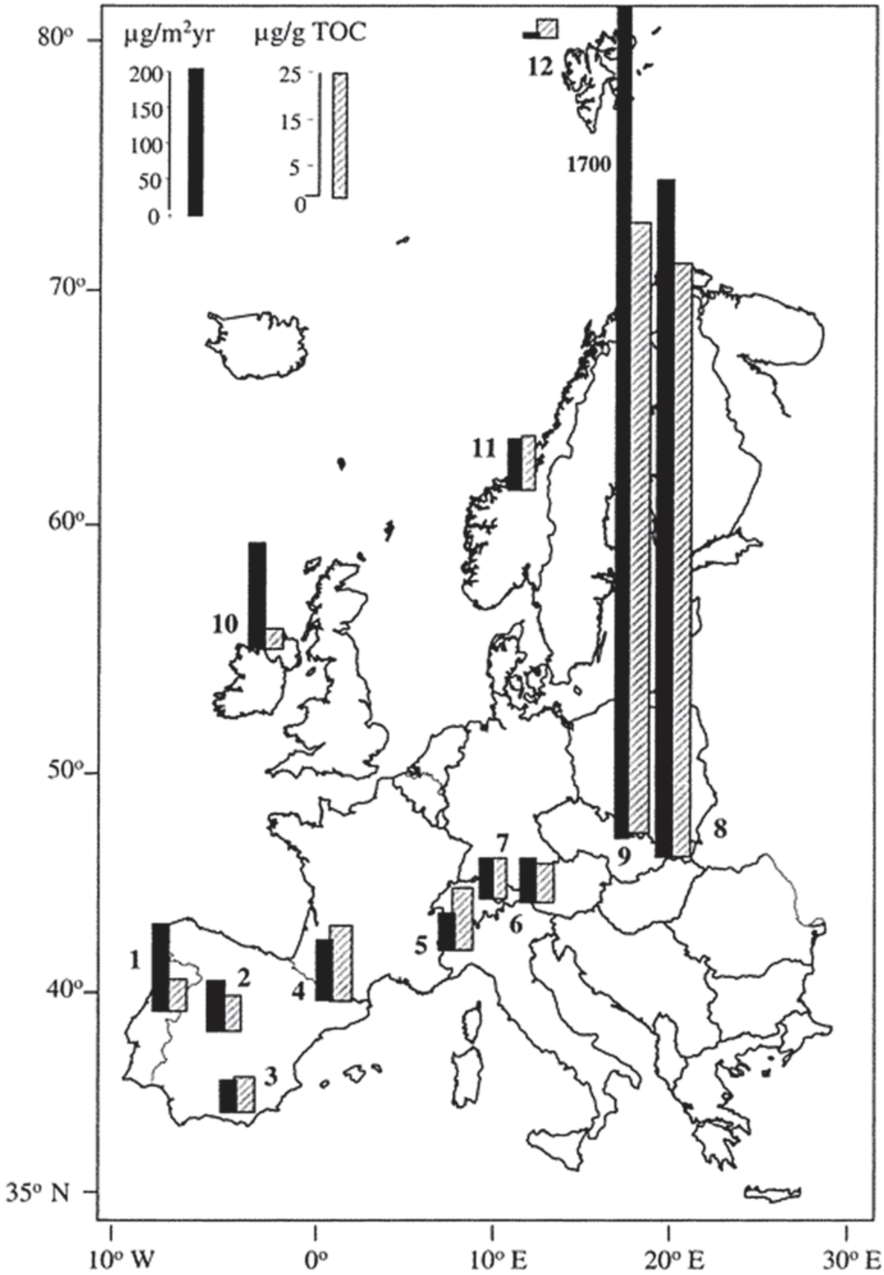

Fig. 3 PAH fluxes and PAH concentrations normalized to total organic carbon (TOC) in sediments from high altitude mountain lakes during the last decades. *1*, Escura (Serra Estrela, Portugal); *2*, Cimera (Sierra Gredos, Spain); *3*, La Caldera (Sierra Nevada, Spain); *4*. Redòn (Pyrenees, Spain); *5*. Noir, (Alps, France); *6*. Schwarsee ob Sölden (Alps, Austria); *7*. Gossenköllesee, (Alps, Austria); *8*. Dlugi (Tatras, Poland); *9*. Starolesnianske (Tatra, Slovakia); *10*, Maam (Donegal, Ireland); *11*. Øvre Neådalsvatn (Caledonian, Norway); *12*. Arresjöen (Danskoyab, Norway). Reprinted with permission from (Fernandez et al. 1999). Copyright 1999 American Chemical Society

in some lakes of the Tatra Mountains (Central Europe) and Julian Alps (Slovenia), to 5 µg m^{-2} y^{-1} in Arctic islands (e.g., Svalbard) (Fernandez et al. 1999). The highest fluxes were similar to those found in lakes situated near urban or industrial areas. In general, the European mountain lake sediments show an industrialization fingerprint screened through a long-distance transport; the composition is dominated by benzo[b+j]fluoranthenes, indeno[1,2,3,-cd]pyrene, chrysene+triphenylene, benzo[k]fluoranthene and fluoranthene, among other less abundant PAHs of pyrolytic origin. Throughout Europe, the increase of PAH fluxes in mountain sediments started during the last decades of the nineteenth century and achieved the maximum between 1960 and 1990 (Fernandez et al. 2000; Muri et al. 2006). The ratio between the maximum flux and the background levels was 12–34 in the broad central geographical core (Alps, Tatras, Pyrenees) and <7 in the periphery, both Northern (Scandinavia, Arctic) and Southern (Iberian Peninsula mountains). The exceptional high concentrations and fluxes in the Tatra Mountains correlated with the average sulfate deposition in the area before the 1990s (Fernandez et al. 1999). PAHs decline in many sediment records since the mid-1990s in response to an international agreement to reduce combustion emissions. In Lake Ladove, in the Tatras, PAHs concentration declined to half from the early 1990s to 2000 (Van Drooge et al. 2011). There are no European studies to evaluate the decline progress during the twenty-first century.

The number of studies investigating PAHs variability within lake districts that consider a large number of lakes is limited. A top-bottom palaeolimnological approach was followed by Van Drooge et al. (2011) in the Tatra Mountains. A northwest to southeast gradient was found, which is consistent with EMEP (European Monitoring and Evaluation Programme) estimates that identified a large area in southern Poland as a focus of high emission, just west of the Tatras. A handicap of the top-bottom approach is that fluxes are more difficult to estimate without dating or at least complementary data to evaluate the differences in accumulation rates and focusing degree among lakes. However, as a large number of lakes were evaluated at each sub-region, diagnostics at a sub-range scale should be acceptable. Different standardization procedures (e.g., lake size, organic carbon content, titanium, ^{210}Pb amount) may help in the interpretation. Some high mountain lakes may receive contaminants from a point source rather than regional background pollution, when the source is not far away and there are no topographic barriers in between. PAHs loadings may stand out over similar places not directly affected by orders of magnitude (e.g., Snyder Lake catchment of Glacier National Park affected by a local aluminum smelter (Usenko et al. 2010)).

The information from Asian mountain areas comes mostly from studies in China and usually not from archetypical mountain lakes. In fact, lakes in high elevation plateaus or in exceptionally large mountain valleys are extremely different from a typical alpine lake. Sometimes they are in arid areas and become saline; in others, with more suitable conditions, human populations may settle in the catchments. All in all, studies in this type of lakes have provided some indications of the background PAHs emissions for some parts of this vast territory. Compared to Europe, the records show an increasing tendency of PAHs deposition that started a decade

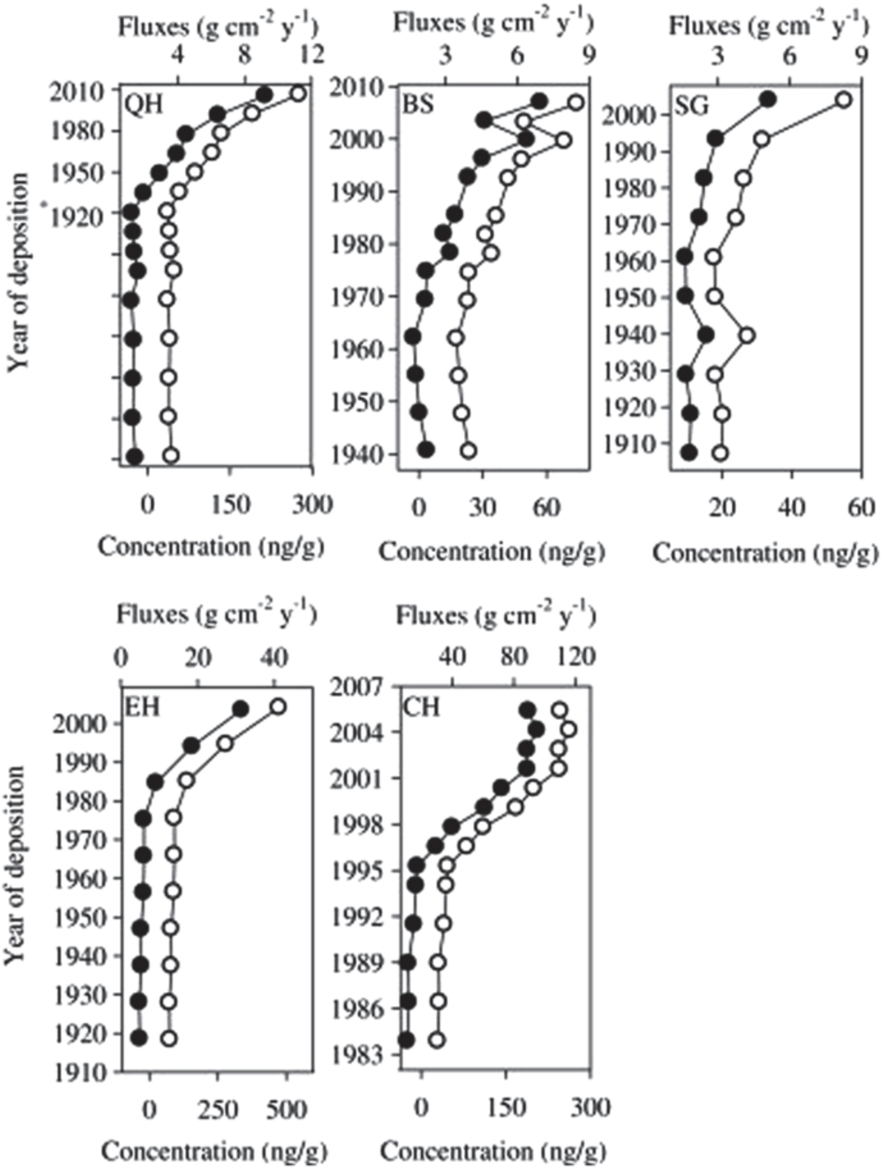

Fig. 4 Concentration and flux profiles of PAH_7 (sum of benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benz[a]pyrene, dibenzo[ah]anthracene and indeno[1,2,3,-cd]pyrene) in lake sediments of Western China: *QH* Qinghai Lake; *BS* Bosten Lake; *SG* Sugan Lake; *EH* Erhai Lake; *CH* Chenghai Lake. Solid circles indicate fluxes and open circles: concentrations. Reprinted from Guo et al. (2010), Copyright (2010), with permission from Elsevier

or two later than in Europe and is still rising (Guo et al. 2010) (Fig. 4). On the other hand, there is a higher contribution of biomass burning and domestic coal combustion, although the contribution of high temperature combustions is growing.

In some records, PAHs show a high correlation with Hg, Pb and other trace metals, indicating a common source related to progressive industrialization (Wang et al. 2010b). This was also a feature in Europe. The shift from low to high temperature combustion sources is reflected in the decreasing proportion of the simplest PAHs, with two and three rings, from 1860s to the present. In fact, the sediment PAHs records reflect the industrialization avatars in China: increased deposition since the "Westernization movement" in the 1860s; short interruption during the period of the "Cultural Revolution" (1966–1976); and steep increase during the last 30 years of unprecedented industrial and urban growth (Wang et al. 2010b).

Phenanthrene is a PAH that is abundant (even dominant) in the air and deposition measured in mountain sites, but it usually plays a secondary role in the sediments (Fernandez et al. 2003). The underrepresentation of phenanthrene in the sediments may be related to the water-particle partition in the water column. Low temperature may mitigate the discrepancy between air and sediments. Phenanthrene is the main PAH in the sediments of lakes in the Svalbard islands in the Arctic [Arresjöen Lake, (Fernandez et al. 1999); Ny-Alesund Lake (Jiao et al. 2009)]. There, the source was unclear. Biogenic origins, enhanced condensation because of the low temperatures, and local sources have been suggested as possible alternative (Rose et al. 2004). Phenanthrene was also dominant in the highest southernmost lake of Europe (La Caldera, 3050 m a.s.l., Sierra Nevada (Fernandez et al. 1999)), where temperature is high in summer.

Retene is common in most mountain lake sediment profiles, although in low quantities, and usually do not correlate with the dominant pyrolytic PAHs. Wood combustion is a source of retene, but it also has a diagenetic origin (Grimalt et al. 2004b), for instance, from abietic acid, which is found in conifer resin and other plant lipids. Conifer forest may cover a large proportion of some mountain slopes. Retene has been identified as the main PAH in soils of the montane stage in the Pyrenees (Quiroz et al. 2011). One way to investigate the origin of retene is to compare its sediment profile with that of the ratio between 1,7-dimethylphenanthrene and 2,6-dimethylphenanthrene, which is an indicator of wood combustion. There are sites where they closely match (e.g., Noir (French Alps), Escura (Serra d'Estrela, Portugal), Gossenköllesee and Schwarsee ob Sölden (Tyrolian Alps, Austria)), indicating a wood combustion origin, and others where they substantially differ (e.g. Redòn (Pyrenees), Starolesnianske pleso and Dlugi (Tatra Mountains), Øvre Neådalsvatn (Norway), Cimera (Sierra de Gredos, Spain), indicating the diagenetic origin of a large proportion (Fernandez et al. 2000). In Planina Lake (Julian Alps, Slovenia), retene was linked to forest fires in the lake vicinities (Muri et al. 2003), concentrations reaching exceptional values (ca. 1000 ng g^{-1} DW). The retene potential as a mountain forest fire indicator has not been explored sufficiently yet. It could be used complementing other fire indicators (e.g. charcoal particles).

Perylene sediment profiles also tend to differ from pyrolytic PAHs. At some sites, it suddenly increases at relatively deep sediment layers, as a result of diagenesis. In some areas, barely affected by industrial and urban pollution, it is largely dominant in the sediment profile (e.g., some Chilean mountain lakes; Barra et al. 2006), which has been related to coniferous signatures.

Organohalogen Compounds

Organohalogen compounds are numerous and diverse in their properties, applications and periods of use. Recent results from the Global Atmospheric Passive Sampling (GAPS) network (Pozo et al. 2009) indicate that the latitudinal distribution of OHCs reflect the estimated spatial variability of global emissions, with the highest concentrations observed at mid-latitudes of the northern hemisphere, including PCBs, which have been long banned.

PCBs can be viewed as a benchmark set for OHCs because different congeners cover a broad range of physicochemical properties and their distribution can reflect regional background conditions as its production stopped in the 1970s. They are found everywhere. The lowest PCB total concentrations found in remote mountain lake sediments are around 1 ng g^{-1} DW (Guzzella et al. 2011). Within a region, PCBs tend to increase with altitude in lake sediments, particularly the less volatile congeners (penta- and hexa-PCB). This was first observed by Grimalt et al. (2001) in a survey of European high mountains lakes covering different ranges to achieve a larger temperature gradient. In this study, it could be criticized that the highest altitudes (lower air temperatures) corresponded to areas of central Europe, which were potentially closer to regions of higher emissions (Daly and Wania 2005). However, the article showed that, within the subset of lakes in the Alps, although the gradient was shorter, the relationship was also significant. In addition, the variation of each compound was partitioned into air temperature and location influences using appropriate statistical techniques (Borcard et al. 1992), being the explicative power markedly in favor of temperature for the less semi-volatile compounds. Later, altitudinal PCB patterns in lakes have been found in sediments (Guzzella et al. 2011) and fish (Gallego et al. 2007; Felipe-Sotelo et al. 2008; Demers et al. 2007). More interestingly, comparison of OHC composition in atmospheric deposition and sedimentary records in geographically distant sites demonstrates a selective trapping of the less volatile compounds. Trapping efficiencies increase at decreasing air temperatures of lacustrine systems (Carrera et al. 2002). Studies in the Chilean Andean lakes show the highest PCB fluxes in the sediments between 1991 and 1998 (Pozo et al. 2007), which differ from the main peaks in rural Canadian and European lakes, which tend to be in the period 1955–1970.

DDT is usually found in mountain lake sediments as its derivates (e.g., DDE), which indicates that they do not correspond to recent use, and sometimes are reported together as DDTs. They also tend to show a local altitudinal increase as the less volatile PCBs (Grimalt et al. 2001). Although not in use in many countries, in others this insecticide is still a primary element in the fight against malaria. There is little knowledge on how it redistributes with LRAT. In lake sediments at Mt. Sagarmatha (Himalayas), between 4893 and 5293 m a.s.l., p, p'-DDE average levels were 0.19 ± 0.27 ng g^{-1} DW, and no other form was measured above the detection limit (Guzzella et al. 2011). These values are similar to those found in the Arctic and Subarctic and may be considered representative of background concentrations in remote cold areas.

HCHs were used initially as a technical mixture of α-HCH and γ-HCH, and later it was commercialized as lindane (γ-HCH) until it was banned in 2009. The HCHs distribution mainly reflected its broad application in agriculture. For instance, HCHs levels compared to other OHCs indicate whether a mountain range is located in an industrial or agricultural region in Europe (Carrera et al. 2002). In the near future, the recent band of HCHs should be reflected in the sediment archive as they are compounds sufficiently volatile to achieve local equilibrium between different environmental compartments quickly (Liu et al. 2010). In Mt. Sagarmatha (Himalayas) lake sediments, HCHs were below detection limits (<0.1 ng g^{-1} DW) in samples collected in 2007 (Guzzella et al. 2011). HCB, which is no longer used but results as a by-product of certain industrial processes, shows distribution patterns similar to HCHs in remote sites because of the similarity in the physiochemical properties between these compounds. In remote Himalayan lakes, the average levels were 0.08 ± 0.04 ng g^{-1} DW (Guzzella et al. 2011).

Other pesticides have had a more regional use than DDT or HCHs. Toxaphene has been found in Lochnagar sediments in Scotland (Rose et al. 2001), which could be evidence of transcontinental contaminant transport, because it was mainly used in North America. The profile showed two peaks, one in the 1970s and another in the 1990s (PCB had a unimodal distribution centered at 1973). The earlier peak agrees with the U.S. source curve; the second could be related to late use in eastern and south-eastern Europe, although air circulation from these regions only exceptionally arrives to Scotland. The toxaphene issue in European remote sites has not been sufficiently explored. Sediment concentrations in Lochnagar were equivalent for those reported in the Great Lakes, where there were fluvial inputs, and higher than untreated sites in the Canadian Arctic.

PBDEs have been used in different technical mixtures along time, with increasing bromination (penta-, octa-, deca-). The most recent consisted of a molecule fully brominated (BDE-209), with low sub-cooled vapor pressure ($10^{-8.3}$ Pa) and high hydrophobicity, according to its octanol-water partition coefficient ($K_{ow} = 10^{8.7}$), which, consequently, was not expected to be found in remote sites. However, it has reached mountain lakes far away from urban areas (Bartrons et al. 2011) becoming an example of how difficult is to predict the environmental performance of new synthetic substances. The changes in production and use of PBDE mixtures have been rapid and diverse throughout continents, and so have been registered in lake sediments. The presence of some brominated compounds (e.g., BDE-47, 99, 100) could be interpreted straightforward as an indication of the source technical mixture. However, there are indications that PBDEs are biodegraded in anoxic sediments faster than other persistent OHCs (Bartrons et al. 2011). On the other hand, they are also affected by temperature-dependent selective trapping. Specific patterns of PBDEs have been observed in the sediments of the Svalbard lakes (Arctic) (Jiao et al. 2009), showing higher concentrations of lower brominated compounds such as BDE-7, 17 and 28. In temperate mountains, PBDEs levels increase with altitude in lake sediments (Bartrons et al. 2011). Comparisons between PCBs and PBDEs distribution have been made (Fig. 5) because of their similar richness in different congeners, which cover a broad range of volatility, and because PBDE production and use raised fast to levels equivalent to PCBs (Usenko et al. 2007).

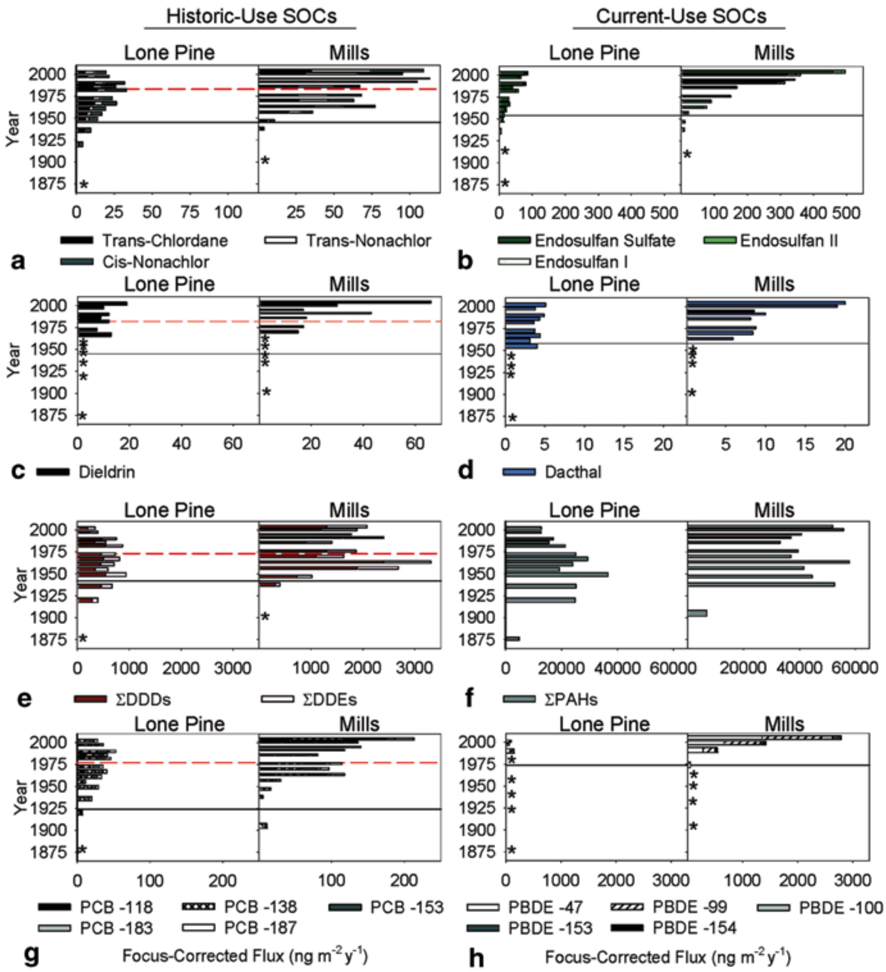

Fig. 5 Focus-corrected flux profiles of current and historic-use of semivolatile organic compounds (SOCs) in Lone Pine Lake (3024 m a.s.l) and Mills Lake (3030 m a.s.l) sediment cores. The lakes are respectively located at west and east of the Continental Divide in the Rocky Mountain National Park (Colorado). Westerly winds predominate in the area, which together with the topographic barrier produce a contrasting pattern of contaminant fluxes between the two slopes. Solid lines indicate U.S. registered use date, *dashed lines* (*red*) indicate U.S. restriction date, and * marks indicate below method detection limit. Reprinted with permission from Usenko et al. (2007). Copyright 2007 American Chemical Society

The number of studies examining perfluorinated compounds in mountain lake sediments is low. In the Canadian Rocky Mountains, the isomer profiles and the temporal trend data suggest that FTOH oxidation is the dominant atmospheric source of PFCAs to high alpine lakes (Benskin et al. 2011). Alpine lakes from Austria presented similar profiles (Clara et al. 2009). Further investigations are required in other parts of the world.

Understanding the Sediment Archive

Mountain lake sediments are recording systems of regional background air contaminants. However, contaminants undergo a complex pathway from sources to the lake and within the lake before being archived in the sediments (Fig. 6). The LRAT of the contaminant can be in gas or particle phase. In this partition, the origin may have some influence but as soon as the travelled distance is sufficiently long, the physicochemical properties of the substance are the primary conditioning factor determining the gas-particle partition. The phase in which a substance is travelling has influence on reaction (e.g., photo-oxidation by high irradiance) and scavenging rates. High mountains are barriers to circulating air masses; particles may deposit in dry conditions by simple intersection by vegetation, rocks and soils, or by adiabatic cooling that may favor rainfall and concurrent scavenging by rain or snow fall. Once deposited, particles will be more or less efficiently transported by water flows to lakes and eventually will settle to the sediments. In water, a new partition between water and particle will take place, under different constraints than the air-particle partition. On the other hand, substances reaching the mountains in gas form will exchange with water according to their solubility properties and temperature conditions. In the water column, the substances will interact with the particles present. These particles are quite different from those present in the atmosphere. In fact, many of them are living organisms, from microbes to large fish. In this case, the water-particle partition will be highly conditioned by the hydrophobicity of the compound, which can be extremely high for some organic contaminants. Sinking

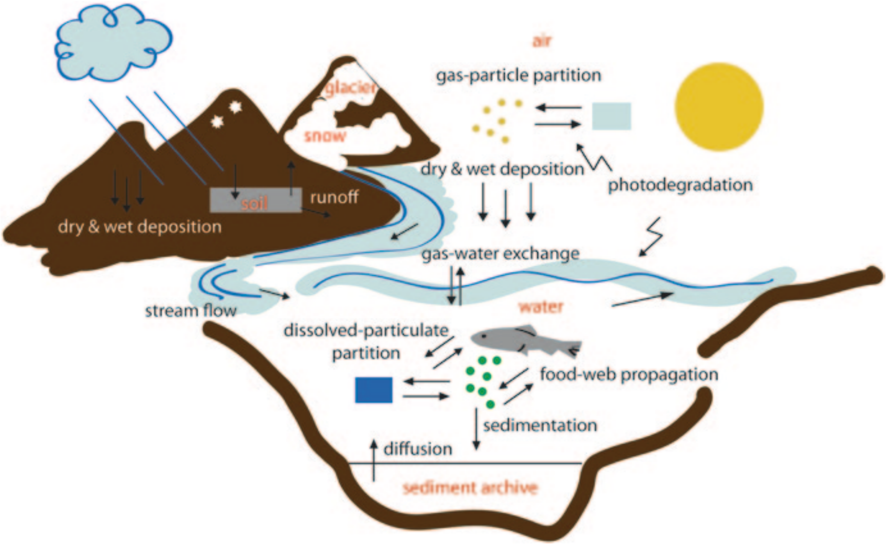

Fig. 6 Processes involved in the transport of contaminants from the airshed to the archive in mountain lake sediments

particles accelerate the transport to the sediments. Bioaccumulation across the food web may delay the deposition of part of the contaminants to the sediment, but eventually, sooner or later, if the suspended matter is not exported down flow, particles with attached contaminants will settle to the sediment surface. Beyond the lake, a large proportion of the contaminants deposited can be stored in soils, vegetation or other catchment reservoirs (e.g., glaciers, peat lands). Depending on the circumstances, these reservoirs are permanent sinks for contaminants or may become a delayed source to the atmosphere or to the runoff.

These complex contaminant pathways to the sediments are not fully understood yet. Some aspects respond to general concepts of contaminant LRAT (Macdonald et al. 2000b) and others require the understanding of processes particular to mountains and mountain lakes. Mountains offer an ideal setting for environmental research as in short distances there are marked physical gradients (e.g., air temperature) and ecosystems are relatively amenable to observation and modelling, particularly mountain lakes. However, the complexity of air circulation at different spatial scales has to be considered.

Atmospheric Transport to the Watershed: The Airshed

Atmospheric transport of contaminants is the ultimate cause and, thus, a key process for understanding the sediment archive. Compared to the watershed, the airshed of lakes—the area that supplies the materials for deposition- does not have defined boundaries and may be changing through time as climate changes. Methods for determining air mass back-trajectories and increased understanding of mountain meteorology have notably improved the capacity for linking sources and sinks in the atmospheric transport of contaminants.

Atmospheric samples from European high mountain areas show that most semivolatile OHCs are predominantly found in the gas phase (Van Drooge et al. 2004). For instance, HCB, the dominant compound in these samples, was exclusively present in the gas phase. Only the less volatile are predominant in the particulate phase (e.g., PCB congeners 149, 118, 153, and 180), and those with extremely low vapor pressure are assumed to be transported exclusively sorbed to particles (e.g., BDE-209). Generally, for a given site, there is an agreement between the amount of particles and amount of contaminants typically associated with them (Fernandez et al. 2003), indicating a relatively homogenous background of contamination. However, the correlation may be lost in areas with contrasting air mass trajectories in which one of them is crossing areas of dust emission. If contaminants are directly measured in the air or in single deposition episodes, the contaminant profile of the different air mass directions can be defined accurately. Unfortunately, in this respect, sediment samples integrate deposition over months, usually years. Therefore, the way to disentangle distinct geographical sources of contaminants has to be by using specific indicators. This has been mainly applied to PAHs, for instance, for distinguishing between low temperature combustions (wood, domestic coal, etc.) and high temperature ones (vehicles, electric stations, etc.) (Guo et al. 2010). When some potential specific point source (e.g., smelter, pesticide factory) adds to the background contamination, the indicators extend to specific trace metals, isotopes or synthetic compounds (e.g. lindane) (Usenko et al. 2010).

Contaminants associated with particle transport are generally better preserved in the sediment record than gas phase components, which tend to have more complex dynamics before being permanently archived. For instance, there is an approximate agreement (e.g., at logarithmic scales) between total PAHs in the air and soils or sediments of remote sites above the planetary boundary layer (Van Drooge et al. 2011). However, sediment PAHs composition generally agrees most closely with the air particulate phase in sites where both have been studied. The air gas phase is largely dominated by lighter, more volatile compounds, such as phenanthrene and fluorene (Van Drooge et al. 2010), which usually have a minor representation in the sediment record, compared to compounds attached to air particles (Van Drooge et al. 2011). This fact may change at exceptionally low temperatures, such as those that can be achieved at high latitudes or extraordinarily high altitudes, where those compounds typically associated to the air gas phase may condense and largely increase in the sediment record (Fernandez et al. 1999).

Atmospheric transport occurs under oxidizing conditions (e.g., UV radiation, free radicals), and some contaminants are more reactive than others. Generally, those compounds carried in the gas phase are more exposed to photo-oxidation and proportionally decay more than those attached to particles. Also, among PAHs and OHCs, there are compounds chemically more stable. Alkylated PAHs are more reactive than the corresponding parent PAHs. Their life time in the air is short; thus, their presence indicates nearby sources (Kalberer et al. 2004). In general, a certain indication of the relative distance of transport can be assessed by the proportion of short life compounds. For instance, benz[a]anthracene and benz[a]pyrene are more chemically labile than benz[e]anthracene and benz[e]pyrene, respectively. Ratios between these compounds have been used as relative indicators of distance to sources (Van Drooge et al. 2010). In endosulfan, the ratio between Endo I and Endo II increases after application because the latter is less stable in the atmosphere. The proportion of endosulfan sulfate may indicate re-emission since it is believed that microbial oxidation of endosulfan in soils is one main source of this form (Pozo et al. 2009). In any case, endosulfan sulfate is the only form usually found when the source of endosulfan is exclusively the long range atmospheric transport, and there are not regional sources (Carrera et al. 2002).

Single point air measurements are not representative of contamination even at remote sites. There is seasonality in the contaminant levels of the mountain air for several reasons. Part of the seasonal change may be related to current use of some compounds (HCHs, endosulfans) (Blais et al. 2001b). High altitude sites in South America appear to be affected by the large use of endosulfans in Brazil, and the concentrations during the summer can be an order of magnitude higher than in winter (Meire et al. 2012b). In the Tibetan Plateau, high summer values of HCHs and DDT-related compounds are due to more contaminated air being blown into the region from the Chengdu Plain, presumably either due to higher pesticide usage in summer or due to higher temperatures leading to higher evaporation in source regions (Liu et al. 2010). In Europe, compounds that have not been manufactured (PCBs) or drastically restricted in their use (4,4′-DDT related compounds) also may show seasonality due to the higher contribution during warm periods of the continental inputs, compared to a more maritime origin during cold periods (Van Drooge et al. 2004). In European mountains, air masses that have been travelling in the high troposphere (>6000 m) carry 4–10 times less background OHCs (e.g., ca. 9 pg m^{-3} PCB and 0.4 4,4′-DDE) than the overall average (Van Drooge et al. 2004). In contrast, in the same areas, PAHs showed an opposed seasonal trend, concentrations in air were higher during the winter. The PAHs seasonality was higher in the particulate fraction, indicating higher winter emission but also the temperature dependence of gas-particle partitioning (Fernandez et al. 2002), which is reasonably well predicted in the case of air-soot partition.

Precipitation

Rain has a large capacity for scavenging particles from the atmosphere and thus their associated contaminants. In addition, water drops can also incorporate contaminants from the gas phase according to its solubility (air-water partition) and temperature. As temperature decreases with altitude, the levels of dissolved contaminants can increase (Wania et al. 1998). This feature, combined with higher precipitation with increasing altitude, has been suggested as a main mechanism for higher contaminant concentrations and selective cold trapping of contaminants at high altitude in mountains (Wania and Westgate 2008). Nevertheless, it has to be taken into account that the increase in precipitation with altitude is not a global general feature in the mountains (Körner 2007). The increase of precipitation with altitude is more marked at latitudes between 40 and 60°, where most of the studies have taken place up to now. The tendency is less marked between 30 and 40°, and there is not such a trend in the rest of the world. In subtropical zones (10–30°), the maximum of precipitation occurs at intermediate altitudes (ca. 1500 m) and decline rapidly towards higher altitudes. At equatorial (0–10°) and polar latitudes (>60°), precipitation decreases with altitude, although with contrasting absolute values, high in the former, and low in the latter, respectively. The spatial heterogeneity can also be large within the same region. Whereas local correlation between altitude and air temperature is always high ($r^2 > 0.80$), the correlation with precipitation is often statistically non-significant (Kirchner et al. 2009). This lack of correlation may be due either to contrasting orientation of the sites respect to the dominant trajectory of the wet air masses (e.g., different slopes in the Andes) or to the micrometeorological complexity occurring in massive mountains. In monsoon areas, the gradient and absolute values of precipitation are higher the lower the average altitude of the mountains in the range. Even locally, precipitation levels are difficult to model (and forecast) from valley to valley (Thompson et al. 2009). Altitudinal gradients of deposition have not been directly studied and sometimes the effect is indirectly evaluated by the concentrations of contaminants in soils, and whether they correlate or not with precipitation (Tremolada et al. 2008). As soils are also dynamically complex, studies of direct measurements of precipitation along altitudinal gradients will be valuable, yet the distribution of sampling points without other influential factors than altitude (and precipitation differences) is not that easy.

In high mountains, a large proportion of total precipitation is in snow form. Snow is even a better scavenger of particles than rain (Franz and Eisenreich 1998), including compounds that are usually in the gas phase (e.g., phenanthrene; Carrera et al. 2001). The highly hydrophobic and scarcely volatile BDE-209 has been recently found in snow (Arellano et al. 2011). Correlation of the OC concentration in snow versus mean annual winter temperature shows higher accumulation at lower temperatures. In the Tatra Mountains, the less volatile PCBs exhibited higher temperature dependencies than the more volatile congeners (Grimalt et al. 2009); contrarily, in sites of western Canada, the more volatile compounds increased preferentially with altitude (Blais et al. 1998). This may be related to the specific range of winter temperature in each area of study.

The quality and quantity of contaminants in precipitation change seasonally, because emissions from urban, industrial and agricultural sources and the stratification of the atmosphere vary from summer to winter. Therefore, a few months of deposition measurements are not representative of the annual load. In addition, snow introduces an added complexity. The snowpack has a complex dynamics, and it cannot be assumed that the load of contaminants that it contains will end-up into the soils and runoff (Finizio et al. 2006). Direct interpretation that higher levels of a contaminant in the snow will contribute to a higher load into the lake sediments is not necessarily correct.

Dust

In mountain lakes close to dust source areas, dust-transport and deposition become key factors for understanding contaminant deposition (e.g., some areas of Central Asia; Wang et al. 2010b). Dust can also be critical for understanding the contaminant deposition patterns in areas affected sporadically by air-masses that bring dust from far away sources. In general, dust has a buffering (Psenner and Catalan 1994) and fertilizing effect on mountain lakes (Camarero and Catalan 2012), which are usually acid-sensitive and oligotrophic. Trace metals are commonly associated with dust (Reynolds et al. 2010) but other contaminants have also been related to dust transport when the source of contaminants and dust are nearby (Wang et al. 2010b). In areas receiving sporadic (but intense) dust loads, dust contribution may jeopardize the correlations between particles and less volatile contaminants (e.g. PBDEs; Arellano et al. 2014), which is normally found when the source of particles is in urban or industrial zones.

Air Mass Trajectories and Distance to Source

Defining the lake's airshed is not a simple task. When considering background contamination in mountain sites, the geographical distance is not necessarily a valid indicator of the potential contribution of a certain source area. Air mass trajectories can make distant sources close and, on the contrary, nearby sources far away.

Generally, high mountain lakes are located above the planetary boundary layer (full theoretical depth ca. 2000 m; nocturnal depth ca. 300 m at mid-latitudes) and are not regularly exposed to contamination from low lands. Therefore, high altitude lakes can be representative of background, long-range atmospheric contamination. However, this is not the case when the lakes are located in inhabited high altitude plateaus (Bogdal et al. 2011). On the other hand, convectional instabilities can develop in warm periods and mix the atmosphere up to several kilometers. Consequently, it has to be locally (regionally) evaluated, whether the lakes studied are permanently above the planetary boundary or not. In the Pyrenees, for instance, researchers have found evidence of trace metal local contamination up to about 2000–2300 m a.s.l. both in soils (Bacardit and Camarero 2010b) and the winter snowpack (Bacardit and Camarero 2010a).

A mountain lake rarely receives all its precipitation from the same direction and usually the different sources have distinctive chemical features; for instance, according to a more maritime (Cl, Na) or continental (Ca) contribution of inorganic compounds (Camarero and Catalan 1996). The cases in which single deposition events are analyzed are rare; more commonly, the samples are a composite of precipitation events covering a certain time. Then, the association between contaminants and air mass trajectories is made based on the relative contribution of different back-trajectories to precipitation of the sampling period (Bacardit and Camarero 2009). There are cases in which the air mass trajectories change seasonally. For instance, seasonality in semi-volatile organic compounds levels in the air of the European mountain is mainly due to a higher occurrence of air masses with strong continental inputs in the warm periods than in the cold periods (Van Drooge et al. 2004). HCHs deposition increased during the monsoon season in East Rongbuk Glacier (6572 m a.s.l.) in the Himalayas (Kang et al. 2009). If there is a geographical segregation of dominant sources (e.g., wood combustion vs. pyrolytic sources for PAHs) the air mass back-trajectories can help to confirm their relative contributions.

Air trajectories from different directions may also travel preferentially at certain altitudes and among complex terrains found in mountain areas, introducing additional sources of variability. Contaminant measurements at high altitude in oceanic islands have been proposed as representative of hemispheric free-troposphere conditions. At the Izaña Atmospheric Observatory (2367 m a.s.l.) on Teide Mountain (Canary islands, Atlantic), air PAHs are an order of magnitude lower than at any remote mountain site in the European continent (Van Drooge et al. 2010). OHCs in mountain ice cores have been related to some main climatic descriptors: DDT and HCH in the Mt. Everest ice to the El Niño-Southern Oscillation, DDT in Mt. Muztaga (Eastern Pamirs) to the Siberia High pattern and DDT in Snow Dome (Rocky Mountains) to North Atlantic Oscillation (Wang et al. 2010a).

Topographical Barriers

High mountains are topographical barriers even for tropospheric circulation. This may result in contrasting patterns between sites at the same altitude but different slopes. For instance, PAHs at high altitude soils showed similar relative composition but contrasting concentrations between northern and southern slopes in the central Italian Alps (Tremolada et al. 2009). As the air mass is forced to ascend to clear the barrier, air cools and precipitation becomes more likely; contrasting precipitation between slopes occurs if some direction dominates the regional air mass trajectories. Disparity in PCB sediment fluxes between lakes in the western and eastern Andes slopes of Chile has been attributed to differences in rainfall and air mass origin (Pozo et al. 2007). Similarly, from a study of 98 semi-volatile organic compounds in two lakes of the Rocky Mountain National Park, one west of the continental divide and another east, Usenko et al. (2007) conclude that regional upslope wind directions and site location with respect to regional sources and topographic barriers were determinant in the composition and magnitude of the sediment fluxes (Fig. 5).

Grasshopper Effect

Mountains are not only sinks for contaminants. Short-term changes in conditions may determine that deposited contaminants during cold periods are re-emitted during warm phases. This affects mostly the more volatile compounds. For instance, PCB summer release in the Alps pastures have been described (1900 m a.s.l.), which can be tracked in seasonal patterns in the contaminants of cow milk (Tato et al. 2011). Concentrations and enrichment in the less volatile congeners were higher in the Northern slope. The remission at low (warmer altitude) may become a supply for high (cold) altitudes. This jumping transport (the so-called Grasshopper Effect) may occur also between mountains (from lower to higher ones) and latitude (temperate mountains towards polar regions).

Catchment to Lake Transport

Ideally remote lakes will act as passive collectors of atmospheric deposition. Even in mountains, with the exception of volcano lakes, the catchment usually occupies a larger part of the watershed than the lake. Therefore, there is always some part of the annual contaminant load to the sediments that will originate from the catchment. The catchment is a reactive surface and, depending on its characteristics, will modify more or less the atmospheric profile of contaminants. Quick superficial runoff, in principle, should be more similar to atmospheric deposition than soil seepage. Soils act as filters for some substances, as has been recorded by comparing trace metals in snow and artesian flows (Shotyk et al. 2010). For lakes with a water budget that includes a significant contribution from catchment runoff, understanding the sediment archive requires understanding of what may happen in the catchment compartments. There have not been many attempts to quantify the direct and catchment-mediated contributions of contaminants [e.g., trace metals (Bacardit and Camarero 2010c), OHCs (Blais et al. 2001b)].

Snowpack

The snowpack is not a simple accumulation of snow that eventually melts. Throughout the cold months, the snowpack develops and changes in some physical properties. There are substances that can be re-emitted to the atmosphere or washout selectively during thaw periods. Emissions from the snowpack back to the air are more likely for the more volatile compounds (Hansen et al. 2006). They can be trapped at very low temperatures, but when the snowpack warms, a fraction of them may return to the gas phase. This is another mechanism of selective trapping of the less volatile compounds. Snow specific surface area, which determines the maximum amount of each organic compound that can be sorbed by snow, has proved useful for describing the distribution of the more volatile compounds (e.g., α-HCH and HCB) in the Tatra Mountains (Arellano et al. 2011).

The snowflakes undergo metamorphic change following deposition. In a simplistic view, flakes transform into grains with an ice core of pure water coated by ice with more solutes and particles. When conditions warm up, the coating ice melts first and, as a consequence, there is a differential elution of substances along the thaw period. The initial runoff from the snowpack is richer in substances than the final one, which is close to distilled water. This was first studied for inorganic compounds (Catalan 1989), but it has also been found for organic contaminants. In Bow Lake (Alberta), the first snowmelts exhibit high concentrations of organic contaminants relative to the snowpack, including the more hydrophobic compounds (Dieldrin, DDTs, and PCBs) (Lafrenière et al. 2006). There are areas of the world where two separate phases of snow accumulation and melting are clearly established, but in other parts, melting and freezing can alternate during many months, increasing the complexity of the process (Felip et al. 1999).

The ice and snow cover of the mountain lakes generally remain until a large part of the snowpack is melted (Catalan 1989). Water entering the lake circulates close to the ice cover, due to the inverse stratification of the water column. This determines that the first flush of snow runoff, which is rich in substances and particles, goes through the lake without much contribution to the sediments if the lake is relatively deep. The late thaw runoff usually does mix with the water column as the lake experiences spring turnover (Catalan 1992). Therefore, the relative contribution of catchment's snow deposition to the contaminants sediment load may vary considerably from lake to lake and year to year. Necessarily, the contribution will differ depending on the geomorphologic and hydrologic setting: lake size and depth; ratio between lake area and catchment area, north and south facing, etc. The differences between contaminants may arise whether they are sorbed to large particles, which may sink quickly, or to fine-particles, or dissolved, which will pass through towards the outflow.

Glaciers

Some mountain lakes receive runoff from glaciers. They are not ideal systems within which to track atmospheric contamination because the glacier's complexity as collectors and archives of contaminants complicates the interpretation

(Villa et al. 2003; Blais et al. 2001b). Even under relatively constant climatic conditions, glaciers are in a dynamic equilibrium. Therefore, they are releasing contaminants during the warm season. The relative contribution of glaciers to runoff may be a relevant source of contaminant inter-annual variability in streams (Lafrenière et al. 2006). Under the current global warming regime, it is interesting to investigate whether and how contaminants archived for decades in the glacier ice are now released with the glacier retreat (Blais et al. 2001a). For some Switzerland glaciers, modelling projections indicate that time for release of the same quantity of contaminants can decrease 10-fold (Bogdal et al. 2010a). Oberaar Glacier is currently increasing the release of OHCs, which account for the observed OHCs increase in the lake of the same name (Bogdal et al. 2010a). In Lake Iseo, one of the large southern Alpine Italian lakes, the PCBs maximum in the lake sediments corresponds to the 1970s (the period of the highest PCB production) whereas DDT shows a sharp increase from the early 1990s, long after their agricultural use was banned in Italy (Bettinetti et al. 2011). This has been attributed to the retreat of the glaciers in the zone. In two lakes of the Bernese Alps (Switzerland), located only 8 km apart from each other, PCBs and DDT levels showed the highest levels in the sediments 30–50 years ago; however, in the one fed with glacier melting water, the peak was followed by a second increase in the 1990s (Schmid et al. 2011).

Soils

Soils play a dual role in the context of contaminant recording in mountain catchments. On one hand, they are an alternative archive to which the sediment register can be compared. On the other hand, similar to glaciers, they may act as a transient storage deposit for contaminants that eventually are released to the lakes. Compared to glaciers, however, dynamics of contaminants in soils may be more diverse and complex. As archive, soils differentiate from sediments by presenting higher bioturbation, lower accumulation rates (hence, there is less chronological control as archive), higher spatial (and seasonal) heterogeneity and different preservation conditions (Kirchner et al. 2009).

PAHs in lake sediments and nearby soils were compared for sites in the Pyrenees and Tatra Mountains (Grimalt et al. 2004b). Both archives showed airborne combustion mixtures refractory to photo-oxidation and chemical degradation. However, the degree of preservation compared to air samples was different (Fig. 7). Soil surface preserved the original air mixture better than the sediment surface. This indicates a PAH differential degradation, either during the water column transport or in the upper sediment before the ‘fossilization’ of the deposition signature. In contrast, lake sediments exhibited higher preservation of the more labile PAHs, indicating a lower degree of post-depositional oxidation than soils. The formation of some PAHs by diagenetic transformation also differs between soils and sediments; perylene usually increases in deep sediment sections, whereas phenanthrene enrichments in deep soils have been observed, which can result from the aromatization of diterpenoids. In several tropical regions, soils have a higher relative abundance of the lighter

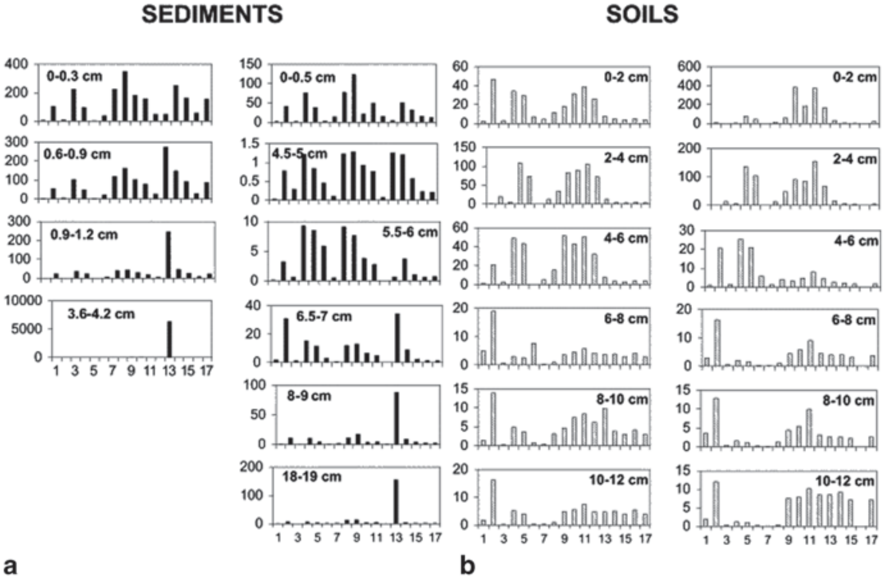

Fig. 7 PAH in soils and sediments from Lake Redòn (Pyrenees). *A* and *B* refer to two different sediment and soil cores analyzed from this site. *1*, fluorene; *2*,phenanthrene; *3*, anthracene; *4*, fluoranthene; *5*, pyrene; *6*, retene; *7*, benz[a]anthracene; *8*, chrysene+triphenylene; *9*, benzo[b+j] fluoranthenes; *10*, benzo[k]fluoranthene; *11*, benzo[e]pyrene; *12*, benzo[a]pyrene; *13*, perylene; *14*, indeno[1,2,3-cd]pyrene; *15*, benzo[ghi]perylene; *16*, dibenz[a, h]anthracene, *17*, coronene. PAH units in ng/g. The PAH composition in the upper layers of both compartments exhibits a high similarity with atmospheric aerosols collected at this site (Fernandez et al 2002). Reprinted from (Grimalt et al. 2004b), Copyright (2004), with permission from Elsevier

PAHs than in temperate regions, which likely reflects a higher contribution from biomass burnings (Daly et al. 2007a).

Soils are the major terrestrial reservoir of persistent organic pollutants (Meijer et al. 2003) and play a control on background atmospheric concentrations. For volatile compounds, there can be direct soil-air exchange (Cabrerizo et al. 2011). Depending on the soil characteristics, the maximum reservoir capacity may differ in many orders of magnitude among compounds (Dalla Valle et al. 2005). The reservoir capacity may change seasonally (and diurnally) with air temperature [e.g., PCBs (Guazzoni et al. 2011), DDT (Tremolada et al. 2011)]. The soils become net emission sources when maximum reservoir capacity is achieved. For semi-volatile compounds, mountain soils at mid-latitudes may be part of a stepwise mechanism of transport to high colder latitudes. Within a mountain range, soils at lower altitudes may become secondary sources for soils at higher altitude (grasshopping mechanism). For instance, soils in the Tibetan Plateau are secondary sources for HCB, HCHs, and low molecular PCBs; whereas they are still sinks for DDE and DDT (Liu et al. 2010; Wang et al. 2012). In the Czech Republic, the highest levels of HCHs and HCB were found in arable soils, but the highest for PCBs, DDTs and PAHs were found in high altitude forest soils, which reflected the legacy from the past high deposition (Holoubek et al. 2009).

Organic matter (OM) content increases the soil's capacity to retain OHCs (Cabrerizo et al. 2011; Wang et al. 2012; Zheng et al. 2012) and particularly the most hydrophobic fraction (Tremolada et al. 2012). However, for PBDEs a better normalization of altitudinal gradients has been found using clay content rather than organic matter in soils (Yuan et al. 2012). Soil total organic matter (as total lipids in organisms) is a heterogeneous catchall that usually provides statistical significance for normalizing organic contamination, yet it may be too crude of a measure for understanding key processes. If the percentage of OM is used for normalizing OHC concentrations among samples, it is always advisable to report the OM values for each sample, so that one can calculate backwards to the original concentrations. This comment also applies to sediments.

The transport of contaminants from soils to streams and, eventually to lakes, is still poorly understood (Bergknut et al. 2011). It is an intermittent process since many of the contaminants are transported with particles or colloidal matter. Soil erosion is highly variable and dependent on multiple factors. In the Pyrenees, the anthropogenic trace metals accumulated in the catchments are three orders of magnitude higher than current atmospheric loads. The Zn soil exportation constitutes ca. 70 % of the lake inputs, yet soils are still a net sink for atmospheric deposition of Zn. In contrast, Pb atmospheric deposition is lower than Zn, and soils have become a net source for Pb, which contribute > 90 % of the lakes Pb loading (Bacardit et al. 2012; Bacardit and Camarero 2010b). In Lochnagar (Scotland) similar contributions have been found for Pb and about 78 % for Hg (Yang et al. 2002b). Consequently, the trace metal contamination legacy from soils may be a general environmental feature in European mountains. The net soil contribution to streams and lakes may last for at least decades (Bindler et al. 2008). This will delay the restoration of the lake system, despite reductions in emissions to the atmosphere, and may confound any evaluation of the reduction in trace metal deposition based on lake sediments if not taken into account. In Flin Flon (Manitoba, Canada), contradictory results between peat and sediment archives identified the soil legacy contribution of Hg and Zn (Outridge et al. 2011).

Plants, Forest

Bare soils and meadows are the common land cover of many high elevation mountain lake catchments. In rainy regions, or descending in altitude, more complex vegetation is often found. Cold and humid areas develop heathlands and peatlands, where plant debris may play a pivotal role in storing and transferring contaminants to the sediments. This has been mainly studied for trace metals, but it should be expanded to the study of other contaminants. In Lochnagar (Scotland), plant debris is the main transport mechanisms for trace metals from the catchment to the lake, a fact that increases the variability from cores taken in the same lake due to the clustered sedimentation of debris (Yang et al. 2002a). Scarcely vegetated catchments are more adequate for studying the chronological sequence of trace metal atmospheric deposition using lake sediments; whereas catchments with thick soils may be more interesting for studying the release of legacy contamination.

A forest has a filter effect on contaminants deposition (e.g., PCB deposition; Nizzetto et al. 2006). On one hand, a forest increases the scavenging of particles and associated contaminants (Davis et al. 2006), due to the large deposition surface that trees offer when air masses circulate through them. In deciduous forests, the filtering capacity may decrease after the autumnal leaf fall (Jaward et al. 2005) and the leaf litter becomes a vector of contaminants to soils, streams and lakes. On the other hand, tree leaves retain volatile contaminants from the gas phase depending on the air temperature. The temperature dependence implies seasonal fluctuations as observed for PCBs (Nizzetto et al. 2008). However, the contaminant concentrations in leaves may (Grimalt and van Drooge 2006) or may not be in equilibrium with average air temperature (Davidson et al. 2003), depending on the patterns of temperature fluctuations.

Confounding Processes

The catchment may be a legacy source for some contaminants, but also may release contaminants from natural sources. This is especially the case for trace metals. The need to always consider the natural sources related to rock weathering has already been mentioned. Alternative historical archives (e.g., ombrotrophic peats) in some cases may track aerial contamination more reliably than lake sediments (Koinig et al. 2003; Outridge et al. 2011). However, in the case where the main interest is in investigating the biological impacts of contaminants in the lakes, one has to consider that organisms do not bother whether trace metals are originating far away or in the same catchment, but it is the level of concentrations in the media that matters. Lakes in catchments with bedrocks rich in metals can achieve naturally high metal concentrations, which will likely fluctuate with climate change. This is the case for high As levels in the lake sediments of the Pyrenees (Camarero et al. 2009), for instance. Rock glacier enrichment in trace metals (i.e., Zn) can cause massive release during climate warming phases in metamorphic bedrocks (Thies et al. 2007), yet not related to atmospheric contamination (Ilyashuk et al. 2014). There can also be natural sources of PAHs. Coniferous forests are relevant sources in mountains, yet there is no confounding effect with pyrolytic PAHs. In Lake Stein (Swiss Alps), high levels of black carbon and PAHs have been attributed to the geological presence of graphite in its catchment area (Bogdal et al. 2011); this may be a quite exceptional case, but warns about the need to locally critically consider any apparent atmospheric contamination.

Air-Water Exchange

Direct exchange between air and lake water may occur in three ways: exchange with the gas phase for volatile compounds; dry deposition of particles; and scavenging by rain or snow. Rain and snow are particularly efficient in effecting the flux towards the lake. Direct air-water exchange has been less studied. Volatile compounds that arrive in the gas phase are exchanged with lake water according to their solubility. Temperature and wind control the kinetics of the process, and the exchange can go both ways, depending on conditions. The relevance of air-water exchange may depend on water residence time. In lakes with short renewal time, water flow will be more relevant (Wilkinson et al. 2005); whereas in deep lakes, with water residence time of several years, air-water exchange may be relevant (Meijer et al. 2006). Patterns that may reflect the temperature control of air-water exchange of volatile compounds in gas phase are: decreasing concentrations with depth of endosulfan, HCB, low molecular weight PCBs and PAHs found in deep lakes (Fernandez et al. 2005), and higher concentrations of PAHs in the dissolved phase of the water column below 6–7 °C in European mountain lakes (Vilanova et al. 2001b), whereas PAHs in particles did not show any temperature relationship. It is usually assumed that there is no exchange during the period in which the lakes are covered with ice and snow.

Water Column-Sediment Exchange

The OHCs distributions in the atmospheric deposition of the three remote sites geographically distant (Redòn, Pyrenees; Gossenköllesee, Austrian Alps; Øvre Neådalsvatn, Norway) were rather uniform and highly enriched in compounds with volatilities larger than 0.0032 Pa. However, more than 90 % of these compounds were not retained in the sediments (Carrera et al. 2002). This is an indication of the profound implications of in-lake processes for understanding OHCs distribution in lake sediments; particularly of the water-particle and water-sediment exchanges, which may determine a selective trapping of the less volatile compounds in the sediments (Meijer et al. 2006).

Both trace metals and organic contaminants are highly insoluble in water. Partition between water and particles are highly biased towards the latter, although differences among distinct compounds are enormous. Particles in suspension in mountain lakes are mainly organic (i.e., plankton); therefore, hydrophobic substances, such as organic pollutants, tend to adsorb to them, and the sinking of these particles will largely control the transport towards sediments (Meijer et al. 2006). In the sediments, the particulate fraction is in contact with porewater. If the solid fraction becomes enriched beyond equilibrium, there is a release of the compound to porewater and, eventually, it diffuses back to the water column. Among OHCs, more volatile compounds achieve equilibrium faster than semi-volatile compounds. In fact, semi-volatile compounds get buried before approaching equilibrium concentrations. Therefore, the latter may appear enriched in the sediment record with respect to deposition. During periods of complete water column overturn, particles may be resuspended from the sediments to the water column and—depending on the relevance of the water flow through the lake at this moment- contaminants can be exported downstream with the particulate matter. Phytoplankton growth and distribution and mixing patterns are extremely seasonal (Catalan et al. 2002); therefore, the pathways of exchange between the water column and the sediment are difficult to be accurately measured. Modelling has indicated that the plankton scavenging to the sediments can be a key factor for understanding selective trapping of some contaminants (Meijer et al. 2006). Unfortunately, accurate field studies of the water-column dynamics are lacking. Some data do not indicate the elevated seasonal variability in OHCs concentrations suggested by the models (Vilanova et al. 2001a; Vilanova et al. 2001b), but the information is too limited for being conclusive.

Active and Fossil Sediments

At certain depth, buried sediments achieve a state of nearly no significant changes in their composition; strictly, this ‘fossilized signature’ is what the sediment archive is about. In fact, there are substances that, from deposition at the top of the sediments to the final buried state, do not suffer any change, but others may experience transformations and/or relocation. The effective ‘fossilization’ takes from years to decades, depending on the sedimentation rates, which is not a problem for studies interested in long-term dynamics (e.g., over the Holocene) but may interfere with the interpretation of recent changes. Some deposited substances in the top sediment may diffuse back to the water column, may be resuspended with particles, may react with other substances, or may be biologically transformed or turbated. The occurrence of each of these potential changes depends on both the properties of the substance and the environmental conditions in the sediments.

Chemodynamics of trace metal in sediments is complex. The seasonal variation differs among trace metals (Anshumali et al. 2009). For instance, Fe and Mn are highly affected by redox changes, but Pb, Zn, Cr, Ni are less affected (Steiner et al. 2000). Cd adsorption by the sediments is pH dependent (Fu and Allen 1992) and thus sensitive to acidification (Borg et al. 1989; Yang et al. 2002a). Nevertheless, the relevance of this complexity appears be secondary compared to the contamination levels generally achieved. The prevalence of the contamination loading upon differential trace metal behaviors is shown by the higher correlation among trace metals concentrations in the most contaminated layers of the lake sediments with respect to their correlation in layers of natural background trace metal concentrations (Camarero et al. 2009). The atmospheric deposition of trace metals from contamination sources is usually rich in several metals and, consequently, increases the trace metal similarity among the sediments of the lakes affected. If contamination is very high, this effect may compensate for local differences in rock composition.

Diagenesis of PAHs in the sediments is still poorly studied, and this includes compounds clearly related to diagenetic processes, such as perylene. Some suggestions of differential preservation have been made based on comparisons between sediment layers. For instance, pyrene, benz[a]anthracene and benzo[ghi]perylene decline in deeper layers compared to their isomeric pairs, chrysene, fluoranthene, and indeno[1,2,3,-c, d]pyrene, respectively (Van Drooge et al. 2011). The latter are usually among the most abundant pyrolytic PAHs in the sediments; therefore, in terms of the reliability of the pollution record, this differential diagenesis is barely relevant.

Sediments usually become anoxic after a few millimeters in the sedimentary profile, even in unproductive lakes. Anaerobic dechlorination of some OHCs may occur (Grimalt et al. 2004c). Recent results indicate that PBDEs profiles can be particularly modified by anaerobic debromination (Bartrons et al. 2011). Higher abundance of anaerobic sites in more productive lakes can increase the proportion of less brominated compounds, with respect the initial deposited mixture. Therefore, the proportion of more brominated compounds at high altitude increases since lake productivity and organic matter content declines with altitude.

Generally, mountain lakes are oligotrophic and, as a consequence, water transparency is high and algal growth can take place along a large part of the bottom, from littoral to deep parts (Buchaca and Catalan 2007). As a consequence, most of the lake is covered with an active biofilm, within which strong gradients can develop in a few millimeters. Recently, it has been shown that even in relatively thin rock biofilms there is evidence of anaerobic microbial activity (Bartrons et al. 2012a). This is in agreement with the changes in PBDE composition from the purely autotrophic biofilms, such as colonies of the cyanobacterium *Nostoc*, common in mountain lakes, which contain OHCs profiles similar to precipitation, to the littoral and deep sediments that show increasing proportion of debrominated compounds (Bartrons et al. 2011). The understanding of OHCs biodegradation in sediments is poor and generally assumed irrelevant. This recent study indicates that, at least for some compounds, it cannot be ignored; otherwise, it will compromise the interpretation of selective accumulation and source attribution of PBDEs, for instance.

Modeling

Air mass trajectories can be traced back confidently at present (Draxler and Hess 1998). This is useful for determining the source areas of some deposition or air transport events (Killin et al. 2004) but, for sediment archives, they have to be applied in statistical terms. It is possible to investigate average back-trajectories for a site, how trajectories change seasonally, and what kind of sources are likely associated with certain trajectories. Weekly air measurements in a remote mountain site in south-western China indicated that HCHs and DDTs were brought preferentially by air masses from northern India, whereas high levels of γ-HCH and trans-chlordane were associated to air masses from southern China and the north of south-eastern Asian countries (Xu et al. 2011). In fact, current computational power can provide increased insights in source apportionment. Monte Carlo techniques allow for exploring the probability space more realistically and increase the characterization of the uncertainty associated with source apportionment (Sheesley et al. 2011).

Beyond the investigation of the routes of atmospheric transport to the mountain sites, modelling can help in the interpretation of the sediment patterns of contaminants. Ideally, a model mechanistically linking from sediments back to deposition would be the target. However, currently, this appears unrealistic as the complexity is overwhelming and uncertainties are too high. Even a comprehensive model from sources to sink appears extremely challenging. However, models targeting specific key steps of the contaminants pathway are quite informative and improve the interpretation of the patterns found. The transport and accumulation of non-volatile compounds (e.g., trace metals) in lake sediments can be modelled on the basis of a conceptual model of the catchment/lake system of a simplified number of compartments and input and output fluxes (Bacardit and Camarero 2010c). This can provide insight into the current influence of the catchment in the total sediment loads compared to atmospheric inputs. Even this simple model requires a significant effort in atmospheric field measurements, which is rarely achievable in many sites.

Trace metal, PAHs and OHCs include substances with a wide range of physicochemical characteristics. The parameters that define these properties are sufficiently known to allow exploring how the dynamics differ across the pathway to the sediment archive. Rather than trying to reproduce the whole process, it is useful to conduct numerical experiments to understand the sensitivity of the final archive to the different parts involved (Bogdal et al. 2010b). The initial step is the air transport and scavenging from the atmosphere (Breivik et al. 2006). Mountains provide a stimulating research area for modelers because of the altitudinal and the seasonal changes in air temperature and precipitation. For OHCs, differential accumulation of compounds with altitude and season appear as a result of their chemical properties (Wania and Westgate 2008). At this point, the key issue becomes understanding precipitation patterns across sites, and whether the rest of the pathway to the sediments is critical to distort or preserve the patterns generated with the precipitation scavenging.

The specific compartments in the lake catchments are each of interest because they serve as an aid in tracking long-range contamination. There are examples of modelling for PCB gas-phase changes between air and snowpack (Hansen et al. 2006), PAH air-soil exchange (Wang et al. 2011), PBDE and PAH uptake by vegetation (St-Amand et al. 2007, 2009), among others. Because of the interest of these compartments, the missing issue is their connection with the lake and eventually the sediment record. In that respect, evaluating the relevant constraints on how much of the contaminants in the snowpack might end up buried in the sediments is a challenge. Multimedia mass balance models have been developed to simulate whole-catchment processes. For the Lake Oberaar catchment, Bogdal et al. (2010a) combined a lake model, with a model of emissions at low land and advective transport to the lake catchment, and a model on the residence time of contaminants in the Oberaar Glacier after the surface deposition. They investigated the current release of legacy OHCs from the glacier and projections under climate change.

PCBs are excellent candidates for OHCs general biogeochemical analysis. The large number of congeners offers a range of physicochemical properties, and the lack of current use prevents from trying to reproduce patterns too locally conditioned. PCB transport in the water column has been modelled for Lake Redòn (Pyrenees) conditions (Meijer et al. 2006). The model assumes that only direct exchange with the atmosphere is relevant, the catchment component is ignored. The simulation clearly shows a selective transport of the less volatile congeners towards the sediment. Also, it shows that there is a re-emission of the more volatile compounds towards the water column, as they achieve equilibrium, which is not the case for less volatile ones, for which the system still has a large uptake capacity. However, the model predicts a highly seasonal and spatially variable distribution of PCBs in the water column that does not correspond with the limited existing observations (Vilanova et al. 2001a). It is an example on how modelling and observation are complementary and foster each other. PBDE and PCB modelling for Lake Thun (Switzerland) also indicated high sensitivity of the whole lake balance on the water-particle partition in the water column (Bogdal et al. 2010b).

There are still many opportunities for investigation using numerical experiments by dynamic modelling. Techniques may involve combinations of statistical, chemical and mechanistic modelling (Boyle and Birks 1999). For global assessments, including a contaminant module in climatic models is important for obtaining long-term projections (e.g., CliMochem; Wegmann et al. 2006), although initial results have challenged observations. Up-scaling may be the only possible way to make assessments over large mountain ranges (Andes, Himalayas, Rocky Mountains, Alps), when the interest is in the mountain themselves as, for instance, for conservation issues (e.g. national parks). Even partial models require a lot of parameters, initial data and certain capacity of validation. There is no substitute for real data, but with the lack of data or with partial information, model sensitivity analysis may provide insights into which can be the relevant processes.

The Mountain Altitudinal Gradients and Contaminants

The first principles behind the dynamics driving contaminant patterns are essentially the same everywhere. However, there is an environmental feature intrinsic to mountains, the altitudinal change in physical conditions, which justifies the specific interest for mountain studies (Fig. 8). The distribution of organic contaminants is frequently investigated with respect to altitudinal patterns. There are features of physical change in the mountains that occur globally, but other features vary according the latitude or the morphological characteristics of the range (Körner 2007). The ‘universal’ mountain gradient includes the decline with altitude of temperature (average lapse rate 5.5 °C km^{-1}), atmospheric pressure (ca. 11 % km^{-1}) and available land area, and the increase of radiation, the proportion of UV-B ((λ 290–320 nm), and the size of the airshed to which sites are exposed. The patterns of altitudinal change of precipitation are not the same throughout the planet, and neither the seasonality of this precipitation (e.g., winter, and summer precipitation in the western, and eastern Andean slopes, respectively). Finally, the length of the growing season above tree line changes with latitude.

Altitudinal gradients of contaminants have been found measuring different matrices in addition to sediments: air passive samplers (Pozo et al. 2009; Loewen et al.

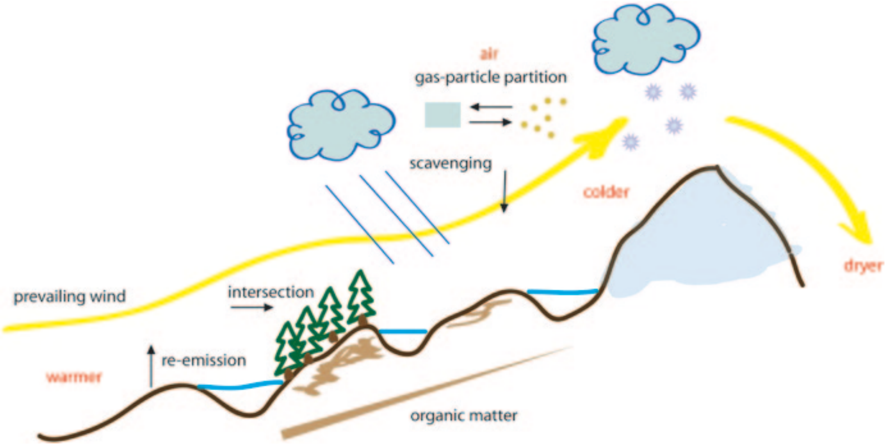

Fig. 8 The altitudinal gradient in mountains includes changes in the physical factors that drive a selective accumulation of contaminants at different elevations

2008; Estellano et al. 2008; Meire et al. 2012a; Meire et al. 2012b; Liu et al. 2010; Li et al. 2006; Shunthirasingham et al. 2011); mosses and lichen (Liu et al. 2005; Grimalt et al. 2004a; Daly et al. 2007c); soils (Chen et al. 2008; Daly et al. 2007c); plant leaves (Wang et al. 2006; Davidson et al. 2003); snowpack (Arellano et al. 2011; Blais et al. 1998); fish (Vives et al. 2004; Blais et al. 2006; Gallego et al. 2007; Yang et al. 2010c; Vives et al. 2005b; Demers et al. 2007); and other aquatic organisms (Blais et al. 2003; Blais et al. 2006). However, there is not necessarily a unique mechanism behind altitudinal gradients of contaminants. The environmental altitudinal gradient in mountains is multivariate as described at the beginning of this section. The physical drivers may generate altitudinal gradients of contaminants by mechanisms such as differential air (or water) compound oxidation, differential compound solubilisation, differential particle loading (i.e., rain scavenging) and combinations thereof. In addition, the changes in physical conditions imply changes in the nature of the land cover (e.g., forest, meadows, bedrock, wetlands, etc.) and biological activity in general, which adds more opportunities for selective trappings across altitudes (e.g. organic matter in soils, forest filtering, etc.).

Complementary to new studies for investigating proposed hypotheses, the repeated observation of similar patterns throughout large geographical areas (or even worldwide) may help in discerning the most likely mechanisms. For instance, in the Bolivian Andes, air samples indicated increasing gas phase concentration of HCHs and endosulfans across an altitudinal gradient from 1820 to 5200 m a.s.l. The differences were attributed to different airsheds (Estellano et al. 2008): the high-altitude sites were exposed to larger airsheds susceptible to long-range transport from more distant (contaminating) regions. A similar altitudinal gradient for endosulfan has been found in Chile; in this case both long-range transport and cold trapping have been suggested as the key factors (Shunthirasingham et al. 2011). Recently, Meire et al. (2012b) found the same increasing pattern of endosulfan with altitude in the

Brazilian tropical and subtropical mountains. Endosulfan was also found as a dominant organochlorine pesticide in the air of Mt. Everest region (4400–5000 m a.s.l) (Li et al. 2006). Such general and consistent patterns point towards a cold-trapping mechanism for endosulfans. Interestingly, PCBs did not show an increase with altitude in the Mt. Everest study, as the values were in a similar range (<12 pg m $^{-3}$) as measurements made in the mountain air of Chile (Pozo et al. 2004). In the case of lake sediments, there is a scarcity of repeated studies in nearby or complementary areas concerning organic contaminants yet, with some exceptions (Landers et al. 2010).

At first, processes driven by temperature are likely to provide more 'universal' altitudinal patterns than those driven by precipitation or any other physical factor that do not change so regularly across the mountain altitudinal gradient. For volatile and semi-volatile compounds, temperature appears to be key factor to consider. Rather than only plotting contaminant levels against altitude, it is worthwhile to plot the log transformed concentrations against the reciprocal of the average air absolute temperature at the corresponding sites and calculate the pseudo-enthalpies (Grimalt et al. 2001; Davidson et al. 2003). The comparison with theoretical enthalpies (e.g., vaporization and solubilisation) may inform whether the process is mainly temperature driven. This is the case, for instance, of the altitudinal gradient shown by some PCBs in lake sediments (Grimalt et al. 2001) and pine needles (Grimalt and van Drooge 2006; Davidson et al. 2003). On the contrary, the lack of minimum agreement between the observed and expected enthalpies may indicate that there is another relevant process behind those considered. For instance, PBDEs showed 3- to 4-fold higher pseudo-enthalpies than expected in the sediments of the lakes of the Pyrenees. The increased availability of anaerobic microsites at lower altitudes was suggested as a mechanism increasing degradation (Bartrons et al. 2011). Differential loss by degradation also has been suggested for soil altitudinal gradients (Daly et al. 2007b).

The altitudinal pattern does not have to be monotonic. Studies of PCBs and PBDEs in soils of Mt Qomolangma in the Tibetan Plateau from 3689 to 6378 m showed negative relationships with altitude below ca. 4500 m and positive dependence above (Wang et al. 2009). Below 4500 m, the distance to source may be the driver. Above 4500 m, physical gradients may dominate. Concentrations of heavier congeners (lower subcooled liquid vapor pressure) increased more with altitude than more volatile congeners, although the latter still were the main contributors to the total. This is consistent with what was found in Western Sichuan (China) by Chen et al. (2008) and the simulations of Wania and Westgate (2008), but opposite from the observation of OHCs in snow of mountains in the western Canada (Blais et al. 1998). Although the temperature gradient is more or less the same throughout, the compounds showing selective trapping may be different because absolute temperatures also matter. Those that are not selectively accumulated at certain temperatures may be affected at lower temperatures. This may explain discrepancies in the compounds selective trapped among snowpacks located at latitudes with different absolute temperature.

The role of wet deposition has been emphasized by some authors (Wania and Westgate 2008), due to its efficiency in scavenging contaminants from the atmosphere. The lower the air temperature, the higher is the partitioning towards the condensed phase. Hence, wet deposition scavenging is more efficient at high altitudes and in winter time, and for compounds less volatile and more hydrophobic. Consequently, relative mountain contamination could be predicted from the respective water-air (K_{wa}) and octanol-air (K_{oa}) partition coefficients of the compounds and precipitation amount. This appears as a reliable mechanism for soils, and the patterns found provide observational support (Chen et al., 2008). Large spatial variability within the same altitude in a geographical area may be related to the soils heterogeneity (e.g. organic content conditioning re-emission properties) but also to the spatial and temporal heterogeneity of wet deposition. In contrast, lake sediments show less variability than soils. This fact points to the question of whether the driving mechanism of selective trapping is the same between sediments and soils. Meijer et al. (2006) have shown that selective trapping can be explained without any connection to catchment processes. Again, differences in the K_{wa} and K_{oa} of the compounds are the key parameters determining the selective trapping. Consequently, it is very difficult to determine whether catchment or in-lake processes can be distinguishable from the statistical analysis of organic contaminants in the sediment patterns. Specific studies in the water column and deposition are required.

Biological Impact and Ecological Risk Assessments

The assessment of the potential impact of air-born contaminants on lakes, mountain ecosystems in general, or on some organisms in particular, can be a complementary goal to studying the LRAT and accumulation of contaminants. This is still an incipient field and different approaches have been tried.

A simple way to tentatively estimate the toxicity of sediments is the use of toxic equivalent factors (TEF) that relate the toxicity of the compound to that of some reference substance. Rather than actual toxicological assessments, TEF are a way to undertake normalized comparisons of the potential toxicity amongst sites. The method consists in weighting the concentration by some toxic equivalency for each compound and adding all the values to obtain an overall degree of toxicity for the sediment sample (e.g. PAH toxicity; Quiroz et al. 2010). A simpler version is to check the contaminant levels respect to some numerical sediment quality guidelines (SQGs) provided by different national or international institutions (MacDonald et al. 2000a). The aim of these guidelines is to rank areas that warrant study on the occurrence of adverse effects. They are useful for comparing the degree of contamination among sub-regions, and to identify which chemicals are elevated in concentration (Han et al. 2011). In general, organisms in high mountain lakes are naturally submitted to harsh conditions (e.g., high radiation, low temperatures, diluted waters, high metal concentration in the sediments). As a consequence, their toxicological response is likely to be different from organisms in low lands. Local adaptation of organisms to some natural stressor tends to also increase resistance to pollutants that may affect similar physiological processes. For instance, frogs show genotoxic co-tolerance to UV and PAH stress, according to the natural exposure to the former (Marquis et al. 2009); those at higher altitude are more resistant to both UV-B and PAH pollution.

Correlation is the simplest way of exploring potential contaminant impacts. Unambiguous statistical associations between pollutants and organism community composition are rare [e.g., diatoms, Moser et al. (2010); chironomids, Brooks et al. (2005)]. When contaminants are combined with another ecosystem stressor (e.g., acid-base conditions, eutrophication), then correlations are more likely to be found, such as trace metals and acidification (diatom changes) or trace metals and oligotrophication (chironomids; Il'yashuk and Il'yashuk 2000), yet the direct toxicity of the contaminants cannot be proven. More informative is the comparison of physiological biomarkers with contaminant levels in the sediments; for instance, Cyp1A gene expression in fish correlated with HCB and 4,4′-DDE levels in the sediments of European mountain lakes (Quiros et al. 2007), which were later confirmed in fish muscle tissue (Jarque et al. 2010). Cytochrome P450 1A (Cyp1A) is an established biomarker for xenobiotics, particularly for the so-called dioxin-like compounds including some PAHs (e.g., benz[a]pyrene) and coplanar PCB congeners. Sometimes contaminants in the sediments are used in 'forensic approaches'. Cascade frog declines in the Mount Lassen area (California) and its potential connection to organic contaminants were investigated measuring 73 semi-volatile contaminants including pesticides, polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs) in sediments and frog tadpole tissue at 31 sites where Cascades frogs had disappeared or are still present across the Lassen and Klamath regions (Davidson et al. 2012). This approach is more useful for rejecting possible causes than confirming them, as it was the case for Cascades frogs, where no connection was found with the contaminants that were measured.

The distribution of contaminants in the lake's food web is generally closer to atmospheric deposition than to concentrations in the sediments. For instance, in Lake Redòn (Pyrenees), phenanthrene is the dominant PAH in both aerial deposition and food web organisms (Vives et al. 2005a), whereas it ranks 7th in the sediments (Fernandez et al. 1999). If the aim is not to investigate a time series, but carry out an assessment of contaminants throughout a large number of lakes in a region, littoral biofilms may more closely reflect the current characteristic of atmospheric deposition than deep sediments (e.g., PBDEs; Bartrons et al. 2011), and sampling is much easier. Fish are the most common organism sampled for contaminant assessment in mountain lakes (Blais et al. 2006), although they are often alien species to mountain lakes (Miró and Ventura 2013), as most mountain lakes were originally fishless due to their steep outlets, produced by glacial erosion, that fish cannot swim upwards or the lack of outlet in seepage and many volcanic lakes. Contaminants in fish may follow similar altitudinal patterns as in sediments (Grimalt et al. 2001), as they integrate food items from different lake habitats (Catalan et al. 2004). This is not the case for any other kind of organism. For instance, PAHs are higher in the organisms inhabiting the littoral habitat than the deep-sediment and the pelagic habitats, although deep living organisms are enriched in those PAHs with higher molecular weight (Vives et al. 2005a). Besides habitat effects, different contaminant composition among organisms also indicate a large variability in the capacity of metabolic degradation, which for PBDEs have been related to the evolutionary trophic history of the studied organisms (Bartrons et al. 2012b).

Bioassays are a direct assessment of toxicity for a specific organism, including humans. Whole sediment and sediment elutriate toxicity tests with fish, amphipods and cladocerans have been used in studies of pollution by acid-mine drainage (Finlayson et al. 2000). Molecular techniques allow for direct evaluation of estrogenic activity using recombinant yeast (Fig. 9), based on a human estrogen receptor, which allow for processing of a large number of sediment samples (Garcia-Reyero et al. 2005) or fish muscle extracts (Garcia-Reyero et al. 2007). If pollutants are measured in the same samples, then the compounds responsible for the potential human endocrine disruption can likely be identified.

Beyond physiological effects on specific organisms, which may be non-native to the system (e.g. stocked fish), there is a need to increase the understanding on how contaminants may modify biogeochemical cycles, particularly, the microbial driven pathways. With increasing molecular facilities, there is a large potential in this field awaiting exploration (Xie et al. 2011; Sanchez-Andrea et al. 2011).

Looking Forward: Research Perspectives in a Changing World

Developing an understanding of long-range transport of contaminants in the current framework of climatic change will demand the merging of various approaches including monitoring, experimentation, palaeolimnology, and modelling, and will require effective international collaboration. It has become apparent that the recovery of lakes from acidification is closely linked with the responses to, and interactions with, other large-scale components of global change (Keller 2009). This has to also be the case for contaminants, such as those considered in this chapter. Mountain lakes provide sites for monitoring and surveillance, but also case studies for understanding mechanisms. In fact, lakes are not absolutely necessary for establishing a network for monitoring atmospheric contaminants at remote sites. Nevertheless, they can provide a unique historical perspective and provide integration of whole catchment processes. With this aim, palaeolimnological studies should merge with the studies of biogeochemical cycling (Bindler et al. 2008) and the fate of organic contaminants in nature (Nizzetto et al. 2010).

Trace metal signatures of air contamination are well recorded in mountain lakes with airsheds influenced by mining activities. The use of mined materials has been increasing at a faster pace than world population. So far, there is no evidence that the growth of global materials use is slowing down (Krausmann et al. 2009). Therefore, although ores have been exhausted in some parts of the world, mining and smelting will continue in others (e.g., Sub-Andean Amazon, Peru; Lindell et al. 2010). The

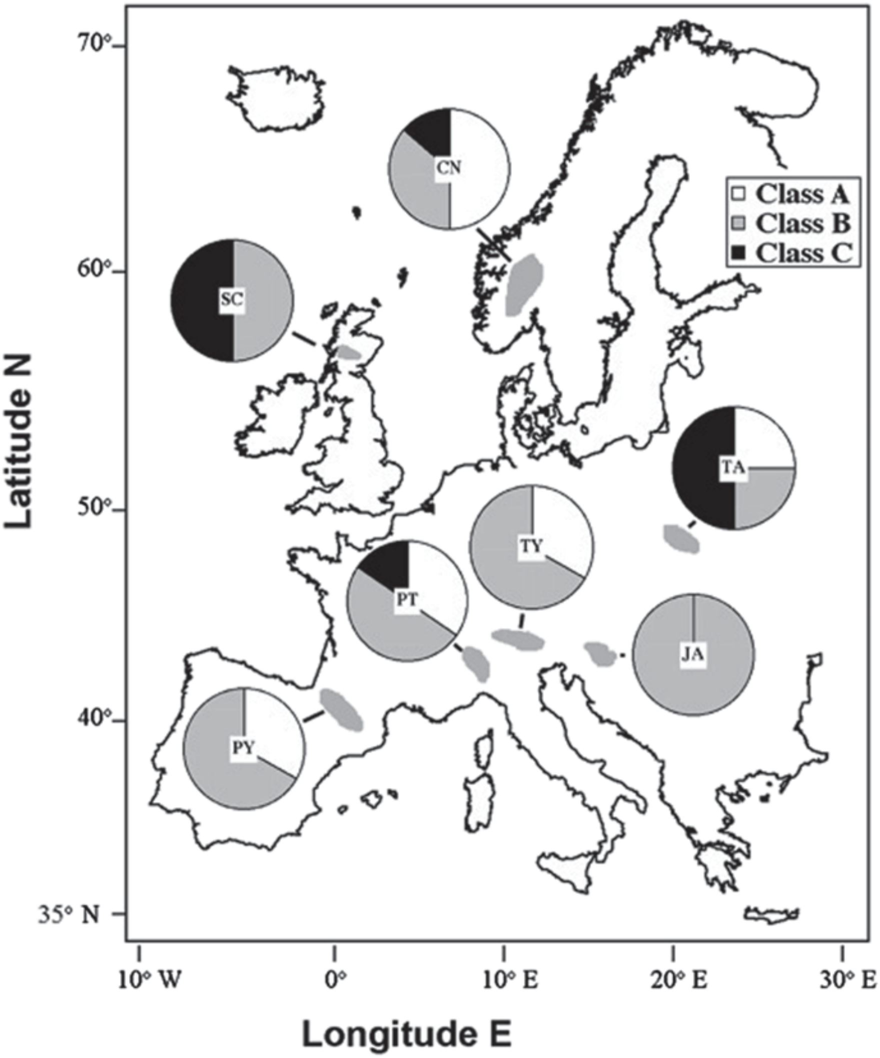

Fig. 9 Evaluation of the endocrine-disrupting potential of lake sediments in 83 mountain lakes across Europe. A recombinant yeast assay (RYA) was used that harbors a human estrogen receptor to which estrogenic endocrine-disrupting compounds binds. The results were classified into three estrogenicity classes (A, non-estrogenic; B, low estrogenicity; and C, high estrogenicity). The proportion of lakes belonging to each category is indicated in the plot for the mountain ranges studied. Reprinted with permission from Garcia-Reyero et al. (2005). Copyright 2005 American Chemical Society

last chapters of the environmental history of mining have not yet been written. The level of mercury (Hg) species in ambient air and precipitation will be of interest in the years to come. Mercury in the atmosphere is largely (~ 95 %) elemental mercury [Hg(0)]. It is a gaseous and relatively insoluble form, which is subject to long-range transport, with a global average residence time for Hg(0) generally considered to be 6 months to 2 years (Schroeder and Munthe 1998). Following the discovery of atmospheric Hg depletion events in polar regions, a significant research effort was made to assess the physicochemical mechanisms behind the rapid conversion of atmospheric gaseous Hg(0) into reactive and water-soluble forms which are potentially bioavailable. The large increase in Hg emissions in rapidly developing countries (i.e., China, India) over the last decade, due primarily to energy production from coal combustion, are not currently reflected in the long-term measurements of total gaseous mercury in ambient air and precipitation at continuous monitoring sites in either Northern Europe or North America. The discrepancy between observed gaseous Hg concentrations (steady or decreasing) and global Hg emission inventories (increasing) has not yet been explained, though the potential oxidation of the atmosphere during the last decade is increasing (Sprovieri et al. 2010). Understanding of the atmospheric Hg fate is a main topic, particularly because projections indicate that Hg emissions will increase in the future, with maximum estimates of a doubling for 2050 respect current values. In addition, the relative emissions of divalent Hg will increase, implying a shift from long-range transport of elemental Hg to local deposition of Hg compounds (Streets et al. 2009). Mountain lake observations may complement latitudinal studies (e.g. Arctic; Muir et al. 2009) to investigate how the issue evolves.

PAHs are extensively used for tracking combustion contamination, yet their actual indicator value still has not been fully exploited. Used with other materials related to combustions, such as SCPs, black carbon, micro and macro charcoal rests and other organic compounds, they can provide an indication on how distinct types of combustion changed trough time (Muri et al. 2006), including the potential for assessing forest fire dynamics in the past.

Among the highest uncertainties regarding advancing global change as a multi-component phenomenon is the question of what will happen with the increasing cocktail of synthetic substances released to the environment that have the potential for interfering with biochemical pathways, many of which are essential to life. OHCs play a primary role in this question. There is a global toxicological puzzle that no one can yet evaluate, neither the magnitude nor the consequences (Rockstrom et al. 2009b). The establishment of the Global Atmospheric Passive Sampling (GAPS) network (Pozo et al. 2009), which mainly focuses on remote sites, will provide global baseline values, and will foster the development and validation of global transport models. Mountain lake sediments can complement the observations with a window to the past. In addition, there is a need to track long range contamination patterns and, simultaneously, toxicological susceptibility from organisms to ecosystems. Remote sites, such as high mountain lakes, provide a less complex setting to evaluate potential interference of synthetic substances with nature, which is now a challenging task under the generalized climatic and environmental changes (Noyes et al. 2009).

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Using Peat Records as Natural Archives of Past Atmospheric Metal Deposition

Sophia V. Hansson, Richard Bindler and François De Vleeschouwer

Abstract Over the last decades, scientists throughout Europe and beyond have been increasingly using peat as archives of past atmospheric metal deposition. Since the pioneering studies using herbaria moss collections to evidence atmospheric metal pollution in the late sixties, the improvements in analytical techniques, as well as chronological controls, have allowed investigations of a variety of scientific questions in various fields, e.g. elemental biogeochemical cycles, atmospheric pollution and archaeology. In this chapter we summarize the various applications and usage of peat cores as archives of past atmospheric metal deposition. The chapter contains an introduction followed by a section addressing the state of the art in the field, providing examples of various elements and a variety of study sites. We then continue with a brief description of the application of metal records stored in peat, i.e. applications to archaeology. To end we present some confounding factors affecting the integrity of the peat record, which must be carefully considered, and lastly we give a few examples of challenges and perspectives for future generations of peat geochemists.

Keywords Peat · Geochemistry · Metals · Lead · Chronologies

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Introduction

Since the late nineteenth century the environmental archive formed by the accumulation of organic matter preserved in peatlands has been of interest to scientists aiming to reconstruct long-term environmental changes (Sernander 1892; Weber 1899). Originally, the focus was on changes in the peat-forming plant macrofossils and the development of the bogs through time (von Post 1913; Granlund 1932; Almquist-Jacobson and Foster 1995), on using pollen as a proxy to reconstruct past changes in climate and also land use (Granlund 1931), and of particular importance today, a focus on peatlands and carbon storage (Gorham 1991; Belyea and Malmer 2004). But since the 1970s interest expanded to include the geochemical record and the information it can provide on past environmental changes (Lee and Tallis 1973; Aaby and Jacobsen 1978). The first metal pollution records from peat were interpreted largely in terms of local histories, such as Roman smelting and local pollution in the UK in proximity to Derbyshire (Lee and Tallis 1973) and in the Gordano Valley near Bristol (Martin et al. 1979). Although these studies focused more on local events, they paved the way for a wider exploration of the geochemical record in peat to study past atmospheric deposition trends not only in relation to local events but also in relation to regional and potentially even global events and scales.

Peatlands are ecosystems that are formed by the net accumulation of fossil plant material. They are widely spread around the world and represent 3 % of the continental area (Gore 1983; Charman 2002). Most of the peatlands around the world developed after the last glaciation, although some older deposits occur in other areas, such as the 700 kyr record of Philippi, Greece (Wijmstra and Groenhart 1983), the 52 kyr record from Lynch's Crater, Australia (Kylander et al. 2007), the 22 kyr record from Kalimantan, Borneo (Weiss et al. 2002) and the 16 kyr record of Harberton, Argentina (Rabassa et al. 2006). Peatlands have three main characteristics: (1) the presence of water at or near the surface; (2) low oxygen contents below the water table leading to anoxic conditions; and (3) specific vegetation adapted to this environment (Charman 2002, and references therein). The main factor needed to form peat is a positive water balance and the presence of plant remains. The slow decay of vegetation in waterlogged and anoxic conditions leads to a gradual accumulation of peat and to acidic conditions, with a pH generally in the range of 3–6.

Peatlands can be simplistically divided into two main categories regarding their genesis, vegetation and hydrological functioning: ombrotrophic and minerotrophic, which are broadly referred to as bogs and fens, respectively. Of course there is a continuum between these two categories, where different classification systems are used within these categories in different countries (Tarnocai and Stolbovoy 2006). Ombrotrophic bogs are by definition supplied with their nutrients, and thus also pollutants (metals as well as organic pollutants), only by atmospheric deposition (i.e., aerosols, rain, snow, fog) and are essentially isolated from lateral groundwater inputs from surrounding mineral soils. In the Northern Hemisphere, their vegetation is dominated by *Sphagnum* spp. together with other bryophytes, as well as *Carex* spp. and *Eriophorum* spp. In contrast, minerotrophic peatlands receive inputs not only from the atmosphere but are to some extent also supplied by lateral groundwater influenced by the surrounding or underlying mineral soils. Besides *Sphagnum*, the surface vegetation of minerotrophic peatlands can include sedges such as *Equisetum*, *Carex* spp, *Menyanthes* spp. and *Molinia* spp., as well as other field-layer plants such as *Calluna*. Trees may also be present, in particular pine species (Charman 2002). It should be noted though that the surface vegetation listed above can occur in both ombrotrophic and minerotrophic environments and their presence is not limited to any one category. For a more detailed description on peatlands in general, i.e. abundance and characteristics, geochemical processes and the behaviour of specific elements stored in peat, we refer readers to two textbooks dealing exclusively with questions linked to peatlands; "Peatlands and Environmental Change" by Dan Charman (2002) and "Peatlands—Evolution and records of environmental and climate changes" by Martini et al. (2006).

Most research on the metal pollution records from peat cores has focused on ombrotrophic bogs because they are by definition supplied exclusively by atmospheric inputs, and thus have the potential advantage of recording more directly the atmospheric signal than other continental archives (i.e., lake sediments). In terms of atmospheric records they are similar to what is found in ice cores, but they present two main advantages: (1) they are geographically more widespread, and (2) they are much easier to access and sample. However, many minerotrophic peatlands can also serve as good records of atmospheric metal deposition (cf. Shotyk 1996; Shotyk et al. 1997; Monna et al. 2004a), but only after careful evaluation of the site, i.e. it must first be concluded that the metals of interest were supplied to the site exclusively by atmospheric sources and not through lateral groundwater flow, or that the two sources can be distinguished. This is done by performing an independent geochemical assessment of the peat profile to establish the existence and thickness of an ombrotrophic zone. In other words, the site has to show geochemical ombrotrophic features, sometimes referred to as ombrogenous, even if the peatland itself is considered minerotrophic (Shotyk 1996).

An important breakthrough that contributed to an expanded interest in exploiting the potential of peat records to monitor past pollution was the development of biomonitoring using forest mosses, particularly in Scandinavia (Rühling and Tyler 1968, 1970; Ross 1990; Steinnes et al. 1992). These programs explored and then developed the use of forest mosses (bryophytes) and lichen as tools to monitor the deposition of heavy metals. Because bryophytes and lichen lack roots, they take up metals supplied essentially via only atmospheric deposition (wet and dry deposition). Furthermore, mosses have a relatively large surface area to intercept deposition and a high availability of cation exchange sites that have a strong binding capacity for metals. Research comparing metal concentrations in forest mosses with the flux of metals in wet deposition has shown that the concentrations of most metals—such as the priority pollutant metals cadmium, lead and mercury—can be directly coupled to annual atmospheric deposition rates (Ross 1990; Berg and Steinnes 1997; Rühling and Tyler 2001; Fig. 1). On this basis, peat records, which are primarily an accumulation of organic material, have the potential to represent a quantitative accumulation record of past metal deposition.

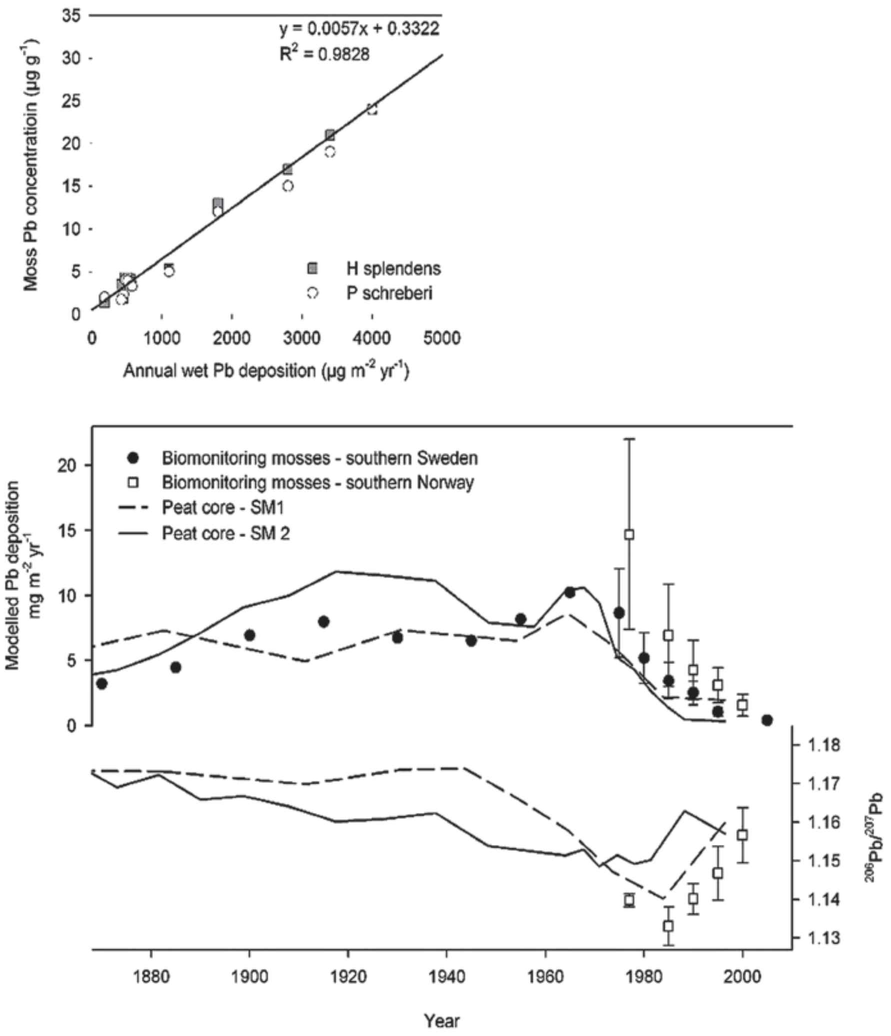


Fig. 1 *Top panel*: Concentrations of lead (µg g^{-1}) in forest mosses (filled circles: *Hylocomium spledens*; open squares: *Pleurozium schreberei*) versus the annual flux of lead in wet deposition (µg m^{-2} yr^{-1}) from biomonitoring in Norway (data from Berg and Steinnes 1997). From the regression line moss metal concentrations in biomonitoring can be used to back calculate wet deposition rates. Bottom panel: Calculated lead deposition (µg m^{-2} yr^{-1}) in southern Sweden from 1870–1960 based on herbaria mosses (filled circles) and 1975–2005 based on the forest moss biomonitoring program (*filled circles* with error bars; data from IVL.se), in southern Norway 1980–2000 based on forest moss biomonitoring (*open squares* with error bars; Steinnes et al. 2005), and two peat cores from Store Mosse, southern Sweden (*solid* and *dashed lines*; Bindler et al. 2004). The lower panel shows $^{206}Pb/^{207}Pb$ isotope ratios in the two peat cores and in the Norwegian moss samples

Research evaluating the utility of peat as a metal pollution archive has taken two main approaches, one evaluating and comparing the temporal record of specific metals between peat sites and between peat and other archives (e.g., lake sediments, glacial ice, herbaria collections and historical documents) and the other evaluating the biogeochemical cycling of metals and other elements to assess the stability or mobility of particular elements of interest. Initially, research on biogeochemical cycling was critical as to whether peat in fact preserved a record of past metal deposition or not, because the interpretation of metal profiles was greatly influenced by research aimed at the remobilization of elements in relation to plant nutrient cycling and redox process, particularly in relation to changes in the water table (Damman 1978; Urban et al. 1990; Stewart and Fergusson 1994). For example, as first stated by Goldschmidt (1937), the elevated concentrations of lead at or near the surface of peat cores was interpreted in large part as a function of plant uptake and recycling (Hvatum 1970; Damman 1978) or as a mobilization/remobilization downwards to the approximate location of the water table where hydrologic conductivity is lower, which would allow a higher proportion of metal cations to be bound to the organic matter (Damman 1978, 1986). Decomposition of organic matter and subsequent mobilization of organic colloids and dissolved organic carbon also have the potential to mobilize metals within the peat (Villaverde et al. 2009). However, as discussed below, the broad consensus from research since the 1990s is that—after careful evaluation—the accumulation records of several metals in peat cores, most notably lead, can be used to reconstruct relative and to some extent also absolute atmospheric deposition rates over the last centuries to millennia.

Linking Peat Records and Biomonitoring Data to Quantitatively Model Past Deposition

Along with establishing long-term patterns, several studies have sought to quantitatively validate the record of metal accumulation in peat against monitoring—either in the form of samples from biomonitoring programs or as archival moss samples from herbaria collections (Figs. 1 and 2). In Switzerland, Weiss et al. (1999) tackled this question by comparing the recent (ca. 150 years) lead isotopic record in peat cores from different parts of Switzerland with analyses of lead in 14 herbaria moss samples, which had been collected since the late 1860s from bogs in the Jura region. The temporal changes in the isotopic composition of this small sampling of herbaria moss fell closely within the range of values recorded in the peat cores from the same region. Furthermore, ice and snow records from Mont Blanc (Rosman et al. 2000) and Monte Rosa (Schwikowski et al. 2004) showed this same temporal pattern in isotopic signals, although the isotopic minimum indicating the maximum influence of alkyl-lead occurs somewhat earlier (1970s) in the ice/snow records than in the peat and lower resolution herbaria records (late 1980s). In general, however, the peat records, herbaria mosses and glacial ice/snow show a cohesive pattern of changes in the lead isotopic composition of deposition over the last 150 years.

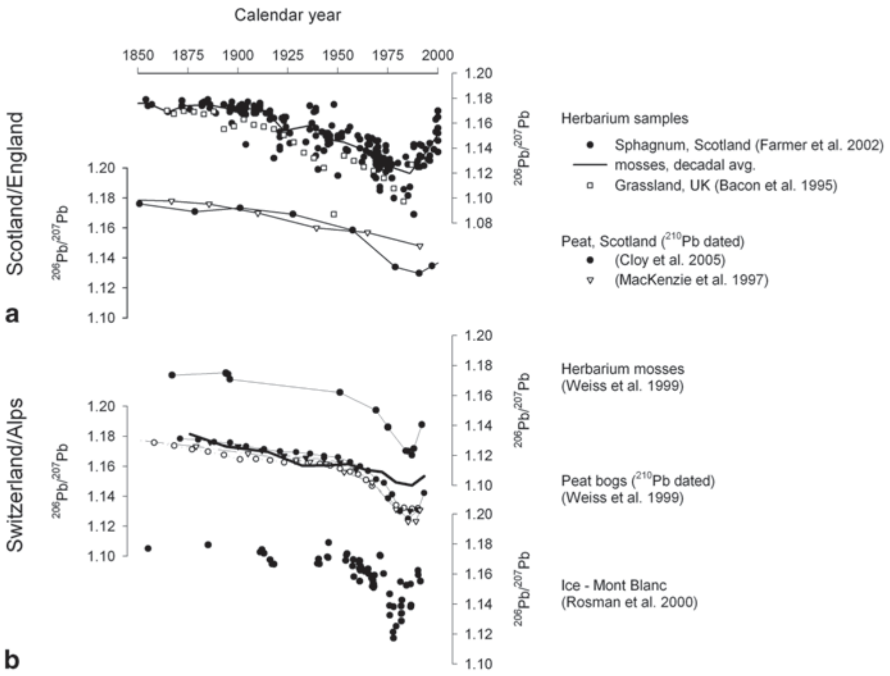


Fig. 2 Regional comparisons of ^{206}Pb/^{207}Pb isotope ratios since the mid-1800s measured in peat versus herbaria collections and ice records: **a** *Sphagnum* moss from herbaria collections in Scotland and a grassland in England (Bacon et al. 1996; Farmer et al. 2002), together with peat data from Scotland (Mackenzie et al. 1997; Cloy et al. 2005); **b** *Sphagnum* from herbaria collections in Switzerland, together with data from four peat records (Weiss et al. 1999) and the ice and snow record from Mont Blanc in the Alps. (Rosman et al. 2000)

In Scotland, Farmer et al. (2002) expanded this approach by comparing the lead isotope composition in a larger number of herbaria moss samples (188 samples) collected throughout Scotland with their earlier results from peat (Fig. 2) as well as lake-sediment records. Although the moss data showed substantial spatial variability amongst sites—between regions within Scotland, but even at individual sites on the same sampling occasion due to widespread local sources (e.g., mining and coal burning)—the general temporal pattern follows the same as that shown for both lake-sediment and peat records. The recent trend in the peat and particularly herbaria mosses from Scotland also fits with biomonitoring data for the period 1977–2000 from Norway, which receives a substantial input of long-range atmospherically transported pollution from the British Isles (Steinnes et al. 2005; data included Fig. 1). The good agreement between herbaria and biomonitoring mosses and the peat records in Switzerland and Scotland is a critical foundation supporting peat as an archive of past lead deposition. Critically, similar attention linking monitoring and archives has not been given to other pollutant metals.

Millennial History of Atmospheric Metal Pollution: The Foundation for Establishing the Utility of Peat as an Archive of Past Pollution

In Europe, trace metals, and more specifically lead, have been abundantly mined, smelted and traded during the last few millennia, and thus also emitted to the atmosphere. Because lead and other trace metals are often released as sulfides, these submicronic to micronic aerosols have a residence time of several days in the atmosphere and can therefore be transported over long distances leading to a regional or even hemispheric pollution signal and thus an environmental change. As lead has been the metal most commonly analyzed and reported in peat records, we use lead here as the primary example to show the utility of peat as an archive of past metal pollution.

Lead in Peat Records

It is not the place of this chapter to present a comprehensive history of the global production and use of lead, but a brief overview is essential to support the use of peat records. Lead became an important metal early in history, particularly after the discovery of the cupellation process about 5500 years ago, which opened a new era of metal mining and exploitation (Settle and Patterson 1980; Nriagu 1983, 1996). From 5500 years ago (Fig. 3), lead production increased slowly until the introduction of coinage about 2700 years ago, after which the production of lead rose dramatically from an estimated 10^2 metric tons yr^{-1} to a peak value of nearly 10^5 metric tons yr^{-1} during the Roman period about 2000 years ago (Settle and Patterson 1980). Global lead production declined during the so-called Dark Ages after the exhaustion of the Roman mines and the collapse of the Roman Empire. Production remained depressed until about the tenth century, when silver mining again expanded in Europe and in particular in Central Europe, such as in the Harz Mountains, Germany. Not until the Industrial Revolution, especially during the latter half of twentieth century with the addition of alkyl lead in gasoline, did global lead production again match and then finally exceed the production during the Roman period. The maximum production in the late twentieth century, by comparison to the Roman period, was $>10^6$ metric tons yr^{-1-1}. In modern times it has been estimated that anthropogenic sources contribute as much as 95 % of the lead in the global lead cycle (Settle and Patterson 1980). This global history of lead production is clearly reflected in millennial scale European lead records from Germany (Hettwer et al. 2003; Le Roux et al. 2005), France (Monna et al. 2004a, b; Forel et al. 2010), Belgium (De Vleeschouwer et al. 2007), the UK (Le Roux et al. 2004; Cloy et al. 2008) and Spain (Kylander et al. 2005). In Europe these signals of lead production are sufficiently ubiquitous that they can be used as an inferred dating tool (Renberg et al. 2001).

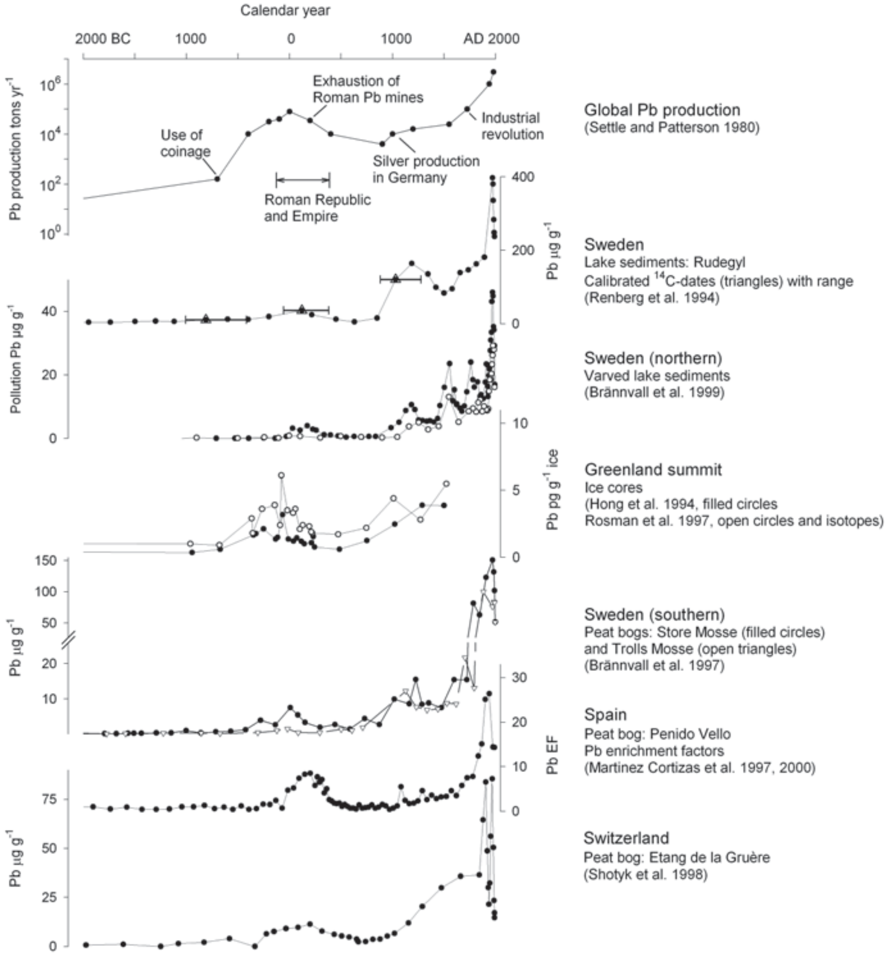


Fig. 3 Comparison of the estimated historical global lead production (Settle and Patterson 1980) and lead records from Swedish lake sediments (Renberg et al. 1994; varved sediments, Brännvall et al. 1999) and the Greenland ice (Hong et al. 1994) with peat records from Sweden (Brännvall et al. 1997), Spain (Martínez-Cortizas et al. 1997) and Switzerland (Weiss et al. 1997; Shotyk et al. 1998). Modified from Renberg et al. (2001).

In the 1990s millennial scale peat records from Germany (Kempter et al. 1997), Switzerland (Weiss et al. 1997; Shotyk et al. 1998), Spain (Martínez-Cortizas et al. 1997), Sweden (Brännvall et al. 1997) and the UK (West et al. 1997), in addition to those studied earlier in the UK (Lee and Tallis 1973) and Denmark (Aaby and Jacobsen 1978), showed a general agreement in temporal trends among records, which broadly traced the economic development of Europe through time as reflected through metal extraction and subsequent emission to the atmosphere. Furthermore, there was also a strong agreement between these peat records and those derived from lake sediments, such as in Sweden (Renberg et al. 1994; Brännvall et al. 1997) and in the UK (Farmer et al. 1997), and from the Greenland ice record (Hong et al. 1994) (Fig. 3). This cohesion amongst records is critical in two ways. First, there is the close match between the long-term changes in lead in European peat records and the estimated historical record of lead production (which was "Eurocentric" in character). The similarity in the temporal changes in lead in peat records obtained from cores sampled in peatlands from different regions and with variable properties, such as hydrology, degree of ombrotrophy or vegetation cover, requires a common external driving force. Second, and more critically, despite fundamental differences in the physical and geochemical properties between lake sediments (including annually laminated), glacial ice and peat, all three archives reflect the same broad changes in the accumulation of lead over time (Renberg et al. 2001).

Stable Lead Isotopes (^{204}Pb, ^{206}Pb, ^{207}Pb & ^{208}Pb) in Peat Records

Further support for the quality of the lead pollution record preserved in peat came from the application of stable lead isotope analyses to pollution studies. Developed especially by Clair Patterson and his colleagues, lead isotope analyses progressed from a geologic dating tool (Patterson et al. 1955) to one that could be applied to separate different sources of lead in environmental samples such as sediments, soils and precipitation (Chow and Patterson 1962; Shirahata et al. 1980). Lead is present as a natural trace element in many types of minerals, such as feldspars and apatite, and can be a significant constituent in sulfide deposits. Lead has four stable isotopes: ^{204}Pb, which is original and does not have a radiogenic origin; and ^{206}Pb, ^{207}Pb and ^{208}Pb, which are the end products from the radioactive decay of ^{238}U, ^{235}U and ^{232}Th. These latter three isotopes have half-lives of 4.5, 0.7 and 14 billion years, respectively. The mixture of lead isotopes varies regionally for geological reasons due to the environment of formation, the initial concentrations of uranium and thorium, and the amount of time that has passed. During formation lead-containing ores are separated from the original host bedrock, which still contains uranium and thorium. The isotope composition of these ores therefore ceases to develop further, whereas the lead isotopic composition of the surrounding host bedrock continues to evolve over geologic time. When applied to peat records as well as lake sediments (see also chapter 6 by Cooke and Bindler), lead isotope analyses revealed that the changes in lead over time indicated by concentration analyses were connected with changes in the lead isotopic composition. As with lake-sediment and glacial ice records, these changes in isotopic composition could only be explained by lead sources having an isotopic composition similar to that found in lead-bearing ores (Stos-Gale et al. 1995; Rosman et al. 1997; Monna et al. 2000).

A classic example of these changes in lead isotopic composition is the peat record from Etang de la Gruère in the Jura Mountains, Switzerland (Fig. 4). From about 14,000 until 3500 years ago the isotopic composition as reflected in the ^{206}Pb/^{207}Pb isotope ratio was >1.19, reflecting natural background values characteristic of soils and bedrock in this region of Europe (cf. Monna et al. 1999, 2004b; Thevenon et al. 2011). Despite small changes in lead fluxes associated with soil

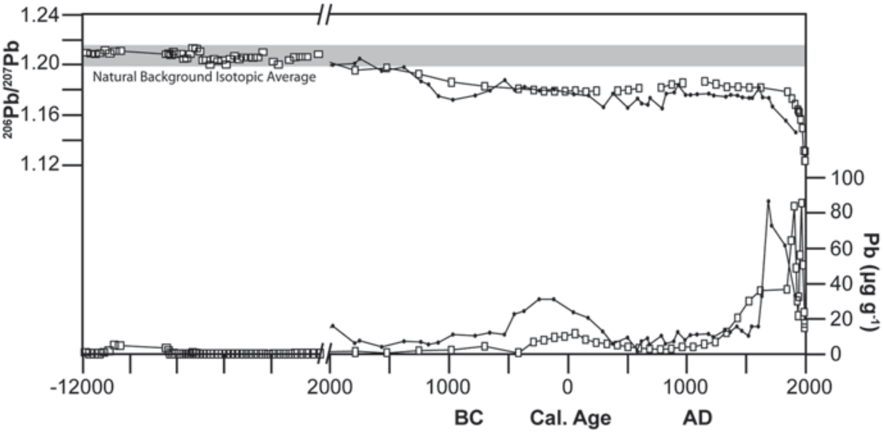


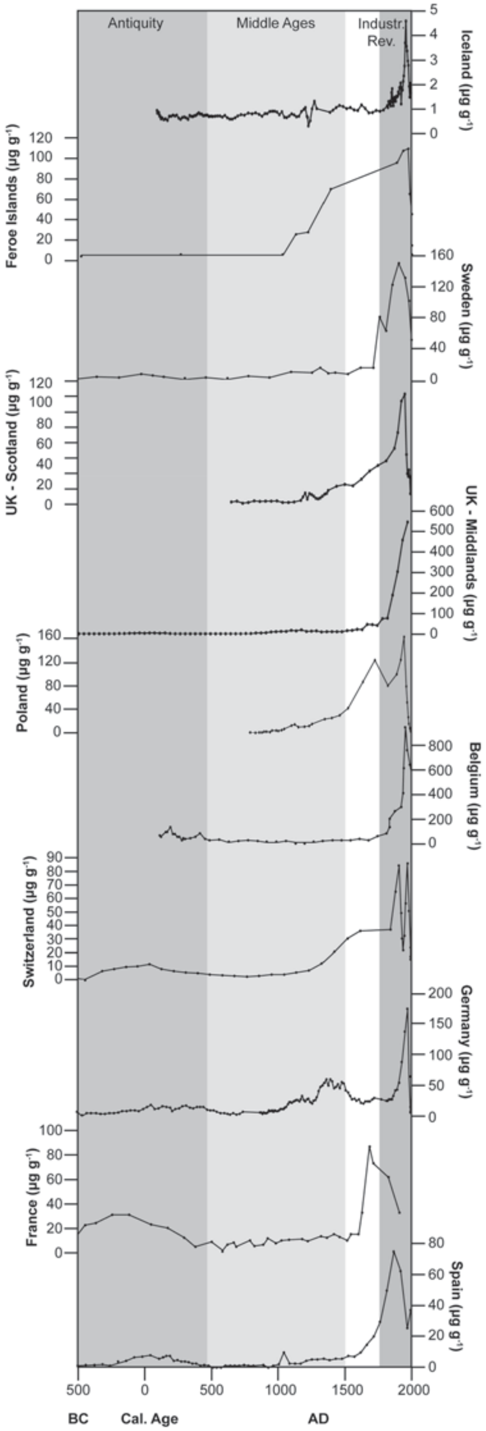
Fig. 4 Changes in lead composition (concentrations and ^{206}Pb/^{207}Pb isotope ratios) over the Holocene in Etang de la Gruère, Switzerland (open squares; Shotyk et al. 1998), and in the nearby region of Morvan, France (filled circles; Monna et al. 2004a). From the end of the last ice age until about 3500 years ago, the lead composition reflected natural background sources, but from 3500 years ago the composition shifted increasingly towards values characteristic of ore sources of lead in conjunction with increasing lead concentrations

dust early in the Holocene, the isotopic composition varied only slightly, which reflected small changes in local soil dust sources or grain-size fractionation associated with changes in climate (Shotyk et al. 2002). From about 3500 years ago, however, there was a distinct and permanent shift towards lower ^{206}Pb/^{207}Pb isotope ratios as lead concentrations increased, which indicated the addition of a new source of lead with an isotope ratio of about 1.18. A similar decline is recorded, for example, in other regional peat records such as that from Morvan, France (Fig. 4; Monna et al. 2004b), about 225 km to the west of Etang de la Gruère, although the ^{206}Pb/^{207}Pb isotope ratio is slightly lower at Morvan because of the closer proximity of mines operated since the Antiquity. Up until the 1930s the ^{206}Pb/^{207}Pb isotope ratio at both sites was characteristic of regional ores, but from the 1930s the isotope ratio in these and most European records declined below the range of values characteristic of European ores, which mostly fall in the range of 1.16 to < 1.2 (Rosman et al. 1997; Monna et al. 2000). This twetieth century decline coincides primarily with the introduction of alkyl lead in gasoline in the 1920s, which had a dominant component of lead derived from Precambrian lead ores from Australia having a ^{206}Pb/^{207}Pb isotope of 1.04. Nearly identical changes in lead inputs and isotopic composition to those at Etang de la Gruère and Morvan are found in other peat records from nearby areas in southern Germany (Le Roux et al. 2005) and eastern France (Forel et al. 2010).

As with lead concentrations, temporal changes in the isotopic composition of the European peat records are similar to those found in the other types of environmental archives including the Greenland ice (Rosman et al. 1997) and lake sediments from disparate regions such as Sweden (Brännvall et al. 1999) and Switzerland (Thevenon et al. 2011). Although this long-term atmospheric lead pollution signal is visible throughout much of Europe and as far afield as the summit of the Greenland ice sheet and follows a common historical narrative as outlined by Settle and Patterson (1980), there are important regional differences (Fig. 5). These differences arise from the specific economic developments surrounding mining and metallurgy through history, which have varied regionally. For example, peat records from Spain (Martínez-Cortizas et al. 1997, 2013), France (Monna et al. 2004a, b; Forel et al. 2010) and southwestern Germany (Le Roux et al. 2005) show a pronounced lead pollution peak that is clearly visible on the basis of lead concentrations alone during the period between approximately 400 BC and AD 200. This peak is also discernible in Etang de la Gruère, but only slightly discernible further north in Belgium (De Vleeschouwer et al. 2007), and detectable in Swedish peat records when the additional information from stable lead isotope analyses are included (Bindler et al. 1999; Klaminder et al. 2003). This geographic variability reflects the importance of mining in the Roman Empire and the Mediterranean region, where the Iberian Pyrite Belt in particular was a major center for mining and metallurgy. However, further north, such as in Scotland and in Sweden, this early peak consisted of a very small increase in lead of only 1 $\mu g\ g^{-1}$ accompanied by a small decline in isotope ratio. The period of trouble and re-organization that followed the fall of the Roman Empire saw a decline in the trading and smelting of metallic ores, and thus a decline in pollution lead recorded in peat cores. From the late tenth century the emission of metals began to increase again, but particularly in the Germanic countries such as in the Harz Mountains region of Germany, due primarily to the extraction and smelting of silver ores, which also contained substantial amounts of lead (Le Roux et al. 2005). This is clearly recorded as a large peak in lead concentrations in German bogs, where concentrations in the medieval period can be as high as 1500 $\mu g\ g^{-1}$ (Kempter and Frenzel 2000); values we would typically associate with modern industrial pollution such as near smelters (Novak et al. 2003; Klaminder et al. 2008). This medieval peak is also seen in Switzerland and as far afield as Iceland (Marshall et al. 2009).

The lead pollution record since the Industrial Revolution is characterized by higher concentrations and deposition rates than in any prior period (with local exceptions, such as the Medieval peak in the Harz Mountains). The Industrial Revolution saw the expansion of modern industries, coal and ore mining, smelting of an increasing variety of ores, fossil fuel combustion (coal and oil) and the introduction of the combustion engine and finally the introduction of alkyl lead in gasoline from the 1920s. Whereas calculated lead deposition rates from peat records in remote sites removed from emission point sources were about 10-fold higher during the Roman period than natural background levels recorded through most of the Holocene (0.1–0.5 versus 0.01–0.03 $mg\ m^{-2}\ yr^{-1}$, respectively) and about 100-fold higher during the Middle Ages (1–3 $mg\ m^{-2}\ year^{-1}$), the deposition rate of lead by AD 1970 (10–15 $mg\ m^{-2}\ yr^{-1}$) was about 1000-fold higher than the natural background values estimated from peat records in many areas of Europe (Shotyk et al. 1998; Bindler et al. 1999; Klaminder et al. 2003; Kylander et al. 2005; Le Roux et al. 2005; Forel et al. 2010; Fig. 6). By AD 2000 lead deposition rates had declined to about 1 $mg\ m^{-2}\ yr^{-1}$, which is less than 10 % of the deposition rates during

Fig. 5 Regional comparison of lead concentrations in peat records from Western Europe, presented geographically from Scandinavia southwards to central Europe and westwards to the Iberian Peninsula



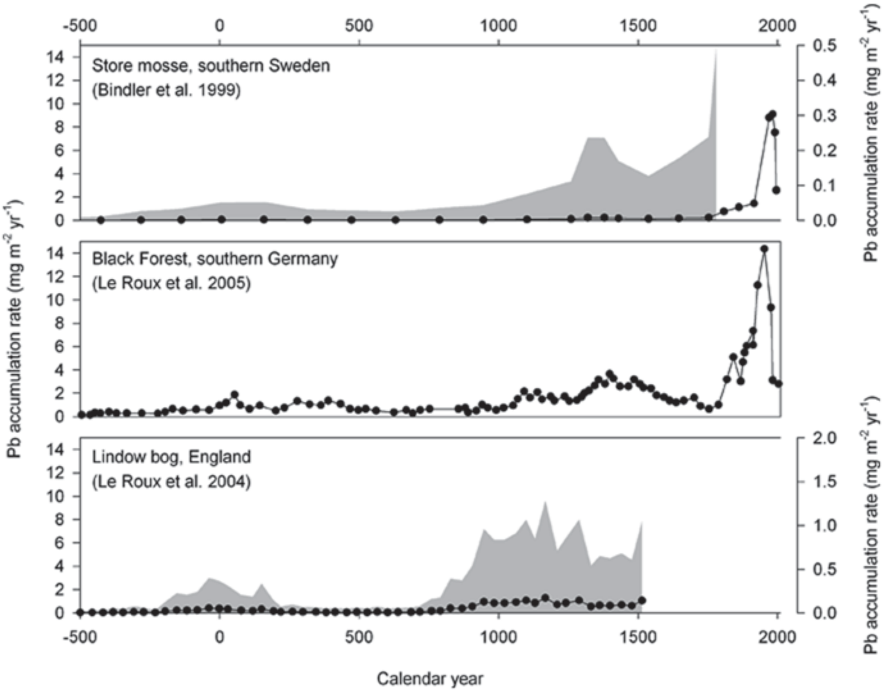


Fig. 6 Lead accumulation rates from Store Mosse, Sweden (Bindler et al. 1999), Black Forest, Germany (Le Roux et al. 2005) and Lindow Bog, England, UK. (Le Roux et al. 2004)

the pollution peak period in the 1970s following implementation of stricter emission regulations and removal of alkyl-lead additives in gasoline (Bindler 2011); but this rate is still substantially elevated in relation to estimated natural background levels. Still, from a contamination perspective, the burden of historical pollution was significant. Although industrial pollution levels are an order of magnitude or more higher than historical and ancient pollution levels, the cumulative burden of lead pollution deposited per unit area from the pre-industrial period, spanning from about 3000 years ago until AD 1800, is equal in many parts of Europe to the burden of pollution lead deposited over the past 200 years (Bindler et al. 1999; Le Roux et al. 2005; De Vleeschouwer et al. 2009).

The above estimates of past pollution are based, as noted, on bogs removed from specific point sources, and thus these values represent background atmospheric pollution levels. Lead concentrations at such sites are typically less than 1 µg g^{-1} in pre-anthropogenic levels (≥2500 years ago) and peak at about 50–150 µg g^{-1} in levels dated to the 1970s (Fig. 5). By contrast, for sites that are located near large pollution emission centers, e.g., in coal or ore-mining districts, near smelters or coal-fired power plants such as sites in several areas in the UK or Belgium, for example, lead concentrations can be closer to 1000 µg g^{-1}. As observed by Novak et al. (2003) in the Czech Republic and De Vleeschouwer et al. (2009) in Poland, the coal industry (production and burning) and related trace metal emissions have remained important during the last 50 years in some areas of Europe and still contribute substantially to lead emissions, thus blurring some of the positive effects of the lead gasoline ban.

Mercury in Peat Records

Mercury is one of the priority metals from a global pollution perspective. A number of mercury records from peat profiles from scattered regions of the globe have been reported over the past 15 years, and there is a general agreement amongst these peat records, although there are as of yet some unresolved discrepancies with other archives and results from monitoring studies. Analyses of millennial scale peat records from Spain (Martínez Cortizas et al. 1999), Switzerland (Roos-Barraclough et al. 2002), Sweden (Bindler 2003), Canada (Givelet et al. 2003), southern Chile (Biester et al. 2003), northeastern USA (Roos-Barraclough et al. 2006), Scotland (Farmer et al. 2009) and Belgium (Allan et al. 2013) yield rather similar background net mercury accumulation rates in the range of approximately 0.5–3 µg m^{-2} yr^{-1} (Biester et al. 2007). Based on whole lake-basin studies of mercury accumulation and studies where sediment fluxes have been corrected for the effects of sediment focusing or watershed size in the upper Midwest and northeastern USA (Engstrom et al. 1994; Landers et al. 1998; Lorey and Driscoll 1999; Lamborg et al. 2002), the pre-industrial deposition rate of mercury was about 3–5 µg m^{-2} yr^{-1}, which is somewhat higher than the accumulation rate in peat.

By comparison to the fairly similar estimated background accumulation rates in peat and lake-sediment records of 0.5–5 µg m^{-2} yr^{-1}, the late-twentieth century deposition rates calculated from lake-sediment records from sites located far from point sources are about 10–30 µg m^{-2} yr^{-1}, a range comparable to that obtained from direct measurements of atmospheric mercury deposition (Engstrom et al. 1994; Iverfeldt et al. 1995; Wängberg et al. 2001; Lamborg et al. 2002; National Atmospheric Deposition Program database). However, for most peat records mercury accumulation rates thus far largely exceed the deposition rates suggested by lake-sediment records and those measured in direct deposition (Biester et al. 2007 and references therein). Maximum mercury accumulation rates in peat records range from 25 to as much as 200 µg m^{-2} yr^{-1}, which is as much as an order of magnitude greater than measured deposition rates during the last two-three decades of monitoring. This apparent overestimate of modern mercury deposition rates in peat records remains a current topic of investigation. Hypotheses presented to explain the differences between the peat records and other data include decomposition of organic matter and mass loss (Biester et al. 2003) and uncertainties in radiometric dating particularly in the recent (past 150 years) uppermost peat (discussed later in the chapter).

Nonetheless, peat records do yield valuable data on relative trends in mercury accumulation through time. Whereas there is clear evidence for a long, pre-industrial history for atmospheric lead pollution in European peat records, as well as regionally for other metals, the evidence for pre-industrial (i.e., pre AD 1800) atmospheric mercury pollution is very limited. In an analysis of one mountain bog from northwestern Spain, Martínez Cortizas et al. (1999) observed clear increases in mercury from the Islamic period, ca. 1000–1500 years ago, and possibly as early as the Roman period. This early regional mercury pollution is quite likely, given that coastal sediment records from the Iberian Peninsula provide clear evidence from about 2000 years ago of waterborne mercury pollution (Leblanc et al. 2000, Serrano et al. 2013) and 1000 years ago in French coastal sediments (Elbaz-Poulichet et al. 2011). At Etang de la Gruère, Switzerland, mercury accumulation rates increase slightly over background values during the period from AD 1500–1800 (Roos-Barraclough et al. 2002), and possibly beginning in the 1700s in the Misten bog, Belgium (Allan et al. 2013). However, in the Misten bog, this increase is not unequivocal because only one of four cores indicate this early industrial increase in accumulation rate, and as observed in other peat records the maximum accumulation rates are 100–200 $\mu g\ m^{-2}\ yr^{-1}$—about an order of magnitude above deposition monitoring data.

Other Pollutant Metals

Mining and metal processing from Antiquity to the present have involved many metals, which have been frequently extracted from complex ore bodies hosting several major metals (e.g., iron and copper—where concentrations are often reported as percentage) and a broad range of metals and metalloids present typically in trace quantities (e.g., antimony, arsenic, bismuth, cadmium, chrome, cobalt, copper, gold, lead, manganese, mercury, nickel, silver, tin and zinc—where concentrations are often reported as $\mu g\ g^{-1}$). Although lead has been the metal most commonly analyzed and reported in peat records, as presented earlier, other pollutant metals have also been studied, although less extensively (Steinmann and Shotyk 1997: Krachler et al. 2003; Novak et al. 2005; Weiss et al. 2007; Rothwell et al. 2010) One factor is that anthropogenic inputs of lead have greatly dominated over natural sources and thus lead pollution is easier to trace. A second factor is the possibility of using stable lead isotope analyses to trace different lead sources. Although other metals also have the possibility of isotope analyses, these metals—such as copper and zinc (Weiss et al. 2007)—are subject to isotopic fractionation in the environment, and isotope records cannot be interpreted in terms of changing sources as for lead. A third factor is that several interesting metals or metalloids are subject to different degrees of mobility, especially in the low pH environment within peatlands, and profiles of these metals must be evaluated carefully (Rausch et al. 2005). Experimental studies by Villaverde et al. (2009) have shown that lead and copper are effectively bound to the solid peat phase, but that a significant fraction of the cadmium can be in the dissolved phase and thus potentially mobile.

As an example, Rothwell et al. (2010) approached the question of metal mobility from a field-based perspective. In their study of a blanket bog in the Lake District in NW England near the industrial centers of Manchester and Sheffield, they found at the dome of the bog that arsenic and antimony profiles followed those of copper and lead (including stable isotopes). The peak concentrations and accumulation rates of all four metals occurred at the same level, dated to ca. AD 1890–1915. This coherence in the accumulation records of the metals is similar to what has been shown in lake-sediment records from the UK (Yang and Rose 2005). Iron and manganese showed a contrasting profile to these trace metals, with both metals enriched in the upper several centimeters due to the changes in redox conditions that occur in the upper peat in conjunction with the higher water table at the dome. However, in a peat profile collected from an eroding gully, where the water table can fluctuate by upwards to 60 cm, Rothwell et al. observed that the peak in arsenic and a secondary peak in antimony occurred together with a subsurface peak for iron and manganese rather than with the ca. 1900 peak in copper and lead. The main peak for antimony did coincide with that for copper and lead. Whereas arsenic and iron were decoupled in the dome profiles, in the more dynamic hydrologic setting near the gully arsenic mobility and immobility (and a fraction of antimony) is governed by the redox chemistry of iron, which has been shown in minerotrophic mires (Gonzalez et al. 2006).

Pollution Records Beyond Europe

Most of the studies focused on lead and trace metal pollution recorded in peat have been performed in Europe. This is mainly due to the long history of interest by European scientists for bogs, but also to the fact that European bogs are easy to access and geographically widely available. In North America, studies of lead pollution using peat archives have focused largely on analyzing the progression of pollution following European colonization and the effects of industrialization from the 1800s onwards. Furthermore, in North America, South America as well as Asia more extensive studies of past pollution have been done using lake-sediment records.

In the USA, for example, Schell (1987; Schell et al. 1989) in Pennsylvania, Norton et al. (1990, 1997) in Maine, and Kamenov et al. (2009) in Florida, studied short peat cores to reconstruct increases in lead and associated metals during the last ca. 150 years. A similar example from Canada can be seen in Pratte et al (2013) who also studied short-term metal records in peat. As described above for peat records in Europe, the increasing accumulation of metals in peat records traced industrialization and the increasing combustion of fossil fuels, smelting and especially vehicle emissions. In surface cores from Big Heath, a bog on the Maine coast, which is downwind of emission sources in New England as well as industrial regions in the Midwest and thus a good regional integrator of metal deposition history, there was an increase in lead accumulation rates beginning in the latter half of the 1800s, which accelerated from about 1900, with a peak period of deposition during the 1970–1980s (Norton et al. 1997). In the North American studies, fluxes in metals have generally increased by 10–100 times over pre-industrial levels. As in Europe, lead concentrations and deposition declined steeply after implementation of the Clean Air Act and its subsequent amendments from 1970 onwards, which included the progressive removal of alkyl lead additives in gasoline.

Application of Peat Metal Records—Archaeology and the History of Mining and Metallurgy

When historical texts and archaeological facts are limited or lacking in the vicinity of known mining or metallurgical sites peat bogs have served as useful archives to reconstruct pollution histories at a local scale. These metal pollution records in peat can, in turn, also be extended to answering archaeological questions focused on tracing the earliest mining and metallurgy and the landscape changes that followed. Mining and metallurgical activities have had a profound effect, not only on the emission of trace metals to the atmosphere through history, as indicated by the millennial scale lead records, but also directly on the surrounding landscape. Mining activities required resources, manpower and energy. Most often, ancient and historical mining and smelting activities were accompanied by human occupations, which included deforestation to open the landscape for agriculture and grazing as well as to provide wood resources for the mine or for smelting. A strong link between mining activity and deforestation for charcoal production, in addition to clearance for agriculture, is also suspected in many places in Europe (e.g., Küster and Rehfuess 1997; Baron et al. 2005; Monna et al. 2004b; Martínez-Cortizas et al. 2005; Mighall et al. 2009). These practices led to rapid changes in the landscape, which may be recorded in peat bogs either through changes in pollen or changes in soil dust fluxes. For example, in southern Bavaria Küster and Rehfuess (1997) observed an inverse relationship between *Fagus* and lead concentrations, where a decline in *Fagus* pollen and an increase in lead began during 2200–2600 BP, a time period corresponding to the *Halstatt* and *La Tène* cultures in Europe.

In mountain sites in northwestern Spain, Martínez Cortizas et al. (2005) and Pontevedra-Pombal et al. (2013) observed a similar inverse relationship between tree pollen, as a proxy for forest cover, and enrichments in lead and other trace metals related to regional atmospheric pollution (Fig. 7), where major peaks in metal pollution coincided with lower percentages in total tree pollen during established cultural periods. These Spanish peat records also exemplify the multi-metal complexity of historical metal pollution, which included more than only lead. Furthermore, the different metals (nickel, zinc, arsenic and zinc) also reveal different pollution patterns through time, which are coupled to metallurgical developments in Antiquity. The first decline in tree pollen, i.e., deforestation, occurred 3500–2800 BP during the Bronze Age and coincided with a clear enrichment in nickel at all three of the study sites. A smaller pollution phase occurred during the late Bronze–Iron Ages, but with enrichments in cadmium, arsenic and zinc. Thereafter, the well-established pollution peak of the Roman period was accompanied by peaks not only in lead, but also nickel, arsenic and cadmium, which reflected the complexity of the ores from the Iberian Peninsula. Over the last thousand years, deforestation and metal pollution were no longer directly connected, because other factors were most important for deforestation, namely expanding cultivation and grazing. All of the measured pollution metals gradually increased about 1000 years ago, but which accelerated first from about 500 years ago with the rise of the Spanish empire, and then with industrialization until peaking in the 1970–1980s, as discussed for other regions.

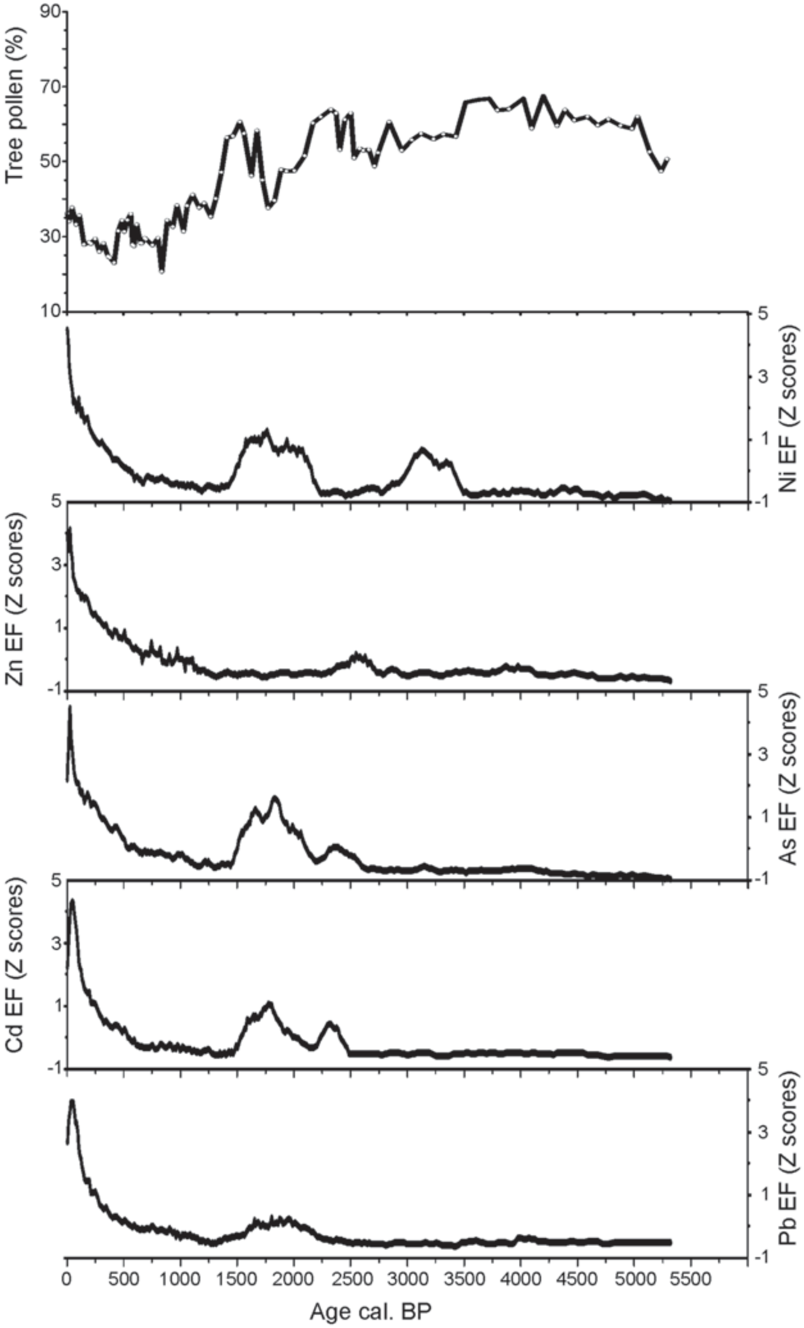


Fig. 7 Changes in total tree pollen (as percentage of total terrestrial pollen) and trace metal enrichment factors from peat records in northwestern Spain. (Martínez-Cortizas et al. 2005, Pontevedra-Pombal et al. 2013)

This interplay between deforestation and farming in association with expanding mining and metallurgy has also played a role in increased soil dust released to the atmosphere and deposited into bogs (Görres and Frenzel 1993; Hölzer and Hölzer 1998; Martínez-Cortizas et al. 2005). This soil dust can be traced using elements such as titanium and scandium (e.g., Hölzer and Hölzer 1998; De Vleeschouwer et al. 2007; Kempter and Frenzel 2008), as well as through changes in pollen (Monna et al. 2004b; Mighall et al. 2004; Martinez Cortizas et al. 2005; Jouffroy-Bapicot et al. 2007; Breitenlechner et al. 2010) or fire indicators such as charcoal particles (Monna et al. 2004b; Mighall et al. 2004; Baron et al. 2005).

Dating Peat Records

When tracing historical pollution and linking trace metal profiles in peat with known periods of pollution, it is fundamental to accurately date events in the geochemical records. The two commonly used techniques to date peat sections are radiocarbon dating and short-lived isotopes such as ^{210}Pb and ^{137}Cs (Oldfield et al. 1979; El-Daoushy et al. 1982), where the latter are used to date approximately the last 150 years. With a half-life of 5720 ± 30 years, it is possible to use radiocarbon dating to date peat samples or sediments back to ca. 50 kyrs. Carbon-14 (^{14}C) is formed in the high atmosphere and then incorporated in plants as atmospheric $^{14}CO_2$ via photosynthesis. Peat being almost exclusively composed by plant residues, it is relatively easy to find enough carbon to perform radiocarbon measurements. For dating of surficial peat deposits and soil organic horizons, the radiometric isotope ^{210}Pb is frequently used (Oldfield et al. 1978; 1995; Klaminder et al. 2006; Appleby 2008; Kaste et al. 2011) providing dating on a 100–150 year time scale. Lead-210 has a half-life of about 22 year and is formed through the alpha decay of ^{226}Ra in soil into ^{222}Rn, which escapes to the atmosphere and decays through several intermediates into ^{210}Pb. Once in the atmosphere ^{210}Pb is attached to aerosols and deposited by dry and wet deposition (atmospheric residence time $=4.8 \pm 0.3$ day, Lal and Suess 1968). For further information on both ^{210}Pb and ^{14}C dating, see the respective chapters in Volume 1 of the Tracking Environmental Changes series, as well as references therein.

In order to know the age and uncertainty of any given sample level in a peat core, it is necessary to build up an age-depth model. Several software programs have been developed over the years, proposing ways of refining the accuracy of the model. The essential point is that a model needs to accurately represent the probability of distribution of ages at each depth and that the output ages at any depth should at least contain a minimum and a maximum age. Several models are specifically designed for peat sequences, with some of the most recent models being BCal, BPeat, Clam.R and BACON (Blaauw 2010; Blaauw et al. 2003; Blaauw and Christen 2005, 2011). The latter model integrates the full probability of age distributions and reports these in the proxy vs. age graphs.

A series of confounding factors arise from the dating techniques described above. They originate both from the technique itself, or from the processes which are behind the accumulation of ^{14}C and ^{210}Pb in a peat sequence. The conventional ^{14}C-dating technique was widely employed and is still in use. However, limitations occur in the fact that a large amount of sample is required (5–100 g of dry peat). Therefore, bulk peat samples are most often dated with this technique, leading to potential problems because a bulk sample will contain roots that can transport recent atmospheric carbon downwards, which can result in age discrepancies between radiocarbon dates of bulk peat in comparison to specific fractions or moss fragments (Nilsson et al. 2001). These problems can be overcome with AMS dating, which requires very low amounts of material (5–50 mg of dry peat) and enables the dating of plant macro-remains or even pollen concentrates. Therefore, aerial parts of plant macrofossils can be selected and dated accurately. If possible, one should prefer moss macrofossils, such as *Sphagnum*, because mosses have no roots and do not mobilize carbon form the underlying peat.

For peat layers deposited since the 1950s, it is also possible to use the radiocarbon produced by nuclear bomb testing to date the peat (Goodsite et al. 2001). Comparisons between ^{210}Pb and ^{14}C bomb pulse age-depth models show a general agreement. However, the comparative results from both Goodsite et al. (2001) and Piotrowska et al. (2010) indicate that there are differences between the two dating methods of a few to several years per sample. The discrepancies could occur because carbon can be taken up in aerial parts of the mosses and transferred through the roots of vascular plants on the bog surface to sub-surface layers, as well as the possibility for a downward displacement of ^{210}Pb due to downwashing (discussed below). From a simple chronological perspective of pollution this difference may not be critical, that is, if the aim is to generally ascertain when pollution levels were highest, such as in the 1970s or in the 1980s. However, from the perspective of calculating metal accumulation rates and thus inferring metal deposition rates, the difference in the results of the two age-depth models may have important implications. The differences would critically affect the calculation of accumulation rates and the quantitative calibration of the peat data to monitoring data. These differences have thus far not been specifically addressed.

In recent peat layers, Olid et al. (2008, 2013) evidenced other issues in using only the ^{210}Pb age-depth model to date maxima of metal pollution and metal fluxes in peat cores from NW-Spain. In particular, Olid et al. (2013) showed that the maximum lead flux predated the maximum lead concentrations by 10–20 years. The authors explain this discrepancy by the fact that not all of the atmospherically supplied ^{210}Pb originates from natural sources, but that some small fraction of this ‘unsupported’ ^{210}Pb at their study site may have originated from atmospheric metal pollution. They proposed a correction method to adjust the age-depth model by calculating the percentage of ^{210}Pb that could be associated with the pollution fraction which is the focus of an ongoing study.

Some studies have also hypothesized that ^{210}Pb accumulation does not occur only in the uppermost (growing) parts of the peat-forming plants, but that some may be transported to and found at depth within the peat (Oldfield et al. 1995; Lamborg et al. 2002). Oldfield, one of the pioneers in radiometric dating techniques for recent sediment and peat records, and co-workers raised the issue of a potential downwash in their review of radiometric dating techniques of recent peat (Oldfield et al. 1995). Specifically they discussed 'Processes displacing Pb-210 in peat' that would affect ^{210}Pb chronologies. One important factor is that well-aerated hummocks could be subject to some rapid downwashing (see more detailed discussion regarding downwash in Hansson et al. 2014), for which there was suggestive evidence. This was exemplified in a following study by Oldfield et al. (1997), where they noted a mismatch in a peat core from northern Sweden between the age of a tephra layer and the dates based on ^{210}Pb. The tephra layer was identified as originating from the AD 1875 eruption of Askja, but the ^{210}Pb CRS date was set to 1927 for that level in the peat. A second factor discussed by Oldfield et al. is the potential for re-mobilization, which had been discussed previously, for example, by Urban et al. (1990), who had suggested that in some peat cores metal mobility could affect ^{210}Pb chronologies based on their study of the mobility of lead through the uppermost layers of peat. Lamborg et al. (2002) invoked both downwashing and remobilization in their analyses of Nova Scotian (Canada) peat records, for which they were unable to establish a ^{210}Pb-chronlogy due to the depths at which unsupported ^{210}Pb was measured, together with sub-surface peaks at or near the water table.

Despite these confounding factors and difficulties that can arise when trying to determine the age of a specific peat layer, in most cases researchers have been able to successfully establish a reliable age-depth chronology after careful evaluation (cf. Appleby et al. 1997; Olid et al. 2013), often using a combination of dating techniques (e.g. using supporting information from known events such tephra layers, peaks in the radiometric isotopes ^{137}Cs and ^{241}Am connected to nuclear bomb tests in the 1950s or the Chernobyl accident in mid-1980s etc.) to determine a reliable long-term chronology that allows reconstructions of relative changes over time.

Confounding Factors that May Influence Metal Accumulation Records in Peat

Although in the ideal case of ombrotrophic bogs the supply of metals is solely via the atmosphere, the use of peat cores as natural archives is not always as simple and straightforward as it may seem. Further to the factors specifically influencing the age-depth modeling, several studies over the last decades have identified factors and processes that can affect the integrity and temporal accuracy of the recent peat record. Studies have also shown that there can be both a between-bog variation as well as a spatial variation within one and the same bog. In this section we discuss some factors and processes that may affect the geochemical record in peat and our interpretations of it.

One factor that can easily be identified is the variation of topography at the peat surface. The surface of a peatland can generally be divided into three main features: hummocks, which are elevated areas raised by *Sphagnum* colonization; hollows, which are permanently or seasonally filled with stagnating water and where aquatic plants and Sphagnum species are developing; and lawns, which are a more homogenous and flat area covered predominantly by mosses. The lawn is generally situated between the hummocks and the hollows but is not present on all bogs. Studies have shown that hummocks, being isolated above their immediate surroundings and not influenced by stagnating waters and the anoxic conditions of a hollow, constitute the best location to core to investigate past atmospheric pollution (De Vleeschouwer et al. 2010). For example, Norton et al. (1997) showed that, although vertical and temporal trends for lead were similar between hummocks and hollows, trace metal accumulation rates could be 3 times higher in the hummock cores than in cores from adjacent hollows. Furthermore, the accumulation rates in the hummock cores were in closer agreement to measured deposition rates. Differences between hummocks, hollows and *Sphagnum* lawns have also been shown for ^{210}Pb accumulation (Oldfield et al. 1995; Malmer and Wallén 1999).

Hummocks and hollows are a very direct example of small-scale variation in topography at the peat surface, yet other small-scale and not so obvious differences exist that can also affect the geochemical record preserved in the peat. For instance, a spatial heterogeneity in trace metal accumulation rates can occur due to variations in vegetation. As it has been shown in biomonitoring studies (Ceburnis and Steinnes 2000), different plants have different abilities to scavenge and retain elements, aerosols and particles from the atmosphere. For instance, there is strong evidence that variations in plant species on the bog surface exhibit different capacities to intercept and bind metals (Le Roux et al. 2005; Kempter et al. 2010; Rydberg et al. 2010), which is well known from biomonitoring studies (discussed earlier). Other studies have shown that within small distances, the accumulation and concentration of total lead, ^{210}Pb (used for radiometric dating) and mercury can vary by a factor of 2–4 within the same bog, even when the cores are only taken from hummocks (Bindler et al. 2004; Coggins et al. 2006; Olid et al. 2010; Martinez Cortizas et al. 2012).

Beside variations in microtopography of the mire and plant composition, the actual form of atmospheric deposition will also play an important role in recording the geochemical signal in peat. Atmospherically derived elements can be deposited in various forms onto the bog surface; some will be completely dissolved in rainwater, while others are deposited as aerosols or as particulate matter. Due to a difference in chemical properties the elements associated with each fraction may also show different behaviors once deposited in the peat. Some may be mobile, e.g., cesium (Oldfield et al. 1979; Urban et al. 1990; Vinichuk et al. 2010) and sulfur (Novak et al. 2005), while others, e.g., lead, titanium and zirconium—the latter two associated particularly with soil dust, are considered immobile (Shotyk 1996; Shotyk et al. 2002). Other elements, e.g., calcium, potassium, phosphorus and zinc, are subject to nutrient cycling and plant root uptake (Damman 1978; Malmer 1988; Vinichuk et al. 2010), while some, e.g., iron and manganese, are strongly redox sensitive (Steinman and Shotyk 1997). It is therefore of utmost importance to take into account the chemical behavior of each element investigated before drawing specific conclusions of the long-term geochemical record in terms of pollutant metal inputs.

Even after deposition onto the peat surface, the geochemical signal can still be altered before being permanently incorporated into the record. One process that has been shown to influence the geochemical record is the decomposition of the peat itself. For instance, Biester et al. (2012) have shown that processes connected to decomposition, such as mass loss and increasing peat density, strongly influence the concentration of some elements whereas others may remain unaffected. They observed that elements associated with the lithogenic (soil dust) fraction (zirconium, titanium and silicon) were exponentially enriched by mass loss and increasing density, whereas biophilic and organically bound elements (nitrogen and halogens—chlorine and bromine; Biester et al. 2004), were linearly enriched through mass loss and not affected by increasing density. They also found that redox-sensitive and mobile elements such as chromium, manganese and iron, but also calcium and zinc that are originally bound to the organic substrate of the peat, were released and recycled during peat decomposition. Hansson et al. (2013) showed that quantitatively determining decomposition itself can also be difficult. They found that although bulk density (Shotyk et al. 2005), humification (presented as light transmission) (Blackford and Chambers 1993) and C/N ratios (Kuhry and Vitt 1996) are all commonly used as proxies for the degree of peat decomposition, they can show both a clear spatial variability within the same coring area on a bog, but more importantly these three proxies show great variation between them within one and the same core. The results of Hansson et al. (2013) clearly indicate that peat decomposition is not fully captured by any single proxy. What these studies highlight is that although this particular research topic, i.e., peat decomposition and its influence on peat geochemistry, is still poorly investigated, it does indicate that post-depositional, diagenetic processes can have an effect on some elements in the geochemical record and thus influence our interpretations in terms of past atmospheric deposition. One should therefore always use a multi-core and multi-proxy approach when studying geochemical records preserved in peat, e.g. peat accumulation and decomposition, as well as past metal accumulation rates.

Future Outlooks

The strongest support for the utility of peat to study spatial and temporal patterns of metal pollution comes from the extensive number of studies on the lead record in peat. The agreement in the lead record between peat, lake sediments, ice and herbaria samples—despite significant differences in biogeochemistry and other physicochemical properties of each of these natural environmental archives—is strong evidence for the utility of peat as a record. This is further supported by the fact that mosses have been well established as a contemporary tool to monitor pollution patterns. As discussed, however, this cross-validation between different archival media has relied almost exclusively on lead, and there is room to develop this link further for other metals.

Another area of development is to utilize the metal records in peat not only in the context of tracing pollution patterns through time and space, but also to use these data to study other environmental questions. For example, changes in the composition of metals within the peat may reflect different atmospheric or climatic regimes, whereby air masses transporting metals to a particular site change over time, or that differences in climate (e.g., wind strength or intensity) promote grain-size fractionation and thus changes in trace metal composition. As an example of the latter, Shotyk et al. (2002) observed varying relationships between scandium, titanium and zirconium, which are all associated with the deposition of atmospherically transported soil dust. The elements occur preferentially in different size fractions and thus differences between them within the peat profile would reflect different potential grain sizes transported to the Swiss bog site. This was also shown by Martinez Cortizas et al. (2002) who invoked physical fractionation to explain the difference in Ti and Zr content in two cores from bogs located at different elevation in NW Spain. Other trace metals, and in some cases also their stable isotopes, would potentially aid in the study of past changes in soil dust sources, as was suggested by Kylander et al. (2010) in a synthesis of lead isotope data from pre-anthropogenic levels in peat records from around the globe. The application of metal records in peat to dust and climate change-studies is an arising and exciting area, which likely will become important for the future utility of peat cores as a natural archive.

An increasing number of studies have also applied multivariate statistical techniques (e.g. principal component analysis—PCA—or projection of latent structures—PLS) to identify the main processes responsible for the chemical signature within the peat cores and improve the identification of signals and drivers that control changes in peat chemistry through time (Muller et al. 2008; Schofield et al. 2010; Biester et al. 2012; Gallego et al. 2013; Martinez Cortizas et al. 2013). Although the benefit of applying multivariate statistical tools such as principal components analysis (PCA) and partial least squares (PLS) when interpreting geochemical records has been shown, the application of these in peat-based geochemical studies is still not extensive. A continuous development and increase in the application of these statistical tools is therefore very likely in the near future.

Finally, there is always a need to improve our process understanding between the deposition of an atmospheric signal—be it metal pollution or soil dust, for example—and the preservation of the signal within the archive. While some signals, such as lead, remain essentially unaltered, others must be interpreted more carefully. Also, the changes that occur within the peat may provide valuable information on environmental changes, such as processes associated with decomposition and the resulting enrichments of trace metals.

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Historical Contaminant Records from Sclerochronological Archives

Jessica Carilli, Branwen Williams, Bernd R. Schöne, Richard A. Krause and Stewart J. Fallon

Abstract A number of marine and freshwater organisms, including scleractinian and proteinacious corals, coralline algae, sclerosponges, and bivalve mollusks, secrete skeletons that grow larger over time and may record environmental contaminants over the lifespan of an individual. Most of these organisms also form periodic growth patterns (growth increments, lines or bands) that can be used to accurately date contaminant archives produced from chemical or physical analysis of sequential skeletal samples (termed sclerochronology). The majority of records produced from these organisms thus far have focused on paleoclimate reconstructions, but there is a vast potential for information on changes in contaminant levels over time. Importantly, sclerochronological archives offer the potential for pre-anthropogenic baselines of naturally occurring substances to estimate the magnitude of anthropogenic pollution. This chapter presents an overview of existing contaminant records and discusses the limitations and potential for future work using archives derived from marine organism skeletons.

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Introduction

Environmental contaminants are any substance introduced in potentially harmful quantities by human activity, and include inorganic (e.g., heavy metals, radionuclides, rare earth elements) and organic pollutants (e.g., sewage, PCB, PAH, DDT). Sources of contamination to the ocean and freshwater bodies include: (a) land-based runoff delivered by rivers, surface runoff, groundwater, and sewage outfalls; (b) leaching or spills from boats; and (c) atmospheric deposition. Land-based pollution represents the largest fraction of contaminants and has received the most attention in sclerochronological studies. Specific sources of land-based runoff considered detrimental to coastal ecosystems include: (a) sedimentation, which can cause physical smothering or abrasion of benthic organisms, reduced light levels for photosynthesis, or enhanced delivery of sediment-bound contaminants; (b) toxic runoff (heavy metals, pesticides, etc.) from industrial and agricultural activities; (c) mining activities; and (d) sewage, especially when raw or not treated completely before discharge.

Contaminants can be measured by direct chemical analysis of water and sediments, but these methods provide no information about the concentrations of bioavailable toxins–those available for uptake and accumulation by living organisms—or more importantly, variability over time. Bioavailable toxins ultimately pose the largest health risks to humans and other organisms, and are thus important to monitor (Rainbow 1995). Samples of soft tissues and skeleton from aquatic organisms are therefore commonly utilized as environmental biomonitors. For example, since the initiation of the Mussel Watch program in the mid 1970s (Goldberg 1975), thousands of studies have been conducted worldwide to monitor water quality using bivalve mollusks. However, most of these studies have analyzed pollutants in soft tissues or whole bivalve shells (e.g., Purchase and Fergusson 1986; Nicholson and Szefer 2003; Bellotto and Miekeley 2007), presenting several drawbacks. Tissue samples provide only a brief temporal snapshot of contaminants, and while multiple organisms can be sampled over time to construct time series of changes in pollutants, artifacts from baseline contaminant concentrations among individuals may bias estimates of temporal variability (e.g., Carriker et al. 1982). On the other hand, analyses of whole shells provide only a time-averaged perspective over the life span of the organism. Further, soft tissue contaminant concentrations can be misleading because some organisms, such as *Mytilus* spp. bivalves, depurate certain inorganic elements very quickly (Lares et al. 2005) while other elements remain in the tissues for long periods of time (Boisson et al. 1998).

More promising are highly temporally resolved records of contaminants obtained from skeletal archives. Numerous marine organisms secrete skeletons from seawater that accrete over time, which have the potential to record a history of water quality at the time of skeletal deposition. Organisms such as scleractinian (stony) corals, bivalve mollusks, coralline algae and proteinaceous corals contain annual or subannual growth banding, similar to tree rings, which allows precise

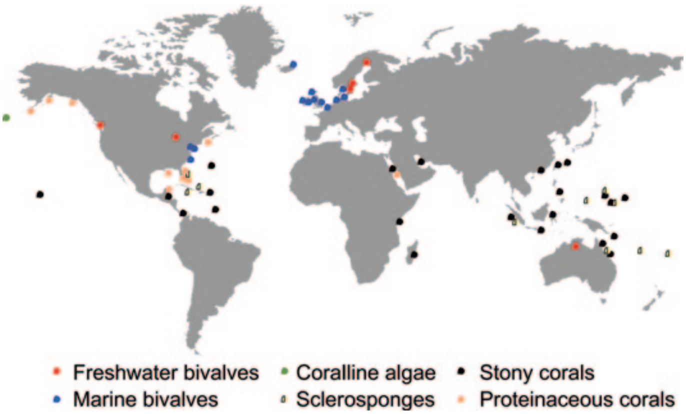


Fig. 1 Map showing approximate localities of multiyear historical sclerochronological contamination records referenced in this chapter. *Red* = freshwater bivalves; *blue* = marine bivalves; *green* = coralline algae; *yellow* = sclerosponges; *black* = stony corals; *salmon* = proteinaceous corals

dating of skeletal-derived records of water quality when properly calibrated. Time series of water quality proxies obtained from sclerochronological archives have the advantage that they are well dated, geographically diverse, serve to both provide baselines before studies began in a region, and provide temporal averaging as compared with discrete snapshots obtained with water or tissue samples.

In this chapter we will discuss records of contamination produced by analyzing the skeletal structures/biominerals of scleractinian corals, proteinaceous corals, coralline algae, bivalve mollusks, and sclerosponges (Fig. 1). We describe the physiology and biomineralization processes for each organism, review the types of contaminant archives that have been produced, and discuss the potential and limitations of records from each organism.

Physiology and Archive Development

Corals Corals are animals in the phylum Cnidaria, which includes sea anemones and jellyfish. Corals are mostly colonial, comprised of numerous polyps that each contain a ring of tentacles with stinging nematocyst cells surrounding a mouth that opens into a gastrovascular cavity and also acts to expel waste products. Corals are suspension feeders, capturing plankton and detritus with their tentacles (Lewis and Price 1975), and can also feed on dissolved organic matter (Sorokin 1973). Many shallow-water corals contain symbiotic zooxanthellae algae that photosynthesize and at least partially sustain the host corals (Muscatine and Porter 1977; Bo et al. 2011). Corals used for sclerochronological studies can be divided into two major groups: the scleractinian, or stony corals, and the proteinaceous corals, which include both "gorgonin" Alcyonaceans (soft corals) and Antipatharians (black corals).

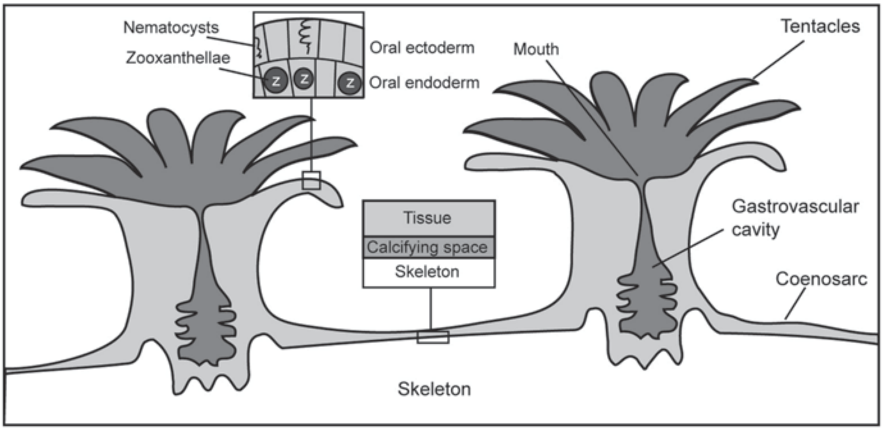


Fig. 2 Schematic of two coral polyps showing major morphological features

Scleractinian corals have a relatively thin tissue layer sitting atop an aragonitic calcium carbonate ($CaCO_3$) skeleton that the coral produces (Fig. 2). Most shallow-water stony corals contain zooxanthellae, from which they obtain the majority of their energy. Stony coral colonies take on a range of morphologies: branching, plating, encrusting, or massive (boulder-shaped; Fig. 3). Stony corals continuously grow larger by adding onto their skeletons; new skeleton is formed in the "calcifying space" between the tissue and the existing skeleton. The mechanisms of coral calcification are still not completely understood. In the most recent models of calcification, some seawater can enter the calcifying space directly, either through tight passages between the tissue cells or via vacuolization through the tissue layer, or ions may diffuse or be actively pumped through the tissue layer, thus delivering contaminants to the site of calcification (Allemand et al. 2011). Through active pumping, the pH in the calcifying fluid is increased until aragonite crystals precipitate; an organic matrix helps control the morphology of the skeleton

Fig. 3 **a** Reef dominated by branching and plating coral colonies. Transect tape across image is 1 cm wide. Tabuaeran Island, Republic of Kiribati (photo J. Carilli). **b** Reef dominated by large massive coral colonies. Kingman Reef, United States of America (photo M. Kospartov)

(Cohen and McConnaughey 2003; Allemand et al. 2011; Tambutté et al. 2011). During the calcification process, contaminants are incorporated into the skeleton, often in concentrations reflecting the environmental conditions during skeletal deposition and thus creating an archive of those conditions over the lifetime of the coral (Corrège 2006). Analyzing the concentrations of various contaminants in coral skeletal samples gives an indication of their relative concentrations in the surrounding seawater when that skeleton was formed. Note that there is some evidence that skeletal calcification rate affects at least some elemental and isotopic compositions in corals (e.g., Cohen and Hart 1997; Gagan et al. 2012); thus a better understanding of calcification mechanisms and contaminant incorporation is needed to utilize coral records to their full potential.

In the early 1970s, Knutson and colleagues described annual growth banding revealed by x-ray in corals from Enewetak atoll (Knutson et al. 1972). This finding paved the way for studies using the chemical composition of coral skeletons to reconstruct environmental conditions with high temporal resolution by allowing precise date control on the reconstructions. Massive corals are typically used for reconstructing records of contaminants because they lend themselves to having cylindrical core samples removed with a specialized drill, thus leaving the majority of the colony intact. Annual growth banding is also most easily assessed in massive corals; these can be imaged using x-rays (Knutson et al. 1972) or CT scans (Cantin et al. 2010), or measured via gamma densitometry (Chalker and Barnes 1990) (Fig. 4).

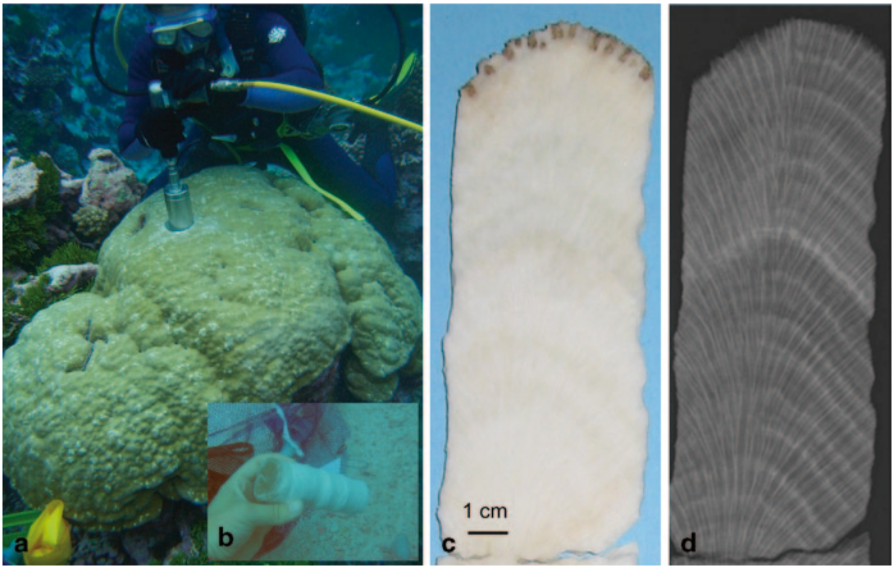


Fig. 4 **a** Collecting a coral core sample using an air drill. **b** resulting core with live tissue on top. **c** slab removed from center of core to be used for geochemical analysis, and **d** x-ray of coral slab showing annual high/low density couplets similar to tree rings

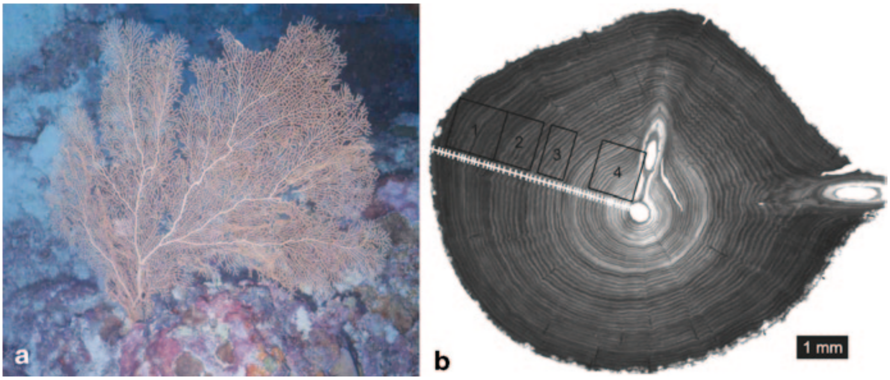


Fig. 5 **a** Gorgonian soft coral gross morphology. **b** Basal thin section from the axial skeleton of the *black* coral *Stauropathes arctica*. White dashes indicate annual growth rings (reproduced from Sherwood and Edinger 2009)

Proteinaceous corals are colonial cnidarians that form a protein-rich, organic skeleton. They have a global distribution from surface waters to several thousands of meters deep. Specimens below 100 m depth are often called deep-sea corals. Although often living in the deep ocean, these corals can record changes in surface waters because they obtain at least some portion of their food from particulate matter and/or zooplankton exported from surface waters (Roark et al. 2005; Sherwood et al. 2005a). In shallow water, inorganic nitrogen taken up by zooxanthellae serves as an important nitrogen source to gorgonian corals (Wainwright 1967; Ribes et al. 1998; Baker et al. 2010a). Therefore, contaminants in surface waters, such as terrestrial effluent, may be recorded in the skeletons of proteinaceous corals (Williams et al. 2007a, Baker et al. 2010b).

Gorgonians have a gross morphology resembling an underwater tree affixed via the holdfast to hard substrate on the seafloor (Fig. 5a). The skeleton consists of a central axial core composed primarily of gorgonin, a flexible, horny material, covered by a layer of polyps connected by living tissue. Each polyp has a columnar body ending in a mouth, surrounded by eight tentacles. Gorgonians have calcite sclerites in the tissue of the polyps often used for taxonomic identification. Some species also have calcite in the skeleton. Corals in the family Isididae (bamboo corals) form solid calcareous internodes alternating with gorgonin nodes along the axial core. The solid axis in corals in the family Primnoidae have concentric layers of calcified material embedded in the gorgonin skeleton. Specimens from within these two families are most commonly used as sclerochronological archives in deep water (e.g., Williams et al. 2007b; Sherwood et al. 2009; Hill et al. 2012). In shallow water, a variety of taxa are used including *Gorgonia* sp. and *Pseudopterogorgia* sp. (Ward-Paige et al. 2005; Baker et al. 2010a).

Black corals have a similar gross morphology as the gorgonians but form a skeleton composed primarily of protein-rich chitin, surrounding a central canal in the axial core (Fig. 5b). Small spines in the skeleton are used for taxonomic identification. The black corals have polyps with six tentacles and are covered with a layer of tissue. No calcite is present in the skeleton, polyps, or tissue.

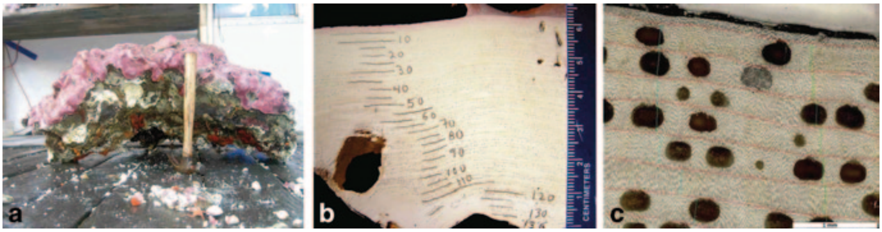


Fig 6 Coralline algae: **a** *Clathromorphum nereostratum* from the Aleutian Islands. **b** Section of specimen with annual growth increments marked. **c** Details of cross-section with circular conceptacles (reproductive) structures. (Modified from Halfar et al. 2011)

Proteinaceous corals can be long-lived: on the order of hundreds of years for gorgonians and thousands of years for black corals (Risk et al. 2002; Roark et al. 2009). The gorgonians and black corals can form skeletons laid in concentric, coeval rings where the outer ring is the most recently formed. In some taxa, radiometric dating and staining techniques indicate annual periodicity in the growth rings (Andrews et al. 2002; Sherwood et al. 2005b; Prouty et al. 2011). Therefore, there is potential for annually-resolved records of environmental contamination dating back millennia from these animals.

Coralline Algae Coralline algae, family Corallinaceae in the phylum Rhodophyta, have a global geographic range. Coralline algae rely on photosynthesis for energy and are thus limited to shallow coastal waters. They form a calcite skeleton containing elevated amounts of magnesium (Mg) but otherwise display a wide range of biological adaptations resulting in a high morphological variability and making taxonomic identification of living and fossil specimens difficult (Cabioch 1988; Foster 2001).

The thallus (body) of coralline algae is composed of a chain of cells (filaments) that may fuse laterally and/or form secondary lateral pit connections. Cells add to the tip of each cell filament—the meristem—to grow the algae from a thin crust. Calcification in the meristem occurs directly in the vegetative cell wall as a deposition of high-Mg calcite crystals (Borowitzka 1982). The epithallus comprises the cells directly above the meristem that are not involved in photosynthesis. These cells are continuously sloughed off at the surface and/or grazed by limpets, chitons, and sea urchins (Keats et al. 1997; Steneck et al. 2002). Below the meristem is the perithallus, which is largely preserved after formation with the exception of conceptacle development; conceptacles are cavities containing the reproductive organs of the plant (Fig. 6).

There are two theories to explain calcification in the coralline algae. The first is the Organic Matrix Theory by which polysaccharide complexes, possibly cellulose, in the cell walls act as nucleation sites to concentrate calcium or bicarbonate ions (Borowitzka 1982). This is supported by the location of crystals within an organic matrix (Borowitzka and Vesk 1978) and could explain why the coralline algae precipitate calcite while the green algae precipitate aragonite (Johansen 1981). A second theory is the Bicarbonate Usage Theory in which bicarbonate is used as a photosynthetic substrate; this stimulates calcification by increasing extracellular pH high enough to increase the concentration of carbonate ions through the extrusion of hydroxyl from the cell, leading to precipitation of calcium carbonate in the presence of calcium ions (Borowitzka 1982). In addition to calcification linked to photosynthesis, calcification in coralline algae can occur in the dark (Pentecost 1978) as some species are able to thrive in areas with substantial winter ice cover (Adey and Hayek 2011) due to their ability to use stored carbohydrates and CO_2 dark assimilation (Kremer 1981; Freiwald and Henrich 1994).

Lithothamnion and *Clathromorphum* are the two primary genera of coralline algae used as sclerochronological archives. Plants in these genera are non-articulated with monomerous thalli. Species used for sclerochronologial archives are primarily from higher latitudes, possibly because strong seasonal cycles in temperature and light drive variability in cell characteristics. During the cold dark winter season, cells shorten and widen creating clear growth banding patterns in the skeleton (Fig. 6). In the genus *Clathromorphum*, seasonal variations in calcification generate interfilament crystals in the summer in addition to inner wall crystals formed year round (Adey et al. 2013). These coralline algae genera are a major producer of calcium carbonate grains at higher latitudes (Freiwald and Henrich 1994). Temperature likely determines the lower latitude distribution, probably due to restrictions on reproduction or competition including grazing.

Lithothamnion spp. are a type of rhodolith (maërl): free-living nodules composed at least partially of branching crustose benthic marine algae. As the orientation of the rhodolith relative to the surface may change over time, the entire surface of a rhodolith is photosynthetic. They are slow-growing and single specimens may be more than a century in age (Frantz et al. 2000). They are able to grow in environments generally unfavorable to faster growing non-calcified macroalgae. Individual rhodoliths of various species, sizes, abundance, shape, and both dead and alive, can accumulate to form communities called rhodolith beds (Foster 2001). These beds can accumulate over thousands of years (Freiwald et al. 1991; Kamenos 2010).

Clathromorphum spp. are an encrusting coralline algae consisting of a thallus with a single system of contiguous filaments linked solely by cell fusions. Specimens are generally fixed to the substrate and only grow upwards toward the surface. The meristem is sunken underneath the overlying primary photosynthetic tissue, protecting newly formed calcite from grazing by other organisms (Adey 1965). Limited marginal growth results in dome shaped plants in some species that may form crusts up to tens of centimeters thick (Adey 1965). Single plants can grow for hundreds to potentially thousands of years in both the northern North Pacific Ocean and the northwest Atlantic Ocean (e.g., Halfar et al. 2007; Adey et al. 2013), and potentially the southern hemisphere as well.

Bivalves Bivalve mollusks (class Bivalvia) belong to the phylum Mollusca, one of the most diverse groups of the animal kingdom. Together with the gastropods, bivalves constitute 95 % of all mollusk species and form the clade Pleistomollusca (Kocot et al. 2011). Bivalves inhabit nearly every aquatic environment including shallow waters and deep-sea environments, the tropics to high latitudes as well as freshwater, marine and brackish settings. The majority of these more or less sedentary and solitary organisms live attached (e.g., Mytilidae) or cemented (e.g., Ostreidae) to hard substrates or floating objects (pterioid bivalves), resting on the sea floor, or within burrows in soft sediment, wood (e.g., *Xylophaga* spp., *Teredo* spp.) or rock (e.g., *Hiatella* spp., *Pholas* spp.). While some burrowers ascend to the sea floor to feed, others with a reduced foot cannot reposition themselves in the sediment as adults and are therefore essentially stationary below the sediment-water interface (as deep as 140 cm in the case of *Panopea* spp.) for most of their lives. In order to feed, these bivalves extend long inhalant and exhalant siphons to the sediment-water interface. Feeding modes are diverse (Purchon 1968), ranging from filter/suspension-feeding (phytoplankton, resuspended organic debris; e.g., *Cerastoderma* spp., *Mya* spp., *Mytilus* spp.), deposit-feeding (organic debris and diatoms from the sediment surface; e.g., *Arctica islandica*, *Macoma* spp., *Scrobicularia* spp.), detritus-feeding, carnivorous (*Poromyoidea* spp.), photosymbiotic (e.g., *Tridacna* spp.) and chemosymbiotic (e.g., *Bathymodiolus* spp., *Keletistes rhizoecus*).

All organs of these bilaterally-symmetric animals are encased by the mantle that in turn is protected by a two-pieced shell: a right and left valve (Fig. 7a). Both halves of the shell are dorsally connected by an elastic organic structure, the ligament (Fig. 7b), interlocking ridges (“teeth”), and grooves stretching in an approximately anteroposterior direction. The ligament forces the valves open when the adductor (closing) muscles are relaxed. The outer shell surface is protected against dissolution and microbial attack by the periostracum (Fig. 7b, c), a thin, often yellow to brownish organic layer (Fig. 7a) that can also serve as a camouflage against predators. The periostracum is secreted by specialized cells of the periostracal mantle groove located between the outer and middle folds of the mantle (Fig. 7c). Since the periostracum is connected with the mantle (Fig. 7c), the extrapallial spaces—the sites of shell formation—are isolated from the ambient water (Wilbur and Saleuddin 1983). Ions from the ambient water reaching the extrapallial fluids (EPF; actually more gel-like than fluid; Addadi et al. 2006) must pass through the mantle epithelia by active (ion pumps) or passive (ion channels) transport mechanisms (e.g., Wheeler 1992; Cohen and McConnaughey 2003; Carré et al. 2006). Likewise, pollutants derived from food and detoxification processes have to pass the semipermeable membranes of the mantle to reach the EPF (Marigómez et al. 2002) and eventually end up in the shell.

The shell can be considered as a bioceramic consisting of $CaCO_3$ (typically aragonite and/or calcite, rarely vaterite; Nehrke et al. 2012) and organic substances (chitin, proteins, lipids, mucopolysaccharides and glycosamides). The exact processes involved in the biomineralization of bivalve shells are still debated, but it is clear that biominerals are formed away from elemental equilibrium with the ambient environment (e.g., Marin et al. 2012).

It is commonly assumed that the cells of the outer mantle epithelium produce an organic template (Wilbur and Saleuddin 1983) of chitin (Addadi et al. 2006) that acts as a matrix (scaffolding), which orchestrates and mediates the formation of $CaCO_3$ and controls which ions become incorporated in the shells. These organic

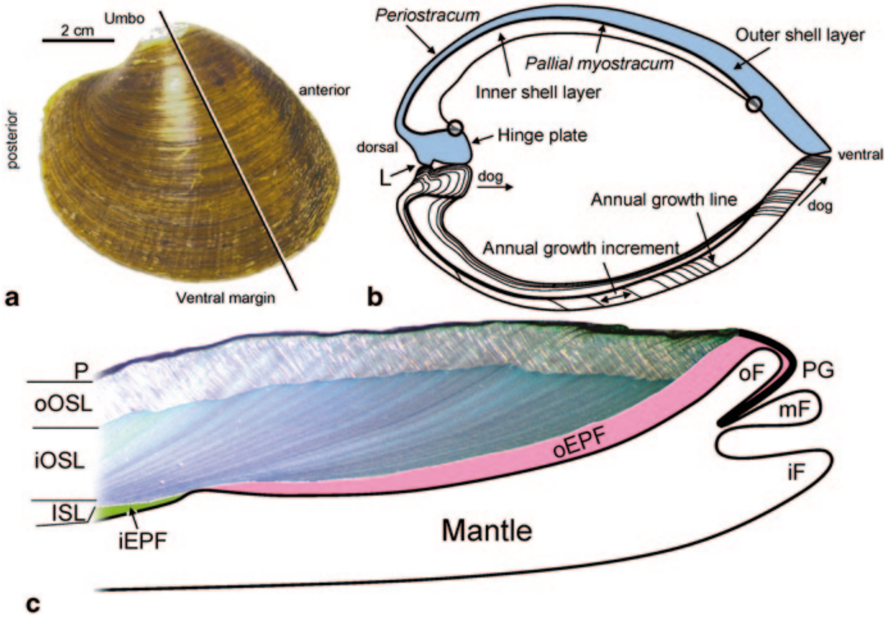


Fig. 7 Shell formation in bivalve shells. Dorsoventral cross-sections (**a**; *left* valve of *Arctica islandica*) are used to study shell internal growth patterns and crystal fabrics (**b**; *A. islandica*). Open circles denote pallial lines where the mantle is attached to the shell. **c** The outer and inner shell layers are formed by the outer and inner extrapallial fluids, respectively (example species: *Margaritifera falcata*). Note distinct annual growth lines in the outer shell layer. *dog* direction of growth; *P* periostracum; *L* ligament; *oOSL*, *iOSL* outer, inner sublayer of the outer shell layer; *ISL* inner shell layer; *oEPF, iEPF* outer, inner extrapallial fluid; *oF, mF, iF* outer, middle, inner mantle fold; *PG* peristracal groove

constituents become part of the biomineral as an intercrystalline matrix (Marin et al. 2012). $CaCO_3$ is probably transported to the site of calcification in the form of membrane-coated vesicles (Jacob et al. 2008) containing amorphous calcium carbonate (ACC; Weiner et al. 2003). In these vesicles, which are released by mantle epithelial cells into the EPF by exocytosis, enrichment in trace and minor elements, specifically Mg (Raz et al. 2003), prevents ACC from crystallization prior to reaching the site of calcification. Only within the EPF does ACC become destabilized and converted into a crystalline polymorph of $CaCO_3$ (Addadi et al. 2006), initially vaterite and then aragonite or calcite. The crystalline phase represents a nanocrystal assemblage (also known as mesocrystals; Cölfen and Antonietti 2005) containing the organic macromolecules that mediated and controlled their formation. Amongst other tasks, proteins, sugars, lipids as well as trace and minor elements promote and modulate mineral growth (Gotliv et al. 2003), and determine the habit, size and orientation (crystal fabrics; also known as 'shell microstructures') of the mesocrystals (e.g., Isowa et al. 2012). Some organic macromolecules become incorporated into the shell as intracrystalline organic substances (Marin et al. 2012), whereas the trace elements can be adsorbed to mineral surfaces (Carriker et al. 1980), bound to organics (Lingard et al. 1992; Schöne et al. 2010), substituted for Ca^{2+} in the crystal lattice (Carriker et al. 1980) or form separate mineral phases (Carriker et al. 1982; Fritz et al. 1990).

Typically, two distinct layers, an outer and an inner shell layer (see Ropes 1984) can be discerned in cross-sections of bivalve shells that differ in overall crystal fabric and chemistry (e.g., Fuge et al. 1993; Carell et al. 1995; Lazareth et al. 2003). Often, the outer shell layer is further subdivided into an inner and outer sublayer (e.g., Simkiss and Wilbur 1989), defined again by different crystal fabrics and chemistry (Schöne et al. 2012). These layers are formed in different extrapallial fluids distinctly separated by the myostracum.

Periodically the biomineralization process slows and stops, producing shell growth lines (Fig. 7b). Periodic shell growth patterns vary from semidiurnal (Evans 1972; Hallmann et al. 2009), to daily (Dunca and Mutvei 2001; Clark 2005), fortnightly (Orton 1923; Evans 1972) and annual (Pulteney 1781; Jones 1980). Annual increment counts have revealed extraordinary life-spans of several hundreds of years for a variety of species (e.g., Shaul and Goodwin 1982; Jones 1983; Mutvei et al. 1996; Schöne et al. 2005; Wisshak et al. 2009; Butler et al. 2012; Selin and Dulenina 2012).

Sclerosponges Of the large number of species of sponges described worldwide, which make up the phylum Porifera, only 15 species of extant sponges construct calcareous skeletons (Willenz and Pomponi 1996). These are the living representatives of groups of sponges from the late Paleozoic and Mesozoic known as Stromatoporoidea, Chaetetida and Sphinctozoa. These groups of coralline sponges (or sclerosponges) were some of the original dominant reef-building organisms before they were out-competed by scleractinian corals (Reitner 1987). Sclerosponges now inhabit low light areas and deep water, where they are not in competition with zooxanthellate scleractinian corals. In shallower areas (~ 10 m) they occupy reef caves and overhangs (Wörheide 1998).

Sclerosponges have a wide geographical distribution. *Astrosclera willeyana* and *Acanthocheatetes wellsi* are found in the Indo-Pacific tropical regions at depths down to 200m (Hartman 1980). In the Atlantic and Caribbean, *Ceratoporella nicholsoni* can be found at depths down to 1000 m (e.g., Böhm et al. 1996; Druffel and Benavides 1986). Geochemical records obtained from sclerosponges can therefore provide information on the history of the upper water column in much of the ocean. Sclerosponges are typically pyriform-half spherical (mushroom-shaped; Fig. 8). They have an in/exhalent water system that extends to the basal skeleton throughout the tissue layer.

Sclerosponges deposit solid aragonitic and calcitic skeletons, growing radially over time with a thin living tissue layer on the outside of the skeleton. Sclerosponges do not, however, exhibit annual growth bands like corals. Therefore, in order to make age and growth rate determinations, radiometric dating techniques are needed. The most often used techniques are ^{210}Pb, ^{14}C and U/Th (e.g., Benavides and Druffel 1986; Böhm et al. 2002; Swart et al. 2002; Fallon et al. 2005). These ageing techniques have led to estimates of skeletal accretion rates of 0.1–0.4 mm yr^{-1} for *C. nicholsoni* (Böhm et al. 1996, 2002; Swart et al. 2002) and 0.2 to 1.9 mm yr^{-1}

Fig. 8 Examples of sclerosponge species used for geochemical reconstructions: **a** *Astrosclera willeyana* (photo S. Fallon). **b** *Acanthocheatetes wellis* (photo S. Fallon). **c** *Ceratoporella nicholsoni*. (Reproduced with permission from Böhm et al. 2002)

for *A. willeyana* and *A. wellsi* (Wörheide 1998; Fallon et al. 2003; Grottoli et al. 2010). Earlier studies using direct staining techniques (Alizarin Red-S and Calcein) determined extension rates of 0.1–0.2 mm yr^{-1} in *C. nicholsoni*, which are consistent with the later radiometric estimates (Willenz and Hartman 1985; Grottoli et al. 2010).

Existing Archives

Inorganic contaminants such as heavy metals can be recorded in marine $CaCO_3$ skeletons in a number of ways: particles might become trapped in the skeleton during growth (Barnard et al. 1974), dissolved ions can substitute for calcium in the aragonite or calcite framework (Shen and Boyle 1988), or trace elements can be adsorbed onto the skeleton or otherwise bound in the crystal lattice (Corrège 2006). In most cases, elemental concentrations in calcium carbonate skeletal samples are standardized by calcium concentration to account for differences in skeletal mass between samples, and reported as element/Ca ratios.

Contaminants can also be recorded in the organic fraction of sclerochronological archives, for example in the organic matrix of stony corals or the hard organic skeletons of proteinaceous corals. Ingalls et al. (2003) reported that organic matter is well preserved in massive stony coral skeletons on the order of hundreds of years, especially the inter-crystalline fraction. Indeed, Yamazaki et al. (2013) report preservation of intra-crystalline organic matter in a stony coral more than 3 million years old. While the total organic content of stony coral skeletons is generally quite low (0.02–0.11 % according to Ingalls et al. 2003, but up to 1–2.5 % according to work cited in Allemand et al. 2011), the relative stability of the material indicates that coral organic material offers good potential for constructing records of organic contaminants. In the proteinaceous corals, contaminants may be taken up through heterotrophic feeding or via zooxanthellae, then directly incorporated into the proteinaceous skeleton. The skeleton of these corals is preserved on millennial timescales (Roark et al. 2009; Sherwood et al. 2011).

Boring organisms including fungi (Priess et al. 2000) and algae (Lukas 1974) are ubiquitous in stony coral skeletons, and their organic remains may swamp the coral organic matter signal (Risk et al. 2009a). However, the remains of these organisms might still give a robust measure of contaminants in the water column while they were growing (Risk et al. 2009a). Given that endolithic algae blooms tend to occur just under the outermost portion of the coral skeleton (Hartmann et al. 2010; Carilli et al. 2010), and fungi may then attack these algae (Priess et al. 2000), theoretically these boring organisms would have grown at approximately the same time as the skeleton—on which the chronology is based—was formed (perhaps up to a maximum of 1 year delayed from the time of skeletal formation; Hartmann et al. 2010). Therefore, analyses of the bulk organic fraction of coral skeletal samples may be temporally smoothed, but still offer the potential for useful records. However, the influence of population fluctuations of boring organisms (Carilli et al. 2010) might influence the incorporation of organic pollutant signals in coral skeleton over time.

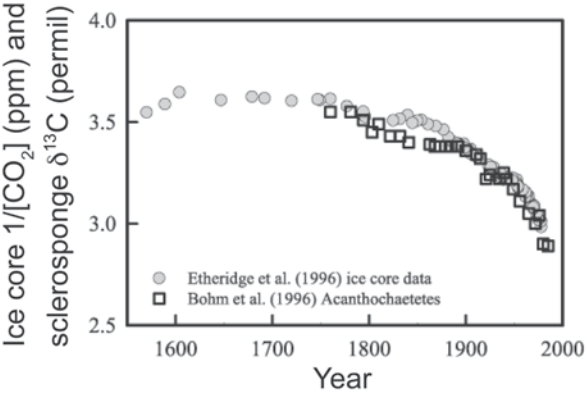
Below, we present a review of studies that have used sclerochronological archives to reconstruct a range of environmental contaminants, with varying degrees of success.

Anthropogenic CO_2

To date, the majority of geochemical records from sclerochronological archives have been used to reconstruct past water temperature and salinity, often using both $\delta^{18}O$, Sr/Ca and/or Mg/Ca (e.g., *sclerosponges*: Druffel and Benavides 1986; Böhm 1996; Wörheide 1998; Swart et al. 2002; Haase-Schramm et al. 2003; Fallon et al. 2005; Rosenheim et al. 2005; *corals*: Ren et al. 2003; Cahyarini et al. 2008; *bivalves*: Jones et al. 1989; Wefer and Berger 1991; Schöne et al. 2004; *coralline algae*: Bond et al. 2005; Halfar et al. 2007; Hetzinger et al. 2009; Gamboa et al. 2010; Kamenos 2010; Chan et al. 2011; *gorgonian corals:* Bond et al. 2005): These records are useful to place current anthropogenically-induced climate change into context, though they are only indirect records of CO_2 contamination.

Sclerochronological archives can also provide direct estimates of increasing anthropogenic carbon dioxide emitted into the atmosphere by the burning of fossil fuels. Carbon stable isotopic ratios ($\delta^{13}C$) tracks fossil fuel emissions because this CO_2 has very low $\delta^{13}C$ values. Fossil fuel emissions have been steadily decreasing the $\delta^{13}C$ signature of atmospheric carbon—termed the Suess Effect—and consequently marine carbon, over time (Keeling 1979; Quay et al. 2003). This depleted $\delta^{13}C$ carbon is used by primary producers and is transferred up the food web. Records of decreasing $\delta^{13}C$ values towards the present due to the $\delta^{13}C$ Suess Effect have been produced from proteinaceous corals (Sherwood et al. 2005a; Williams et al. 2007a; Baker et al. 2010a), stony corals (e.g., Swart et al. 2010), bivalves (e.g., Butler et al. 2009; Schöne et al. 2011), and coralline algae (Williams et al. 2011). Sclerosponges have been shown to be particularly good recorders of the Seuss Effect, because they incorporate both oxygen and carbon in isotopic equilibrium with

Fig. 9 Ice core CO_2 data from Etheridge et al. (1996) and *Acanthocheatetes wellis* sclerosponge $\delta^{13}C$ data from Böhm et al. (1996)



the DIC of seawater (Druffel and Benavides 1986; Böhm 1996; Wörheide 1998; Fig. 9), unlike organisms such as stony corals (McConnaughey 1989).

Metals as General Anthropogenic Pollution Tracers

A number of studies have used stony corals as biomonitors by comparing metal/Ca of bulk coral skeleton and/or tissue samples between sites influenced by pollution to varying degrees (e.g., Hanna and Muir 1990; Scott 1990; Guzman and Jimenez 1992; Esslemont 1999; Esslemont 2000; Guzman and Garcia 2002; Ramos et al. 2004; Prouty et al. 2008; Pait et al. 2009). For example, Guzman and Garcia (2002) found high Hg/Ca in coral samples throughout Central America, with higher levels closer to point sources such as ports and an oil refinery.

Other studies have focused on reconstructing specific contaminants through time using a single coral core. Inoue et al. (2004) found that non-lattice-bound Sn/Ca and Cu/Ca in a coral core from Pohnpei, Micronesia were well correlated and elevated between the years 1965–1990 when antifouling boat paints containing these metals were widely used (Fig. 10). Wang et al. (2011) linked Pb/Ca, Al/Ca, and Zn/Ca in a Hong Kong coral core to local development and wartime pollution.

Several studies have combined these techniques, constructing contaminant records from coral skeletons both over time and from several locations with varying pollutant levels to investigate the relative magnitude and timing of various contaminants affecting the studied reefs (e.g., Carilli et al. 2009). In addition to comparing low and high-impact sites, Al-Rousan et al. (2007) added a novel unpolluted baseline by measuring metal/Ca from fossil corals.

In proteinaceous corals, Chan et al. (2012) found that gorgonian corals bioaccumulated Cu, Zn, and Cd in tank experiments. Prouty et al. (2014) found that Re values in black corals were elevated over the past 150–200 years, consistent with anthropogenic Re enrichment in major world rivers.

In one of the first chronological records of heavy metals in bivalve shells, Carriker et al. (1982) measured 16 elements including biologically non-essential heavy

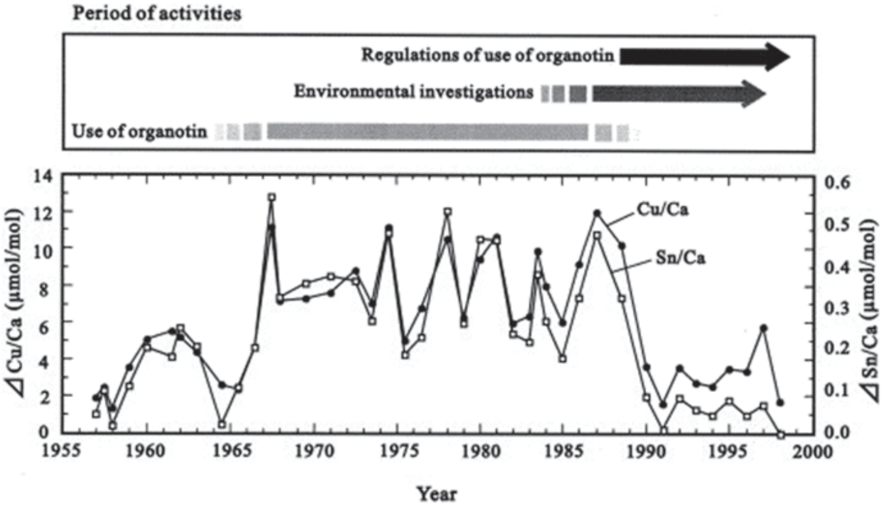


Fig. 10 Time series of extra-skeletal Cu/Ca and Sn/Ca ratios in a ***Porites*** coral collected from Pohnpei Island, Micronesia. The symbol Δ denotes the difference between the value determined with subsequent cleaning treatments. The *upper* panel shows the period of activities related to the worldwide use of organotin (TBT) anti-fouling paint. (Reproduced with permission from Inoue et al. 2004)

metals (e.g., Cr, Zn) in the recently deposited shell material in the ventral margin from three specimens of the oyster *Crassostrea virginica* kept in tanks. Element concentrations varied among shells and with ontogenetic age, but generally exhibited similar trends.

Subsequent studies of temporally aligned trace metal records in bivalve shells benefited from technological advances for in-situ chemical analyses, in particular Laser Ablation—Inductively Coupled Plasma—Mass Spectrometry (LA-ICP-MS). Price and Pearce (1997) presented an intra-annually resolved 3-year record of heavy metals (Pb, Cu, As, Zn, U) from four differently polluted localities of the British Isles using shells of *Cerastoderma edule*, a shallow infaunal suspension feeder. Sharp excursions in the element records were interpreted as short-term anthropogenic pollution events or disturbance events during which sediments and metals were remobilized. Likewise, Pearce and Mann (2006) demonstrated that industrial activity could be reconstructed from Pb, Zn, Cd, and U in shells of the bilvalve *Ensis siliqua*, based on 4-year long chronologies from 13 different localities around the British Isles.

Using a transplant study, Klünder et al. (2008) demonstrated that historical Pb contamination could be qualitatively reconstructed from shells of the bivalves *Mytilus edulis* and *A. islandica*. Similarly, in a study that investigated the cardinal tooth of *A. islandica* from a heavily polluted site in the Mecklenburg Bight, Baltic Sea, Liehr et al. (2005) found Pb and Cu concentrations that were significantly higher than in specimens from a less polluted control site.

In the Great Lakes, Al, Fe and Mn was measured in the shells of up to 13 year-old *Elliptio complanata* bivalve specimens and decreased with increasing ontogenetic age, while Cu and Zn increased (Dermott and Lum 1986). The authors suggested that trace metal concentration in these shells are not "directly related to environmental exposures, but reflect availability and physiological exchange rates during periods of growth".

Putten et al. (2000) were the first to assess in detail the variability in trace element concentrations among contemporaneous specimens. They found similar concentrations of Pb, Mg, Sr, Ba and Mn in the calcitic layer of four shells from individuals of the mussel *Mytilus edulis*. Similar results were presented by Richardson et al. (2001) for Cu, Zn and Pb in six shells of the bivalve *Modiolus modiolus* spanning 1968 to 1979. In addition, Putten et al. (2000) noticed a strong co-variation of seasonal Pb/Ca values with Mg/Ca ratios. They concluded that the seasonal variability in lead concentration was unrelated to the chemistry of the ambient water, but was rather associated with seasonally changing levels of metal-binding organics in the shell; alternatively the incorporation of Pb into the shell may have been directly linked to the Mg levels in the extrapallial fluid. On the contrary, *M. modiolus* shells from a dump site in the North Sea showed significantly higher levels of Pb and Zn than shells from a clean control site and thus did reflect environmental pollution (Richardson et al. 2001). The apparently contradictory results from these studies underscore the potential for organisms to differentially record environmental contaminants, potentially due to varying physiology between species; thus careful calibration studies are needed to best utilize sclerochronological contaminant records.

Others have advocated the immense potential of bivalve shells as universal archives of anthropogenic and natural pollution in aquatic ecosystems, specifically in rivers (e.g., Mutvei et al. 1996; Westermark et al. 1996). Lindh et al. (1988) demonstrated that high spatial resolution (3 µm) µPIXE (µm-scale Particle Induced X-ray Emission) studies can be used to reconstruct seasonal elemental variations in shells of the freshwater bivalve *Anodonta* spp. from Lake Ymsen in Sweden. A 3-year record showed distinct seasonal variations in Mn, Cu and other elements, which the authors related to changes in water chemistry (Lindh et al. 1988). High Mn levels in shell portions deposited during spring were attributed to seasonal acidification. They suggested that sulfur particles accumulated on the snow surface during winter and were released to the water with the snowmelt causing seasonally lower pH levels.

Oil Contamination

Guzman and Jarvis (1996) showed that oil pollution has increased over the last century in Panama using V/Ca from coral cores. Vanadium is elevated in crude oil and can act as a tracer for oil pollution (Guzman and Jarvis 1996).

Readman et al. (1996) reported bands of oil contamination from analyses of solvent-extractable organics in coral heads collected from the Persian Gulf. In a more recent study, Poulsen et al. (2006) also analyzed solvent-extractable organics from Persian Gulf coral cores (Fig. 11). Both studies compared the organic "fingerprints" of different source crude oil samples from the region with the chemical composi-

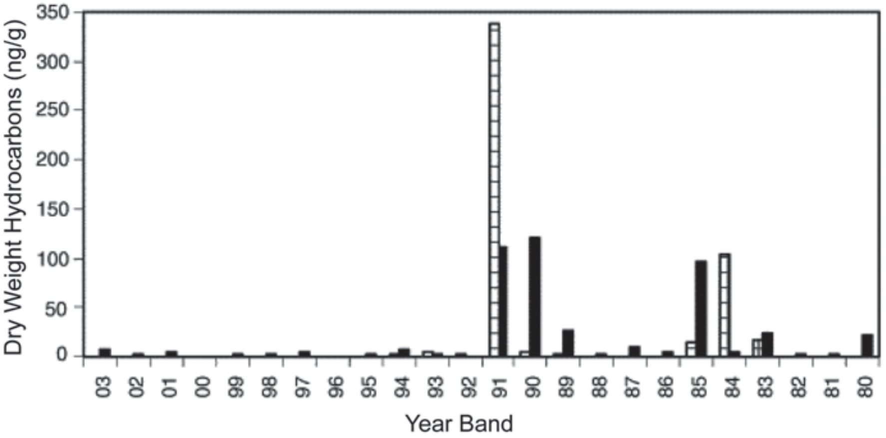


Fig. 11 Sum of triterpane and sterane petroleum biomarkers extracted from annual year-bands of two coral cores (solid and hatched bars) from the Persian Gulf, in ng/g dry weight. Note that time increases from *right* to *left*. (Reproduced with permission from Poulsen et al. 2006)

tion of extracted organics from the corals; both found that although some corals contained elevated levels of oil contamination in year-bands corresponding to the Gulf War, the hydrocarbon fingerprints did not match any of the likely sources. Incorporation and degradation processes for organic contaminants such as crude oil are still unknown for corals, and further study is needed to optimize the use of corals or other sclerochronological archives to pinpoint the source and magnitude of past oil contamination.

Atmospheric Fallout

Shen and Boyle (1987) analyzed lattice-bound Pb/Ca from coral cores at several sites worldwide; their records from Bermuda reflect atmospheric deposition of lead from the introduction and subsequent discontinuation of leaded gasoline in the United States. Shen et al. (1991) also found evidence that Mn/Ca in corals from the Galapagos Islands reflected volcanic ash fallout over the region. Similarly, Gillikin et al. (2005) determined the seasonal and inter-annual Pb/Ca variability from 1949 to 2002 based on shells of 11 live-collected specimens of the bivalve *Mercenaria mercenaria* with partially overlapping life-spans. Although Pb/Ca records of contemporaneous specimens of this species exhibited significant differences, higher Pb contents in shell portions deposited during the late 1970s seemed to reflect the increase in the use of leaded gasoline at that time. This finding was substantiated by a later study that found elevated Pb/Ca levels in shells of *A. islandica* from the East coast of North America, and to a minor degree in shells from the North Sea, which reflected the peak use of leaded gasoline during the 1970s (Krause-Nehring 2012), while a specimen from Iceland contained significantly lower overall levels and no gasoline Pb peak.

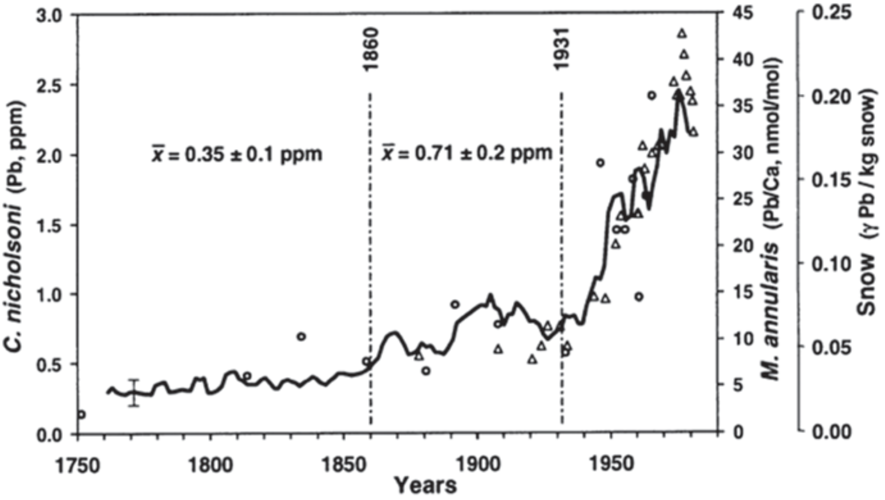


Fig. 12 Sclerosponge Pb concentration in *Ceratoporella nicholsoni* from 1750 to 1990 compared with other Pb records. Solid line: *C. nicholsoni* LA-ICPMS profile from Lazareth et al. (2000); circles: Greenland snow Pb data from Murozumi et al. (1969); triangles: Florida Keys coral Pb/Ca data from Shen and Boyle (1987). (Reproduced with permission from Lazareth et al. 2000)

Similar to scleractinian corals and bivalves, sclerosponges have also been utilized to examine Pb input into the ocean as a proxy for Pb input to the atmosphere. Pb records from Caribbean sclerosponges show strong coherence with Pb levels deposited in Greenland snow (Fig. 12). The Pb record begins to increase ~1750, then a two-fold increase occurs between 1875–1930, followed by a three-fold increase between 1930–1940, again representing leaded gasoline consumption (Swart et al. 2002; Lazareth et al. 2000). The data also show a drop in Pb concentration after 1970, coincident with discontinuation of Pb additives to gasoline in North America (Fig. 12; Swart et al. 2002; Lazareth et al. 2000).

Benninger and Dodge (1986), Lindahl et al. (2012) and Winkler et al. (2012) used coral records to reconstruct fallout of radioactive Pu and U, respectively, from atmospheric bomb testing in mid-century. These records provide the dual function of estimating total fallout due to bomb testing and acting as tracers for oceanic circulation. Similarly, atmospheric bomb-testing increased the radiocarbon content in the atmosphere in the mid-century. This “bomb-pulse” carbon was incorporated into living organisms, and can serve as a tie-point to verify dating chronologies (Grottoli and Eakin 2007; Kastelle et al 2011).

Sewage and Fertilizer

Dodge et al. (1984) found that phosphorus measured in acid-dissolved coral skeletal samples (both total, which included a muffle-furnace step to release organic-bound phosphorus, and inorganic, without this step) appeared to broadly track sewage impacts over 30 years of coral growth at several Caribbean islands. Similarly, Dodge and Gilbert (1984) produced 25-year time series of Pb/Ca from two corals from St. Croix; the coral collected near a sewage outfall had Pb/Ca ratios up to seven times higher than equivalent year-bands in an offshore coral.

Stable nitrogen isotope ($\delta^{15}N$) measurements can also track sewage discharged into the ocean that has not been treated to a tertiary level. $\delta^{15}N$ can be used as a tracer of inorganic fertilizer runoff, which has $\delta^{15}N$ closer to the atmospheric value of 0‰, and/or sewage runoff, which generally has heavier values of $\delta^{15}N$ (Marion et al. 2005; Risk et al. 2009a), in addition to changes in ventilation of nutrient-rich deep water toward the surface (Williams and Grottoli 2010). The preferential elimination of the lighter isotope (^{14}N) in organisms results in a stepwise increase of ~3‰ in $\delta^{15}N$ values with increasing tropic levels (DeNiro and Epstein 1981). As a result, dissolved inorganic nitrogen (DIN) derived from sewage and manure has strongly enriched $\delta^{15}N$ values, typically from 6 to 22‰ (Heaton 1986). In the Caribbean and offshore of Florida, $\delta^{15}N$ values in shallow-water gorgonians were enriched at sites heavily impacted by multiple sources of anthropogenic nitrogen inputs including terrestrial effluent relative to control sites with less anthropogenic influence (Ward-Paige et al. 2005; Baker et al. 2010b; Sherwood et al. 2010). Risk et al (2009b) found increasing $\delta^{15}N$ values in black corals offshore of Jeddah, Saudi Arabia, corresponding to a rise in sewage discharge paralleling population growth in Jeddah. Deep-sea black corals record increased $\delta^{15}N$ values over the past 75 years likely reflecting increased terrestrial effluent via increasing wastewater discharge offshore of the southeastern United States and in the Gulf of Mexico (Fig. 13)

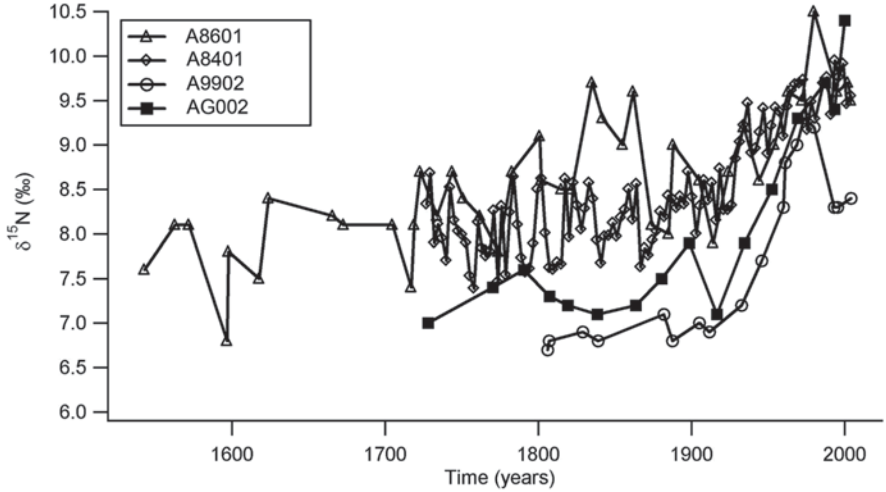


Fig. 13 Increasing skeletal $\delta^{15}N$ values from four *Black* Coral *Leiopathes glaberrima* specimens from the Gulf of Mexico (*black* squares) and offshore the SE coast of the US (open symbols) likely reflect increasing terrestrial effluent to the deep sea. (Reproduced with permission from Williams et al. 2007a)

(Williams et al. 2007a). Decreasing $\delta^{15}N$ values in Caribbean gorgonian corals towards the present likely reflects increasing contribution of nitrogen fertilizers to the ocean (Baker et al. 2010b).

Similarly, Marion et al. (2005) subsampled two stony coral cores from Bali on an annual basis, and analyzed the stable nitrogen isotopic composition ($\delta^{15}N$) of organic matter obtained after decalcifying the samples. Marion et al. (2005) found that the coral from the site adjacent to several large hotel developments had enriched $\delta^{15}N$ (~8 ‰) compared with that collected adjacent to rice paddies (~4–5‰), reflecting untreated sewage discharged into the water from the hotels. These authors also found a trend towards lower $\delta^{15}N$ after the 1970s in the rice paddy coral, reflecting the introduction and increasing use of synthetic fertilizers after that time. Yamazaki et al. (2011) also report success reconstructing nutrient dynamics from stony coral organic matter $\delta^{15}N$, and describe a more efficient laboratory methodology.

Land-Use Changes

Sedimentation negatively affects corals and other marine organisms, and as such has been an area of focus for studies relating land-use change to increases in sedimentation on coral reefs. Barnard et al. (1974) analyzed the amount and mineralogical composition of detrital material trapped in cavities in coral skeletons; they related the timing of gibbsite incorporation in one coral to construction of an adjacent housing development. Ba, Fe, Al, and rare earth elements like Ce, La and Y have all been used as proxies for sedimentation, as these elements are elevated in continental compared to oceanic rocks. Bastidas and Garcia (1999); McCulloch et al. (2003); Fleitmann et al. (2007); Lewis et al. (2007); Jupiter et al. (2008); Carilli et al. (2009); Prouty et al. (2010); Grove et al. (2012); and Moyer et al. (2012) all found elevated levels of these elements with proximity to rivermouths and/or over time, reflecting increases in sedimentation due to land development.

Terrestrial organic matter is characterized by $\delta^{13}C$ signatures lower than that of marine organic matter (Risk et al. 1994). Therefore, land use changes resulting in increased contribution of terrestrial organic matter to the ocean could also deplete $\delta^{13}C$ values in addition to, or separately from, the Suess Effect and/or upwelling of isotopically depleted carbon. Reduced $\delta^{13}C$ values correlated with land development have been recorded in gorgonian coral skeletons (Ward-Paige et al. 2005; Williams et al. 2007b), and stony coral skeletons (Moyer et al. 2012). Another proxy for land-based runoff is stony coral luminescence, driven by humic acid incorporation (Grove et al. 2010).

Mining

Fallon et al. (2002) and Edinger et al. (2008) used corals to track a suite of metals from a range of sites to identify nearshore impacts from gold mining (Fig. 14).

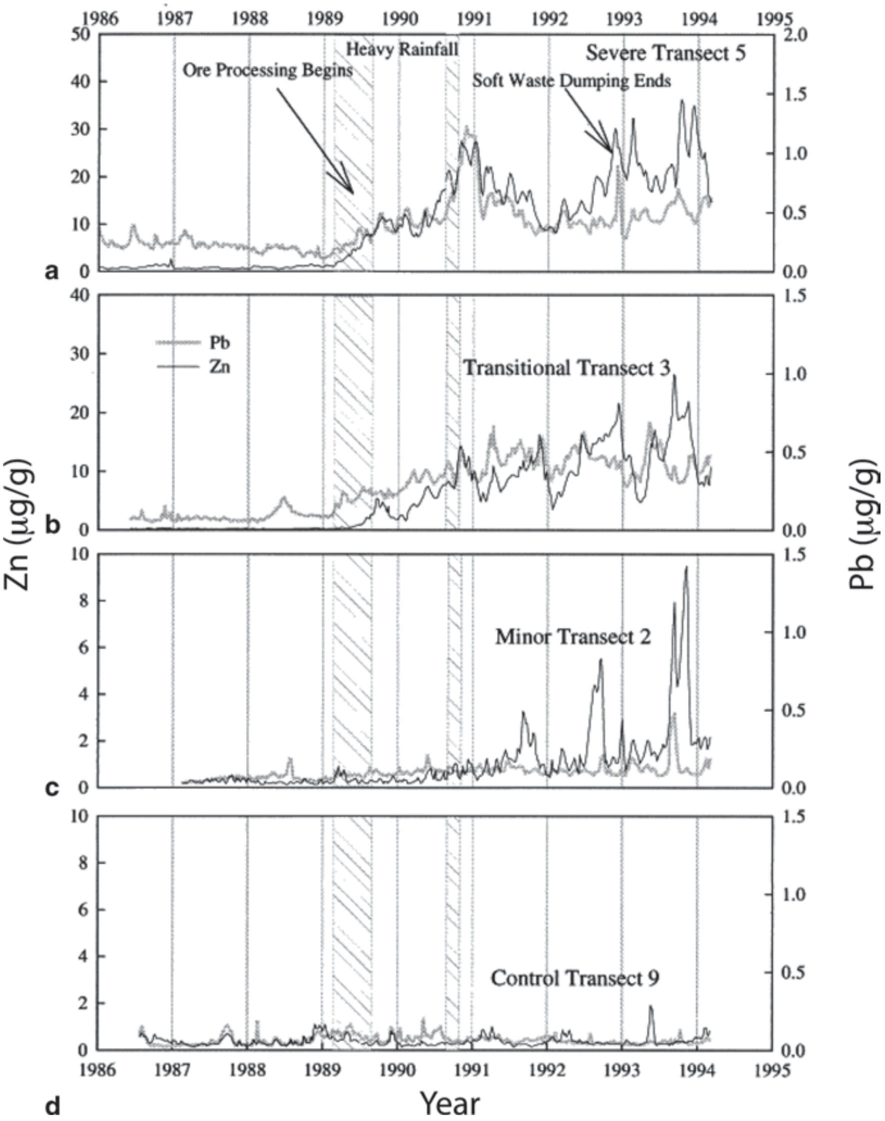


Fig. 14 Zn and Pb (μg g^{-1}) vs. time from four transect sites with increasing distance from mine-waste runoff source (**a–d**). Zn and Pb do not increase until ore processing begins and fresh rock is exposed. (Reproduced with permission from Fallon et al. 2002)

Similarly, David (2003) found higher concentrations of metals in corals closer to and after the timing of accidental release of copper mine tailings in the Philippines.

Using the long-lived deposit-feeder, *Arctica islandica*, Dunca et al. (2009) found higher contents of S, N, Cu and other metals in shell portions formed in the twentieth century than those formed in the preceding century in Sweden, potentially due to an increase in mining and industrial development in the surrounding region.

Markich et al. (2002) used shells of the freshwater bivalve *Velesunio angasi* from tropical northern Australia to monitor and reconstruct mining pollution. Concentrations of heavy metals (Cu, Mn, Zn, Ni, Co) in these shells decreased significantly with increasing distance from a renaturated copper-uranium mine. Shells from more pristine sites provided an approximately annually resolved record spanning 1965–1996, while the bivalves from the polluted sites only started growing in 1986, after the mine was abandoned.

Limitations

General Limitations One major limitation hampering use of all forms of sclerochronological archives is a lack of detailed understanding of biomineralization mechanisms. Importantly, all of these organisms may alter the chemistry of the calcifying medium away from equilibrium with seawater, and thus geochemical records from skeletal material are probably not an exact recording of the concentration of contaminants in the surrounding environment. To a large degree, physiological processes likely control the amount and type of substances reaching the site of calcification. Contaminants may be metabolized or accumulated preferentially in different portions of the organism (the soft tissues, skeleton, or organic matrix within the skeletal material). For example, in stony corals there is some evidence that the zooxanthellae or animal tissues can preferentially take up or sequester some elements, reducing their eventual incorporation into the skeleton (Corrège 2006). In addition, other factors might influence the "recording" of contaminant concentrations in an organism's skeleton, including ontogenetic age, calcification rate, biomechanical needs, amount and type of organic matrix, crystal fabrics, other stressors, etc. A major task for future research is to disentangle and quantify vital and kinetic effects (Cohen and McConnaughey 2003).

A related limitation is a lack of consensus on the best analytical methods. Early coral studies analyzed either non-carbonate material by first dissolving the coral skeleton and retaining the remaining material (Barnard et al. 1974) or investigated total contaminant content in coral skeletal samples (Goreau 1977; Dodge et al. 1984; Dodge and Gilbert 1984). Later, Shen and Boyle (1988) developed a method to extensively clean the coral skeleton, removing detrital material, organic matter, and contamination introduced during sampling, in order to measure only lattice-bound metals. However, some studies have questioned the relevance of these measurements, because including or measuring only extra-lattice metals appeared to produce a more realistic measure of pollution occurring at impacted sites (Guzman and Jimenez 1992; Runnalls and Coleman 2003; Inoue et al. 2004). In addition, Prouty et al. (2008) found that only 5 of 18 intra-crystalline metal/Ca ratios (Ba, Mn, Cr, Cu, and Sb) replicated well within a site. Clearly, more work is needed to understand how individual elements and molecules are incorporated into different parts of an organism (tissues, skeleton, etc.) so that analytical methods can be targeted to produce more accurate records.

Another major impediment to using sclerochronological archives is the possibility of diagenesis. The extraction of chemical records from skeletal archives is built on the assumption that the material analyzed is pristine. However, dissolution of the primary skeleton, or deposition of secondary material can significantly alter these records. Many of the organisms discussed in this chapter secrete aragonite or high-Mg calcite skeletons, both of which are less stable and prone to alteration into the more stable calcium carbonate polymorph, calcite. Skeletal alteration can, however, be ruled out by careful screening. Coarse screening involves choosing skeletal material that does not contain obvious evidence of bioeroders such as worms, boring sponges, or endolithic algae, which directly dissolve skeleton and contribute to alteration in nearby material. More accurate screening uses x-ray diffraction to estimate whether the original material has been altered to calcite, and thin sections or scanning electron microscopy to investigate the crystal fabric and assess diagenesis (e.g., McGregor and Abram 2008).

Sclerosponge skeleton is extremely dense, providing more resistance to diagenesis than, for instance, corals. However, all sclerosponge species have significant secondary infilling of carbonate material. This produces horizontally adjacent skeletal material that has been deposited at different time intervals, instead of being coeval. In *C. nicholsoni* the tissue occupies a depth of 0.5–1 mm in the skeleton (Swart et al. 2002; Rosenheim et al. 2004). In *A. willeyana* and *A. wellsi,* the tissue can occupy upwards of 5 mm (Fallon et al. 2005; Allison and Tudhope 2012), This secondary infilling results in aragonite deposition not only at the outermost skeletal surface but, more critically, throughout the tissue layer. At the base of the tissue, the aragonite infills and thickens to the density of pure aragonite (Fallon et al. 2005; Fig. 15). The time between initial deposition and secondary infilling in *A. willeyana* is several years (Fallon et al. 2005; Fig. 15). In *C. nicholsoni* approximately 80 % of the total mass is infilling with 20 % original older material (Böhm et al. 1996). In *A. willeyana* the skeletal density gradually increases with depth in the skeleton, suggesting continual thickening (Fig. 15; Fallon et al. 2005).

Other limitations include geographic constraints: for example, scleractinian corals are only found in the tropics in the photic zone, covering < 0.1 % of the world's oceans (Spalding et al. 2001). Coralline algae are found in shallow (< 100 m) coastal waters, but many of the long-lived specimens used for reconstructions come from isolated coasts (Fig. 1), presenting significant logistical challenges for sample collection.

Growth banding can sometimes be obscure, limiting the temporal resolution of some records. Fortunately, secondary checks on banding exist, including dating using radioactive elements (for instance U-series in corals, Zhao et al. 2009), matching banding with geochemical records of annual water temperature fluctuation, identification of the radiocarbon bomb-pulse, or cross-dating between multiple adjacent organisms.

One additional limitation is complex behavior of some elements in the water column, which can confuse interpretation of records. For instance, non-conservative metals can be scavenged by particles in the water column, and the rate of scavenging

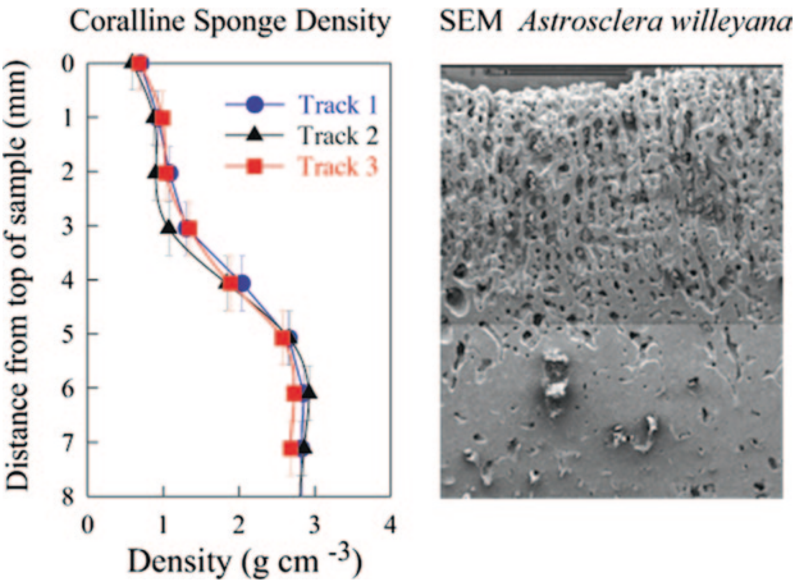


Fig. 15 Density of *A. willeyana* from Ribbon Reef #10, Great Barrier Reef and a scanning electron microscope (SEM) image of the same part of the sclerosponge; the outer surface has lower density. The density increases to near solid aragonite at the base of the tissue layer. Scales are approximately equal

may change over time disproportionally to the input of a particular metal. Thus, even if an organism passively records the concentration of a particular contaminant without altering the signal, the interpretation of resulting records may not be straightforward without additional environmental data.

Conclusions and Future Work

High-resolution analyses of contaminants in the archives discussed here have yielded promising results, despite the generally small number of studies. For example, high-resolution serial sampling of single bivalve shells has been employed by several researchers (e.g., Carriker et al. 1982; Gillikin et al. 2005; Krause-Nehring et al. 2012; Holland et al. 2014). These studies found that despite baseline differences in metal concentrations due to ontogeny or individual variability, temporal changes—including the 1970s leaded-gasoline peak in these studies—were recorded in the shell chemistry. However, studies of this kind are still rare and almost exclusively based on heavy metals, and few studies have been undertaken to calibrate skeletal chemistry with measurements from the surrounding water (for instance Carriker et al. 1982; Rosenheim et al. 2004). The limited number of studies using sclerochronological archives to reconstruct contaminants reflects the challenges involved in the interpretation of the chemical data in skeletons and the complex pathways that elements take from the environment into the skeletal material. Yet, sclerochronological archives provide an enormous potential for retrospective environmental biomonitoring and should be strongly considered as an important complement to existing biomonitoring initiatives.

Future studies must seriously consider the merits of different sampling strategies and provide detailed information on those employed (e.g., individual drill holes, serial micromilling, single spot and line scan LA-ICP-MS techniques, Fig. 16a–d). For example, all existing shell-based historical records of contamination are based on (sub)seasonal snapshots (Gillikin et al. 2005; Liehr et al. 2005; Krause-Nehring et al. 2012). Shell portions between individual laser ablation spots (Fig. 16a) or individual drill holes (Fig. 16c) remain unsampled. To attain an uninterrupted chronology of water chemistry, serial micromilling (Fig. 16b) or a line scan technique (Fig. 16d) might be applied rather than measuring discrete sample spots (Figs. 15, 16a, c; Holland et al. 2014).

Future work might also look into other contaminants that have not been investigated in detail, but that might show promise. A number of pollutants have received little attention in molluscan shell: organic macromolecules, radionuclides and rare earth elements, despite their ubiquitous presence in some environments and known uptake pathways in molluscan tissue (Wang and Fisher 1999; Davies et al 1997; Marigómez et al 2002). Similarly, very-fine-scale sampling might provide higher temporal resolution archives, but differences in chemical composition between assumed equivalent time periods due to biomineralization processes need to be carefully addressed (for instance the type of crystal fabric, Fig. 16e; or secondary infilling, Fig. 15). In mollusks, the relative amount of organics and the crystal fabrics influence the behavior of laser ablation of shell material, and hence the measured chemistry of the shell. Therefore, it is imperative to describe the crystal fabrics of mollusk shells in detail (Fig. 16e). In corals, very fine-scale sampling has shown high variability between different skeletal elements (e.g., Sinclair et al. 2006; Rollion-Bard et al. 2011), underscoring the necessity to either conduct very high spatial resolution sampling or conversely to swamp out differences with bulk sampling methods. For very high-resolution sampling, Nano-SIMS and ion microprobe techniques may prove useful; for example In *Clathromorphum* sp., Nano-SIMS might be used to detect variations in the geochemistry between different crystal structures. Other factors that might affect skeletal geochemical records also should be carefully considered, such as ontogenetic age, growth rate and analytical methods (e.g., pretreatment of material such as removal of organics prior to analyses).

Similarly, compound-specific time series of organic contaminants have not yet been produced, but organic matter in these archives (proteinaceous coral skeleton, organic matrix in stony corals and bivalves, or even potentially endolithic bioeroders like algae and fungi in corals) may allow reconstruction of contaminants associated with humans such as coprostanol (a degradation product of cholesterol and a biomarker for sewage, see Korosi et al. (this volume)), PCBs, hormones, and pharmaceutical products, all of which have been detected in coastal waters. No studies

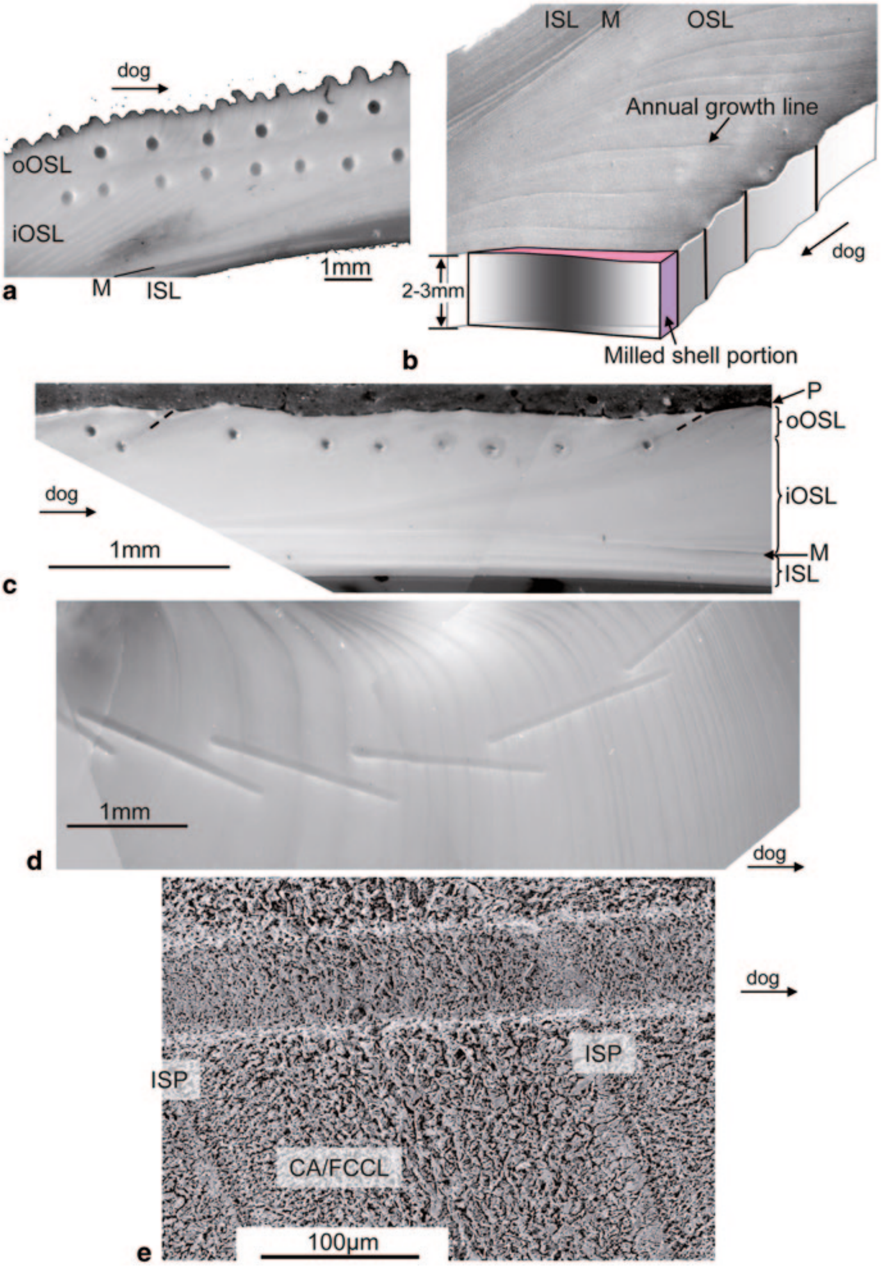


Fig. 16 Typical geochemical sampling techniques in the field of sclerochronology (**a**–**e**) and bivalve crystal fabrics (**e**). For wet chemical analyses, sample powder can be obtained by drilling holes in cross-sections (**a**: *Mercenaria campechiensis*) or micromilling material from shell slabs (**b**: outer shell layer, ventral margin, *Arctica islandica*). For in-situ analyses (here, laser ablation [LA] ICP-MS), the single spot technique (**c**: ventral margin, *A. islandica*) or the line scan tech-

to date have reported results of these kinds of measurements, but hydrocarbon and organic biomarker measurements in stony corals provides evidence that this may be a promising avenue of research (Readman et al. 1996).

Long-term laboratory and natural calibration studies should also be a research priority. For example, detailed calibration studies for water temperature proxies have been undertaken for all three sclerosponge species discussed. In all cases, samples were stained (to obtain a time marker) and in situ temperature monitors were left near the samples for ~2 years before detailed geochemical analyses were conducted and calibrated against the temperature data (Rosenheim et al. 2004; Rosenheim et al. 2009; Grottoli et al. 2010). In contrast, none of the existing bivalve-shell-based historical pollution studies has provided a detailed record of water chemistry (including dissolved ions, pollutants absorbed to sediment grains or bound to particulate organic matter, detritus or phytoplankton etc.) with the same temporal resolution and same time-averaging as the skeletal data. In order to quantitatively reconstruct environmental pollution from skeletal records, controlled calibration studies are essential, especially because calcification of these organisms is not completely understood. Once these critical limitations are addressed, sclerochronological archives will provide highly temporally resolved quantitative records of past contaminants at a wide range of locations and water depths throughout the world's oceans.

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niques (**d**: cardinal tooth, *A. islandica*) can be used. Micromilling and LA line scans provide an uninterrupted chronology of geochemical variables. **e** Crystal fabrics can vary significantly within different seasons. Under scanning electron microscope, the cardinal tooth of *A. islandica* typically shows irregular simple prismatic and irregular spherulitic prismatic (ISP) fabrics at annual growth lines and a mixture of crossed-acicular (CA) and fine-complex crossed-lamellar (FCCL) fabrics within the annual increment. Horizontal line = LA line scan. For legend see caption from Fig. 7

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Contaminant Records in Ice Cores

Paolo Gabrielli and Paul Vallelonga

Abstract Ice cores extracted in polar regions and in high altitude glaciers at low and mid latitudes are important recorders of global to regional changes in climate, ecosystems and human activities (e.g. industry, mining, transport). All of the contaminants found in ice cores are transported through the atmosphere, with the transport mechanism and atmospheric lifetime of these contaminants determining their spatial extent. In this chapter, we consider such ice core impurities as lead, mercury, platinum group elements, other trace elements, black carbon, organic and radioactive species. These contaminants are evaluated over the past few centuries, from the pre-industrial period through the Industrial Revolution and up to the most recent years of atmospheric monitoring, pollutant moratoria and/or abatement technologies. Contamination by most of these compounds is widespread from the higher latitudes of the Northern Hemisphere down to the remotest locations of Antarctica, suggesting that today there are no glaciers on Earth where atmospheric depositions of anthropogenic origin cannot be detected.

Keywords Snow accumulation · Alpine glaciers · Ice sheets · Greenland · Antarctica · Industrial Revolution · Anthropogenic emissions · Long range transport · Environmental reconstruction

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Introduction

Thick ice sheets and glaciers build up over centuries and millennia in areas where snow accumulates at a greater rate than it is lost. Usually this occurs in cold regions at high latitudes, although the highest mountain chains of the tropics and mid-latitudes also contain glaciers. The surface snow layers are gradually compacted by the overlying snow to become dense snow, known as firn, which is then further compacted to form ice. Cold glaciers (characterized by a temperature below the pressure melting point) preserve physical, chemical, and biological evidence of past atmospheric variability, for example changes in stable isotopes (e.g. EPICA community members 2006), soluble and insoluble inorganic impurities (e.g. Thompson et al. 2000) and a multitude of organic species (Grannas et al. 2006), respectively. Ice sheets and alpine glaciers also archive information about the human influence on the past atmosphere retaining contaminants such as, among many others, trace elements (e.g. Boutron et al. 1991), organic compounds (e.g. Legrand et al. 2007) and radionuclides (e.g. Fourré et al. 2006) that are wet- or dry-deposited on the glacier surface (Davis 1991).

Insights into the paleo-environmental information contained in glaciers can be obtained by extracting ice cores. These are ice cylinders of typically ~10 cm diameter that can be recovered by drilling into glaciers hundreds or even thousands of meters thick (EPICA community members 2004). Ice cores extracted from the Antarctic and Greenland ice sheets (N-GRIP-members 2004; Petit et al. 1999) and alpine glaciers (Thompson et al. 1986; Schwikowski 2003) have the potential to provide very detailed information on past atmospheric characteristics, from sub-annual to orbital time scales (10^5 years). Ice core studies offer the considerable advantage that multiple physical, chemical and biological records are obtained from the same ice matrix and thus can be compared on exactly the same time scale (except gaseous species). This reduces the relative temporal uncertainty and allows the examination of synchronous interactions between climate, ecosystems and, more recently, human societies.

Nevertheless obtaining an accurate absolute ice core chronology is often a challenge. Where annual snow layers are thick and preservation conditions are favorable (e.g. Thompson et al. 1986; N-GRIP-members 2004), robust dating can be obtained by counting annual ice layers (typically characterized by seasonal variations in stable isotopes, major ions and/or microparticle concentrations) in combination with the use of time markers. These are chemical signals in the ice which can be linked to known events, for instance the ash or acid fallout of major volcanic eruptions, aeolian dust events and atmospheric nuclear bomb tests (e.g. Knüsel et al. 2003). Thinning of the ice layers in glaciers and ice sheets eventually results in annual layers that are too thin to resolve. At low and mid latitudes rare organic fragments embedded in ice cores can be used for dating by determining their ^{14}C content (e.g. Thompson et al. 1998). Particularly promising is also a recent dating technique employing ^{14}C determined in the carbon fraction dissolved in the ice (Jenk et al. 2009; Sigl et al. 2009). In polar areas, ice flow models of varying levels of complexity can be coupled to time markers, such as the stratospheric products

(^{10}Be) linked to variations in the Earth's magnetic field (Raisbeck et al. 2006), and eventually tuned to other well-dated paleo-records and orbital parameters (Parrenin et al. 2007; Wolff et al. 2010).

The surface of alpine glaciers, and to a lesser or negligible extent that of polar ice sheets, are intermittently subjected to summer melting, percolation and refreezing that increase the glacier temperature and create ice lenses that may cause different degrees of perturbation in the records, especially for the most soluble species (Eichler et al. 2001). In a rapidly warming climate, many cold glaciers that were suitable drilling sites until only a few decades ago are now disrupted by percolation of surface meltwater and are rapidly transitioning from a cold to a temperate state (temperatures at the pressure melting point throughout the glacier) (Gabrielli et al. 2012). Under these conditions untapped glacial paleo-environmental archives are being irreversibly obliterated, and their valuable climatic and historical information are lost.

The structure and dynamics of a glacier are very important to the preservation and extraction of a useful ice core record. The continuity of the ice stratigraphy is critical and can be assured only if the snow accumulates throughout the year and if reworking processes at the glacier surface are limited (e.g. wind erosion and re-deposition, summer melting, sublimation and re-condensation) (Schotterer et al. 2004). Ideally, ice core drilling sites should be characterized by minimal horizontal glacier flow, resulting in parallel ice layers that can preserve the depositional sequence. The Greenland ice sheet is characterized by a central ice divide, the highest point along the ice sheet where horizontal flow is minimized, while Antarctica features a number of ice domes with similar ice flow characteristics. However, closer to bedrock the ice flow dynamics are often poorly constrained and phenomena such as ice folding and shearing may hamper the stratigraphy and therefore the interpretation of ice core records (Chappellaz et al. 1997). The weight of the thickest ice sheets can induce pressure-melting at the base of the ice, resulting in the loss of the deepest and oldest sections of the ice core record. However, the basal ice stratigraphy can also be retained in such areas if the liquid water interface between the ice and bedrock limits folding and shearing.

In order to verify the robustness and reproducibility of the local and regional findings obtained from the polar ice sheets and the alpine glaciers, ice core records are often replicated (Jouzel et al. 1989). For this purpose multiple short ice cores (typically up to ~100 m long) have been drilled in alpine glaciers at the same drilling site (Thompson et al. 2002) while several long ice cores (up to 3.6 km long) have been retrieved in different locations located on the same polar ice sheets (Watanabe et al. 2003). Building a network of ice core drilling sites also allows the identification of impacts and sources of atmospheric emissions on regional, hemispheric or global scales. For example, signals from tropical volcanic eruptions are occasionally found in ice cores from Greenland and Antarctica, confirming the global impact of the eruption and allowing ice cores from around the world to be chronologically synchronized by such global markers (Severi et al. 2007).

If an appropriate sample preparation methodology is adopted and sensitive enough analytical techniques are available, the ice core matrix (essentially distilled seawater with low content of salts and insoluble particles) offers a very low analytical background that allows even small deviations of atmospheric proxies to be detected (e.g. Vallelonga et al. 2010). Depending on the analyte, the process of drilling, handling and transporting ice cores can contaminate the outer surface of the ice cores. Hence strict contamination controls can be a fundamental prerequisite to extracting reliable records from ice cores (Candelone et al. 1994). Trace elements (e.g. lead, zinc, copper, cadmium), biota and organic species are perhaps the most prone to contamination due to their broad diffusion in the modern human environment. During the most recent decades an awareness of the importance of contamination control has increased and thus clean materials, reagents and careful procedures have been developed, allowing pristine and detailed records to be extracted from the ice cores (McConnell et al. 2002a; Candelone et al. 1995).

While polar ice core records can be representative of hemispheric and global atmospheric contamination by humans (Murozumi et al. 1969), alpine ice cores from lower latitudes are in general more indicative of the history of regional or local pollution (Schwikowski et al. 2004; Kaspari et al. 2011). The first striking evidence of an early large-scale human contamination was provided by an ice core extracted at Summit in central Greenland (Hong et al. 1994, 1996). In this core, enrichment of copper and lead relative to the average terrestrial crustal composition was attributed to mining and smelting emissions produced by Roman and Greek civilizations. It is significant that this widespread pollution event occurred well before the beginning of the so-called "Anthropocene" that is commonly attributed to the inception of the Industrial Revolution (Crutzen and Stoermer 2000). Since the beginning of the Anthropocene, the atmosphere has undergone a major change in its chemical composition that, as we will see in detail, is well evidenced by many ice core records extracted from both polar regions and high altitude glaciers.

In this chapter we will review the ice core records that detail the history of atmospheric contamination over the last ~300 years, covering the transition from the pre-industrial to the industrial period up to recent years. We will deal in particular with records of trace elements (including lead, mercury and platinum group elements), black carbon, organic species, and radionuclides, and compare them with corresponding records from other sedimentary archives such as lake sediment cores, peat bogs, etc. Table 1 details the species of presumed anthropogenic origin detected in glacial archives covering the time interval of the last ~300 years. We acknowledge the many other signals of natural and anthropogenic change that are recorded in ice cores, such as gases and major ions and their linked isotopic or physical properties (e.g. acidity, conductivity), but these are not evaluated in this chapter because they do not have direct counterparts in other paleo-environmental archives, as described in this book.

Lead

Unquestionably, the pioneer of environmental lead (Pb) analysis is Clair C. Patterson (Flegal 1998). In his attempts to measure Pb isotopic compositions at μg g^{-1} concentrations in meteorites, Patterson inadvertently discovered that the air, water and

Table 1 List of the species of anthropogenic origin detected in glacial archives covering a time interval that goes from the beginning of the industrial revolution to the present time.

Species	Location	Reference
Pb	Greenland	Murozumi et al. 1969; Rosman et al. 1993; McConnell et al. 2002b; McConnell and Edwards, 2008
	Alps	Van de Velde et al. 1998; Heisterkamp et al. 1999; Rosman et al. 2000; Schwikowski et al. 2004
	N. America	Shotyk et al. 2005b; Zheng et al. 2007; Osterberg et al. 2008; Shotyk and Krachler, 2010
	Asia	Lee et al. 2011; Eichler et al. 2012
	S. America	Correia et al. 2003; Rosman et al. 2003; Hong et al. 2004
	Antarctica	Wolff and Suttie 1994; Hong et al. 1998; Vallelonga et al. 2002; Planchon et al. 2002b; Planchon et al. 2003; Van de Velde et al. 2005; Burn-Nunes et al. 2011
Hg	Greenland	Boutron et al. 1998; Mann et al. 2005; Faïn et al. 2009
	Alps	Jitaru et al. 2003
	N. America	Schuster et al. 2002
	Asia	Wang et al. 2008a; Zhang et al. 2012
PGEs	Greenland	Barbante et al. 2001b; Barbante et al. 2003; Gabrielli et al. 2008
	Alps	Van de Velde et al. 2000a; Barbante et al. 2004
	Antarctica	Soyol-Erdene et al. 2011
Ag	N. America	Krachler et al. 2008
	S. America	Hong et al. 2004
	Antarctica	Planchon et al. 2002a
As	N. America	Krachler et al. 2009
	Asia	Hong et al. 2009
	S. America	Correia et al. 2003; Hong et al. 2004
Bi	Alps	Barbante et al. 2004
	N. America	Krachler et al. 2009
	Asia	Li et al. 2006; Kaspari et al. 2009; Liu et al. 2011
	S. America	Hong et al. 2004
	Antarctica	Planchon et al. 2002a
Cd	Greenland	Boutron et al. 1991; Candelone et al. 1995; McConnell and Edwards 2008
	Alps	Van de Velde et al. 2000b; Barbante et al. 2004
	Asia	Liu et al. 2011
	S. America	Correia et al. 2003; Hong et al. 2004
Co	Alps	Van de Velde et al. 1999
	S. America	Correia et al. 2003

Table 1 (continued)

Species	Location	Reference
Cr	Alps	Van de Velde et al. 1999
	S. America	Correia et al. 2003
	Antarctica	Planchon et al. 2002a
Cs	Asia	Kaspari et al. 2009
Cu	Greenland	Boutron et al. 1991; Candelone et al. 1995
	Alps	Van de Velde et al. 2000b; Barbante et al. 2004
	S. America	Hong et al. 2004
	Antarctica	Wolff et al. 1999; Planchon et al. 2002a; Vallelonga et al. 2004
Mo	Alps	Van de Velde et al. 1999
	Asia	Hong et al. 2009
Ni	Alps	Barbante et al. 2004
	Asia	Correia et al. 2003
Sb	Alps	Van de Velde et al. 2000b
	N. America	Krachler et al. 2005; Krachler et al. 2008; Krachler et al. 2009
	Asia	Li et al. 2006; Hong et al. 2009; Liu et al. 2011
Sn	Asia	Hong et al. 2009; Liu et al. 2011
Tl	Greenland	McConnell and Edwards 2008
	N. America	Krachler et al. 2008
	Asia	Liu et al. 2011
U	Alps	Barbante et al. 2001a
	Asia	Kaspari et al. 2009
	Antarctica	Planchon et al. 2002a
Zn	Greenland	Boutron et al. 1991; Candelone et al. 1995
	Alps	Van de Velde et al. 2000b; Barbante et al. 2004
	S. America	Correia et al. 2003; Hong et al. 2004
	Antarctica	Planchon et al. 2002a
PAHs	Greenland	Masclet et al. 1986; Kawamura et al. 1994; Jaffrezo et al. 1994
	Alps	Gabrieli et al. 2010
	Asia	Wang et al. 2008b
	Antarctica	Fuoco et al. 2012
POPs	N. Europe	Hermanson et al. 2010; Ruggirello et al. 2010
	Alps	Villa et al. 2001; Villa et al. 2003; Maggi et al. 2006; Kirchgeorg et al. 2013

Table 1 (continued)

Species	Location	Reference
	N. America	Gregor et al. 1995; Donald et al. 1999
	Asia	Wang et al. 2008a; Wang et al. 2008b; Wang et al. 2010a; Wang et al. 2010b
	Antarctica	Fuoco et al. 2012; Kang et al. 2012
BC	Greenland	McConnell et al. 2007
	Alps	Lavanchy et al. 1999; Jenk et al. 2006; Thevenon et al. 2009
	Asia	Kaspari et al. 2011
	Antarctica	Bisiaux et al. 2012
Radionucl.	Greenland	Koide et al. 1982; Picciotto and Wilgain 1963
Radiocact.		Merlivat et al. 1973
	Alps	Vincent et al. 1997; Schwikowski et al. 1999; Eichler et al. 2000; Reithmeier et al. 2006; Gabrieli et al. 2011b; Warneke et al. 2002
	Asia	Kehrwald et al. 2008; Thompson et al. 1995b; Liu et al. 2011; Olivier et al. 2004
	S. America	Thompson et al. 1995a; Knusel et al. 2003
	Antarctica	Crozaz, 1969; Jouzel et al. 1979; Koide et al. 1982; Fourré et al. 2006

chemicals he used were thoroughly contaminated with Pb from leaded gasoline. He developed techniques for removing Pb from his laboratory, purifying both the lab water by filtration and sub-boiling distillation in quartz vessels and the air by using HEPA filters. In addition he ensured that the filtered clean lab air was over-pressured with respect to external contaminated air. He needed to produce his own lead-free acid and used only polyethylene or stainless steel apparatus that could be cleaned using his own Pb-free acid and water.

Patterson's legacy was to demonstrate just how pernicious the Pb contamination of modern society was. The pinnacle of this work involved the collection and analysis of snow blocks and ice cores from Antarctica and Greenland in order to demonstrate that Pb concentrations in 1960s Greenland snow were up to 300 times greater than they had been 3000 years ago (Murozumi et al. 1969). This record was instrumental in convincing American policy makers to enact the Clean Air Act in 1970, which mandated the removal of Pb from gasoline in the US. By the start of the twenty-first century, most of the countries in the world had switched to unleaded gasoline, thanks in part to Patterson's tireless dedication to science and environmental stewardship.

Following the careful sample collection and preparation techniques pioneered by Patterson, sensitive analytical techniques and instruments are required to accurately determine ultra-low Pb concentrations in environmental matrices. Instruments such as Inductively Coupled Plasma Sector-Field Mass Spectrometers (ICP-SFMS) and

Thermal Ionization Mass Spectrometers (TIMS) are regularly used to study Pb and its isotopic ratios. Pb isotopes are of interest because they can be used to identify Pb pollution sources (Rosman 2001). Three stable isotopes of Pb (^{206}Pb, ^{207}Pb, ^{208}Pb) are respective end-products of the radioactive decay chains of uranium (^{238}U, ^{235}U) and thorium (^{232}Th). When Pb is incorporated into an ore body, it is removed from its parent U and Th and its isotopic composition is fixed. While the isotopic composition of Pb in an ore body is related to its age, its composition in volcanic emissions is dependent upon the crustal material from which the magma was produced (Sun 1980).

Murozumi et al. (1969) produced the first Pb record from snow blocks carved out of the walls of the Camp Century base in Northwestern Greenland. The results showed a tenfold increase in Pb concentrations from the earliest sample (1 pg g^{-1} at 800 BC) to 1750 AD (10 pg g^{-1}), which marked the early Industrial Revolution. However, there was a greater than tenfold increase from 1750 to 1965 AD (230 pg g^{-1}). This trend was confirmed and further developed by colleagues and students of Patterson over the 1980s and 1990s (Boutron et al. 1991; Ng and Patterson 1981; Sherrell et al. 2000). Candelone et al. (1994) developed an advanced technique for the contamination-free sampling of ice cores which involved the use of a plastic lathe in a clean-air bench located in a cold room. Acid-washed stainless steel chisels were used to scrape away 4 to 6 layers of the external, contaminated, layers of ice. The pristine inner sections were isolated in acid-cleaned polyethylene bottles, then melted and analyzed. The chiseled outer layers were also analyzed to demonstrate the successful removal of external contamination.

Hong et al. (1994) identified a fourfold Pb enrichment in Greenland ice between 500 BC and 300 AD resulting from ancient mining and smelting activities during the height of the Greco-Roman empires. Pb isotopic analysis enabled Rosman et al. (1997) to attribute this Pb to smelters in two regions of southern Spain, with 70 % of Pb pollution originating from the Rio Tinto mines between 150 BC and 100 AD. Post-Roman Pb enrichment in ice occurred after 500 AD with the development of mining and smelting in the Harz Mountains of Germany. Pb isotopes were also used to study twentieth-century Pb deposited in Greenland (Rosman et al. 1993). These authors were able to distinguish between Pb additives used in the USA (^{206}Pb/^{207}Pb 1.21) from those used in European refineries (^{206}Pb/^{207}Pb~ 1.14), thus resolving the mixture of US and European gasoline Pb deposited in Greenland from 1968 to 1988. The data showed a change from US to European sources after the introduction of clean air legislation in the US in 1970 AD. A more recent study of Pb pollution in Greenland resulted from another leap in analytical capability in which McConnell et al. (2002b) developed a technique to continuously melt ice core sections on an acid-cleaned heated plate. The meltwater was pumped continuously to an ICP-SFMS for determination of Pb concentrations. They were able to report subannual variations in Pb concentrations from central and southern Greenland over the past 250 years, thus detailing the history of industrial development at unprecedented high resolution (McConnell and Edwards, 2008; McConnell et al. 2002a).

Alpine records of Pb have been used to reconstruct regional variability in industrial development. Several studies of Pb concentrations and isotopic compositions (Heisterkamp et al. 1999; Rosman et al. 2000; Schwikowski et al. 2004; Van de Velde et al. 1998) have featured snow and ice cores from the Alpine glaciers of

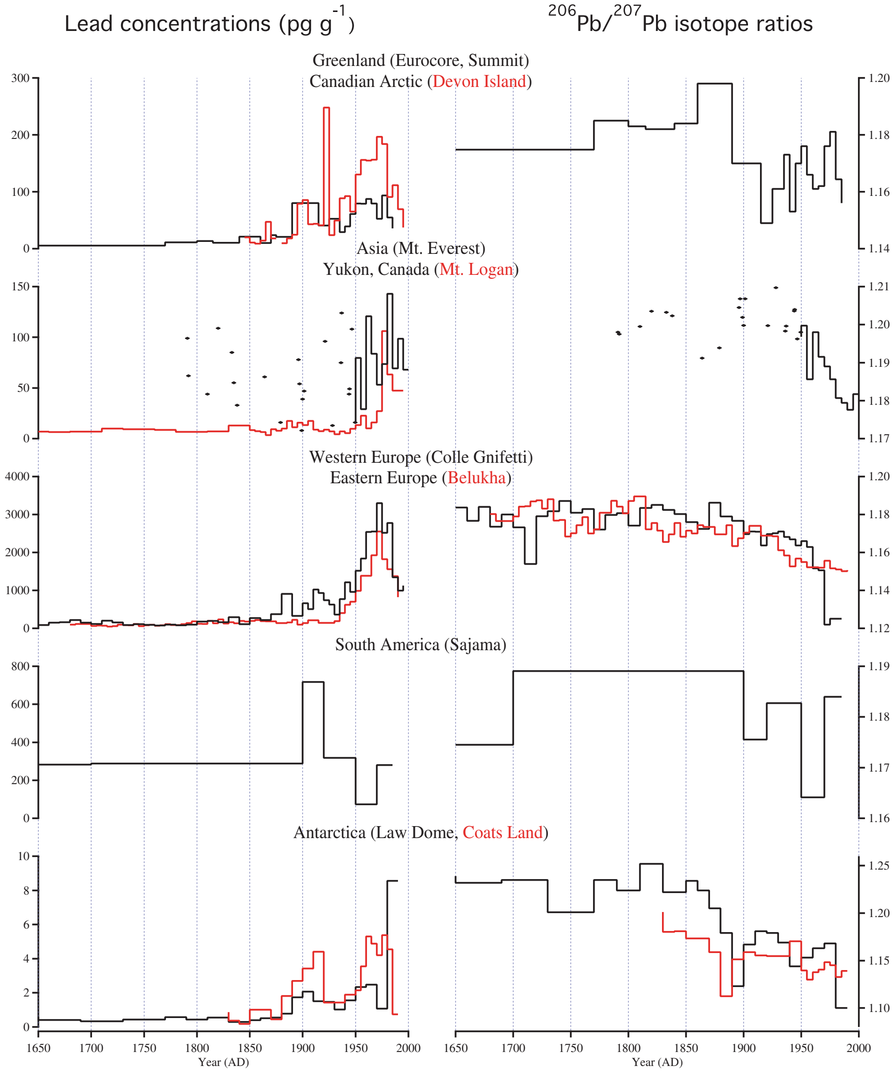


Fig. 1 Lead concentrations (*left column*) and ^{206}Pb/^{207}Pb ratios (*right column*) in ice cores from Greenland (Eurocore, Rosman, pers. comm. and Summit, Rosman et al. 1993) and Devon Island (Shotyk et al. 2005b); Mt. Everest (Lee et al. 2011) and Mt. Logan (Osterberg et al. 2008); Colle Gnifetti (Schwikowski et al. 2004) and Belukha (Eichler et al. 2012); Sajama (Rosman et al. 2003) in South America; Law Dome (Vallelonga et al. 2002) and Coats Land (Planchon et al. 2003) in Antarctica

central Europe to report the development of atmospheric Pb pollution, particularly in Europe during the twentieth century. For example, Schwikowski et al. (2004) reported that Pb concentrations increased from ~0.2 ng g^{-1} in 1800 AD to ~3 ng g^{-1} by the 1970s (Fig. 1). Abundances of industrial Pb emissions from coal burning, mining and smelting were overwhelmed by the emissions from leaded gasoline in the 1960s and 1970s. Through the measurement of Pb isotopes, it was determined that the Pb added to gasoline originated from various mines, including Broken Hill, in Australia, and the Mississippi Valley ore complex in the USA. The findings of these studies corroborate well with lake sediment (Farmer et al. 1996), moss (Rosman et al. 1998) and peat bog records (Kylander et al. 2005; Shotyk et al. 1998) across Europe. However, while these Pb records may agree in the general trends observed, the magnitude of the post-industrial increases in Pb pollution recorded in non-glacial archives remain uncertain as, for example, changes in catchment detrital input or scavenging of metals by organic matter may "magnify" the apparent metal inputs from the atmosphere. This should be kept in mind also when comparing other trace metals recorded in different archives.

Other records of Pb pollution have been reported from glaciated areas of North America, and these generally agree with the Greenland ice cores (i.e. peak Pb concentrations in the 1970s and 1980s followed by sharp decreases in concentration during the last two decades). Records have been reported from ice cores from Devon Island in Northeast Canada (Shotyk et al. 2005b; Zheng et al. 2007) and a peat bog record from Eastern Canada (Shotyk and Krachler 2010). Despite indications of recent lower atmospheric Pb concentrations over continental North America, Pb isotope ratios suggest that air here is still contaminated with Pb from the Asian continent (Shotyk and Krachler 2010; Shotyk et al. 2005b), and one record from Mt. Logan (Yukon, Canada) shows a strong increase of Pb concentrations attributed to the transport of pollutants across the Pacific Ocean from Asia since the 1980s (Osterberg et al. 2008). Recent work by Shotyk and colleagues (e.g. Shotyk and Krachler 2010) highlights the varying responses of different terrestrial compartments to decreasing anthropogenic Pb contributions; Pb is preferentially removed from lake basins, leading to lower enrichments compared to transport media such as streams, or fixed deposition sites such as ice, sediments and peat bogs.

Ice cores have been retrieved from various sites across Asia, from the Siberian Altai to the Himalayas and in the South American Andes. The most coherent Pb record is from the Siberian Altai (Eichler et al. 2012), spanning from 1680 to 1995 AD and demonstrating the influence of leaded gasoline and mining emissions from Russia between the 1940s and 1980s. Pb concentrations decreased after 1995 AD due to post-communist economic collapse. Lee et al. (2011) reported Pb concentrations and isotopic compositions in ice cores from the Himalayan East Rongbuk glacier at an altitude of 6518 m above sea level. The pollution record showed relatively constant Pb concentrations of about 50 pg g^{-1} before 1959 AD, then higher concentrations (70–111 pg g^{-1}) between 1960 and 2002 AD. The data demonstrate the influence of leaded petrol from South Asia (predominantly India) until it was phased out in 1997 AD. Samples from 1997 to 2002 AD still showed high Pb levels which were attributed to fossil fuel combustion and non-ferrous metal production. Two ice core records of Pb pollution have been reported from Bolivian glacier archives. Hong et al. (2004) reported Pb concentrations in the Sajama glacier from 22,000 years ago until 1988 AD. When normalized to mineral dust inputs, Pb showed a clear enrichment from the start of the twentieth century which was approximately six times over pre-industrial levels. Lead isotope ratios, reported by Rosman et al. 2003 (Fig. 1), confirm that this enrichment was anthropogenic in origin. Correia et al. (2003) investigated a suite of heavy metals in an ice core from the Nevado Illimani glacier also in Bolivia, finding that the concentrations and enrichment of heavy metals with respect to mineral dust inputs was seasonally dependent, with the preferential deposition of anthropogenically-emitted pollutants during the dry season (June to August). A well-resolved record of Pb concentrations and isotopic compositions covering the past few 1000 years' atmospheric deposition is still lacking from South America. Nevertheless, Cooke et al. (2008) reconstructed the distribution and intensity of metallurgical and industrial activity over the past 4000 years, from lake sediment records obtained in Peru and Bolivia. These records showed changes in the location and intensity of Pb emissions over the successive periods of Tiwanaku/Wari, Inca, Colonial and modern industrial culture.

A detailed history of Pb pollution in the Southern Hemisphere has been compiled from Antarctic snow and ice cores. Wolff and Suttie (1994) sampled an 8.3 m snow pit, the record from which shows Pb concentrations varying between 2–4 pg g^{-1} from 1920 to 1950 AD, with a peak of ~7 pg g^{-1} in the late 1970s and slightly lower values during the 1980s. Despite the possibility of contamination from overflights in the 1970s, their results agreed with reconstructions of southern hemisphere gasoline consumption. Vallelonga et al. (2002) produced a 500 year record of Pb concentrations and isotopic compositions from Law Dome. They found concentrations of ~0.4 pg g^{-1} and $^{206}Pb/^{207}Pb \sim 1.22$ until the onset of anthropogenic Pb pollution at about 1890 AD. Pb isotopic compositions observed at Law Dome around 1900 AD ($^{206}Pb/^{207}Pb \sim 1.12$) clearly pointed to contamination from the Broken Hill Pb/Ag mine ($^{206}Pb/^{207}Pb \sim 1.04$) in Southeastern Australia. Since the 1950s, Pb isotopic compositions have been consistent with inputs of products of combustion of gasoline added with Pb extracted in Australia, potentially emitted into the atmosphere of both hemispheres and deposited globally. Subsequent studies of Pb isotopes from other Antarctic coastal locations (Burn-Nunes et al. 2011; Hong et al. 1998; Planchon et al. 2003, 2002b; Van de Velde et al. 2005) have demonstrated similar pollution histories across the Antarctic continent, suggesting that the Antarctic cryosphere accurately archives Pb emitted from the continental landmasses of the Southern Hemisphere before the 1950s while afterwards it may also reflect Pb isotopic composition from global transport emission.

Mercury

Gaseous elemental mercury (Hg^0) is the predominant atmospheric mercury (Hg) species, with an estimated residence time of ~1 year which allows long-range transport and inter-hemispheric mixing. However, the discovery at high latitudes of so-called “Atmospheric Mercury Depletion Events” (Schroeder et al. 1998) and post-depositional re-emission of Hg^0 from the snow pack (Durnford and Dastoor 2011) suggests that the residence time of Hg in the atmosphere is more difficult to define. Likewise, understanding to what extent Hg is deposited and preserved in the ice sheets and glaciers is complicated and mostly depends on the specific Hg form retained in the snow. Particulate Hg is intimately linked to the insoluble matrix and

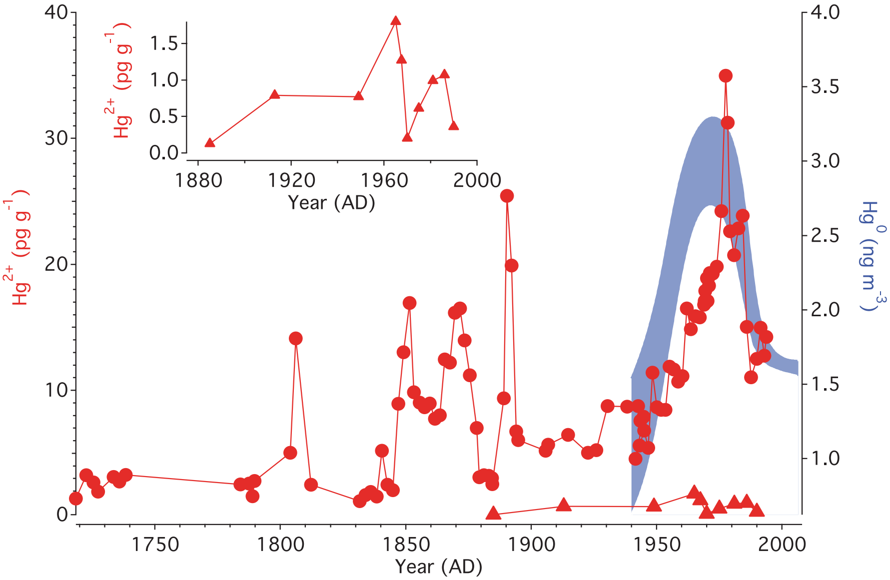


Fig. 2 Hg^{2+} concentrations in ice cores from Wyoming (*dots*, from Schuster et al. 2002) and the Western Alps (*triangles*, also in inset, from Jitaru et al. 2003) are compared with Hg^0 concentrations as recorded in interstitial air from Greenland firn (*shaded area*, indicating a range of maximum and minimum values, from Faïn et al. 2009)

is the most stable species found in glaciers (Jitaru et al. 2009), while Hg^{2+} can react quickly to form Hg^0 and is re-emitted from the snow into the atmosphere (Ferrari et al. 2004). Taking all these processes into account, records of total Hg (here defined as particulate Hg + Hg^{2+}) within snow and ice layers in the Antarctic and Greenland ice sheets may provide some constraints in answering the long standing questions on Hg origin (natural vs. anthropogenic) in the modern atmosphere and whether its deposition is due to local, regional or global sources.

Only a few ice core records reliably report Hg concentrations during modern times. This is mainly due to the fact that most of the early records were affected by contamination during field sampling and/or laboratory analysis. An ice core time series of Hg is available from Greenland (Fig. 2), covering a 40 year period from 1949 to 1989 AD (Boutron et al. 1998). This record basically provides Hg^{2+} concentrations because particulate Hg was not detectable by means of the extraction technique used. In this core Hg^{2+} concentrations ranged from less than 0.05 to 2 pg g^{-1}. Although these values are very low and do not represent total Hg, they could not be explained in terms of a natural contribution alone. Therefore it was suggested that Hg deposition to the Greenland ice sheet was influenced by the anthropogenic input from the North Hemisphere, possibly linked to coal and solid waste combustion. A recent report, however, emphasizes gold mining as an important global source of atmospheric Hg (UNEP 2013). A successive study from a firn shallow core extracted from the same Greenland site confirms Hg concentrations to fall within the range previously determined (Mann et al. 2005).

It is noticeable that the Boutron et al. (1998) Greenland record shows an apparent peak in Hg^{2+} concentration between the late 1940s to the mid 1960s. Similarly, a recent study found that Hg^0 concentrations determined in the interstitial air of the Greenland firn (Fig. 2) started to increase in the 1940s and reached a peak of 3 ng m^{-3} around 1970 AD, subsequently decreasing and stabilizing around 1995 AD (Faïn et al. 2009). In this context, Hg^{2+} and Hg^0 determined in the firn and in its interstitial air, respectively, appear to be correlated to some extent, suggesting that Hg^{2+} determined in firn and ice cores may be linked to atmospheric Hg^0 concentrations. Accordingly both US and Europe sediment and peat record reconstructions show higher deposition of atmospheric Hg during the 1970s (Pirrone et al. 1998; Bindler 2003), which is also broadly simultaneous with the 1970s peak in worldwide production on the order of 10^7 kg y^{-1} (USGS 2006). While Arctic sediment records of Hg^{2+} show a similar global trend (Biester et al. 2007; Muir et al. 2009), it is not clear whether these can be affected by climate-driven biophysical processes, which could modify the recorded history of atmospheric Hg deposition (Goodsite et al. 2013).

A mid-latitude Hg ice core record was also reconstructed from the Upper Fremont Glacier in Wyoming, North America (Schuster et al. 2002). This glacier is temperate and thus is more prone to post depositional processes. However, the low solubility of the Hg compound detected (Hg^{2+}) might have reduced the impact of melting processes on this record, which shows some features that broadly resemble that from the Greenland ice sheet (Fig. 2) and global Hg production. According to the Upper Fremont Glacier record Hg^{2+} concentrations started to rise during the 1950s and peaked during the 1970s and 1980s (20–25 pg g^{-1}), followed by an abrupt decrease in the 1990s (10–15 pg g^{-1}). The 5-fold increase in the Hg^{2+} depositional rate from pre-industrial times to the mid-1980s is consistent with the corresponding increases determined in sediment records from North America (Pirrone et al. 1998), and is perhaps linked to the proximity of this site to industrial sources. A low-resolution Hg^{2+} and methylmercury (MeHg) record was also obtained from an ice/snow core drilled at an altitude of 4250 m in the Col du Dome glacier on Mont Blanc, France (Jitaru et al. 2003). In this case, at the beginning of twentieth century an increase in Hg^{2+} was observed with a maximum six-fold increase at 1965 AD (1.80 pg g^{-1}) compared to 1885 AD (Fig. 2). Here we argue that the large difference in absolute Hg^{2+} concentration between the Upper Fremont Glacier and Mont Blanc ice cores, in addition to the different potential source areas for these regions, could be largely ascribed to the different fractions analyzed by means of the two analytical methods used.

Altogether, the few existing ice and firn records support the hypothesis that a recent deposition of anthropogenic Hg has occurred on a large (continental to hemispheric) spatial scale. The rapid industrial development in the Northern Hemisphere may have caused an increase in atmospheric Hg levels after World War II. Conversely, the decline observed since the 1970s is likely a response to the Clean Air Act of 1970 and similar European regulations. It is now imperative to determine Hg in ice cores from the Himalaya and the Tibetan Plateau glaciers. If regional Hg transport is predominant, records from these ice cores would indeed be well suited to reflect the recent continental increase in Hg emissions due to the rapid ongoing industrialization in this part of the world (Pirrone et al. 2010). So far Hg has been determined in this region only in snow pit samples, yielding results that are indicative of modern deposition in the Himalayan and Tibetan Plateau regions (Zhang et al. 2012; Wang et al. 2008a). In this case concentrations were found to be on the same order as those recorded in the snow and firn records from the other glaciers around the world, perhaps supporting the view of a large scale transfer and deposition of Hg. A ~700 years record of Hg in eggshells from Guangjin Island (South China Sea) indicates a rapid increase in Hg deposition since ~1800 AD (Xu et al. 2011). In other records obtained from Tibetan plateau lake sediment, the most significant increase in Hg pollution was shown to occur since the 1970s, followed by a further marked increase in the 1990s (Yang et al. 2010). This is also consistent with a three-fold increase in atmospheric Hg deposition since the advent of the Industrial Revolution as recorded in Alaskan lake sediments (Fitzgerald et al. 2005).

Platinum Group Elements

Platinum Group Elements (PGEs) are constituted by rhutenium (Ru), palladium (Pd), rhodium (Rh), osmium (Os), platinum (Pt) and iridium (Ir). These metals are depleted in the upper terrestrial crust (0.05–0.4 ng g^{-1}) (Wedepohl 1995) and enriched in the terrestrial mantle and in meteorites (Anders and Grevesse 1989). Since the mid-1970s Pt, Pd and Rh have been widely employed as catalysers to reduce the emissions of unburned hydrocarbons (HC), carbon monoxide (CO), and nitrogen oxides (NOx) from automobile traffic. The first vehicles equipped with catalytic converters adopting Pt, Pd and Rh were constructed in the mid-1970s in North America and Japan and, beginning in the 1980s, in Europe, particularly Germany. This resulted in a well documented decrease in HC, CO and NOx emissions and indirectly a decrease in environmental Pb pollution (Boutron et al. 1991) because the new catalytic converters required the use of unleaded gasoline. However, the increasing use of Pt and particularly Pd and Rh by the automobile industry raised some concerns about their possible toxicity for humans and the environment.

Several studies have demonstrated that urban and roadside PGEs concentrations are higher than in rural areas as a result of automobile emissions (Rauch et al. 2005, 2006; Rauch and Fatoki 2013). However, few studies have shown a temporal increase in PGEs concentrations. Ice cores provide an opportunity to reconstruct such trends. A methodology aimed at determining Pt, Pd and Rh in snow and ice at the pg g^{-1} level by ICP-SFMS was developed by Barbante et al. (1999). Using this procedure Pt, Pd and Rh were determined in the Dome de Goûter ice core which was extracted from Mt. Blanc (French-Italian Alps) and covered the 1778–1991 AD time intervals (Van de Velde et al. 2000a). Pd and Rh concentrations were found to be about two times higher during the second half of the twentieth century than in ancient ice, with values ranging up to 10 and 0.2 pg g^{-1}, respectively. A parallel study, conducted in the Swiss-Italian Alps at Colle Gnifetti, substantially confirms the results obtained for the Mt. Blanc core and also suggests a two-fold increase in Pt concentrations with values up to 0.8 pg g^{-1} (Barbante et al. 2004). Relatively high levels of Pt, Pd and Rh were determined in shallow snow and firn samples from central Greenland dated from the last few decades and were interpreted to be mainly a consequence of hemispheric pollution by these metals due to emissions from vehicles equipped with catalytic converters during the 1990s (Barbante et al. 2001b, 2003).

However, in a more recent study (Gabrielli et al. 2008), Pt was determined a second time in these same 1990s Greenland samples by means of a more sensitive technique which extends detection to the sub fg g^{-1} level (Gabrielli et al. 2004). In this case, only a few Pt spikes were found, with concentrations ranging from 37 fg g^{-1} to 90 fg g^{-1}, 5–15 times higher than the background but lower by about one order of magnitude than the Pt concentrations previously determined. This suggests that the supposed load of anthropogenic Pt to the northern Arctic latitudes was lower than previously assumed. These more recent Pt data, while still suggestive of a hemispheric Pt contamination, re-evaluated the concept of the hemisphere-scale diffusion of atmospheric Pt. Aside from this research, significant recent Pt enrichments were found in the Northern Hemisphere only in urban sediments where a 40-fold increase was observed over the pre-1975 background (Rauch and Hemond 2003; Rauch et al. 2004).

In Greenland snow sampled during the 1990s, low background concentrations of Ir (1–2 fg g^{-1}) were concomitant with the few Pt spikes, possibly reflecting that only traces of Ir were present in the majority of the catalytic converters at that time and that the natural atmospheric budget of Ir was not perturbed at hemispheric spatial scales (Gabrielli et al. 2008). Ir was in fact widely used only in small quantities by chemical and electrochemical industries, and in electronics. Only more recently Ir was included in new generation automobile catalysts but it remains unclear to what extent all these human activities might affect the Ir natural budget. Only a few other sediment studies have attempted to evaluate the recent deposition of Ir and only in the urban environment. For example Ir was found to increase by up to 5 times in Northern Hermisphere lake sediments near Boston (USA), following the introduction of automobile catalysts (Rauch et al. 2004).

Recently Soyol-Erdene et al. (2011) determined Pt, Ir and Rd in snow samples collected from two pits excavated in Queen Maud Land, East Antarctica and covering the 1957–2000 AD period. The average 50-year concentrations in Antarctic snow were: 7 fg g^{-1} (4.7–76 fg g^{-1}) for Pt, 0.12 fg g^{-1} (0.05–0.34 fg g^{-1}) for Ir, and 0.71 fg g^{-1} (0.12–8.8 fg g^{-1}) for Rh. These records illustrate the recent natural (volcanic) and anthropogenic contribution to the Antarctic continent for these trace elements. Significant enrichment in Pt and perhaps in Rh suggested large scale pollution since the 1980s for these two metals (Fig. 3). This was possibly due to anthropogenic sources such as automobile catalysts (introduced in 1987 AD in Australia and 1996 AD in Brasil-Argentina) and metal production processes (South Africa is the single largest PGEs producer). In contrast, no detectable Ir enrichment was observed. The possible anthropogenic Pt enrichment and negligible Ir in Antarctic firn are consistent with the preliminary information from the Greenland snow pit record (Gabrielli et al. 2008), perhaps suggesting a recent and detectable global Pt contamination concomitant with a negligible large scale diffusion of anthropogenic Ir.

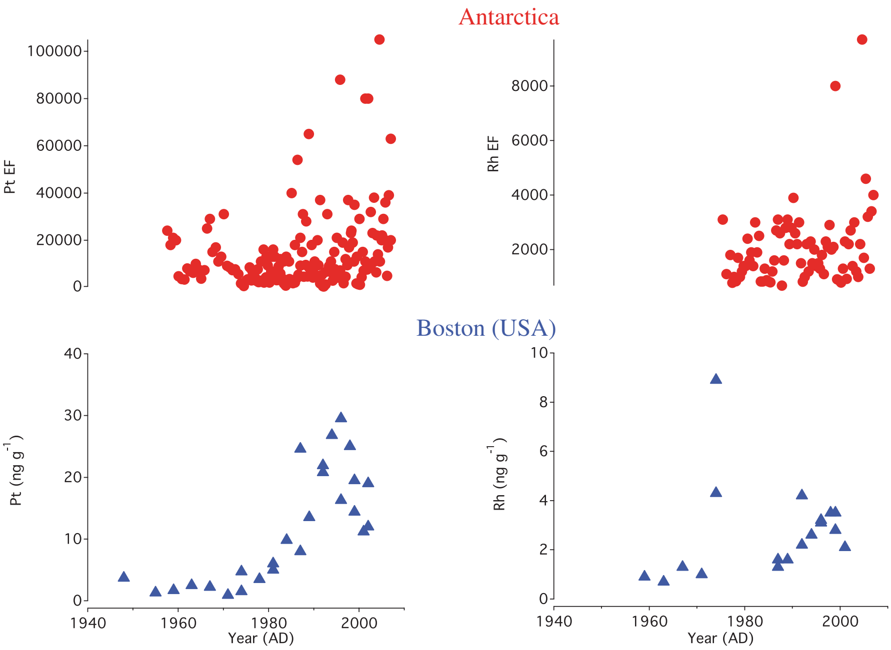


Fig. 3 Crustal enrichment factors of Pt (*top left*) and Rh (*top right*) from two snow pits in Central Antarctica (*dots*; from Soyol-Erdene at al. 2011) and concentrations of Pt (*bottom left*) and Rh (*bottom right*) in two sediment cores from the urban area of Boston, USA (*triangles*; from Rauch et al. 2004)

Other Trace Elements

Investigations on many other trace elements started in the polar ice sheets and are now extending to lower latitudes with the study of firn and ice collected from high altitude glaciers. In central Greenland a recent increase in trace element concentrations in snow and ice dated between 1773 AD and the 1960–1970 AD was found for cadmium (Cd; 8 times), copper (Cu; 4 times) and zinc (Zn; 5 times) (Candelone et al. 1995), indicating hemispheric contamination of the atmosphere for these trace elements (Cu and Zn are displayed in Fig. 4). As a result of the policy initiatives aimed at limiting atmospheric pollution in the USA and Europe, Cd and Zn concentrations have decreased by a factor of ~2 in Greenland snow between the end of the 1960s and the beginning of the 1990s (Boutron et al. 1991). The crustal enrichment factors, or EFc (a comparison of trace element mass ratios determined in the ice and in the terrestrial crust, typically using aluminum as a normalizing factor) of Cd and Zn decreased respectively from 186 and 19 in 1967 AD, to 58 and 6.3 in 1989 AD, suggesting a large scale reduction in the anthropogenic component of these two trace elements that are typically emitted during combustion of fossil fuels, nonferrous metal production, steel and iron manufacturing and incineration

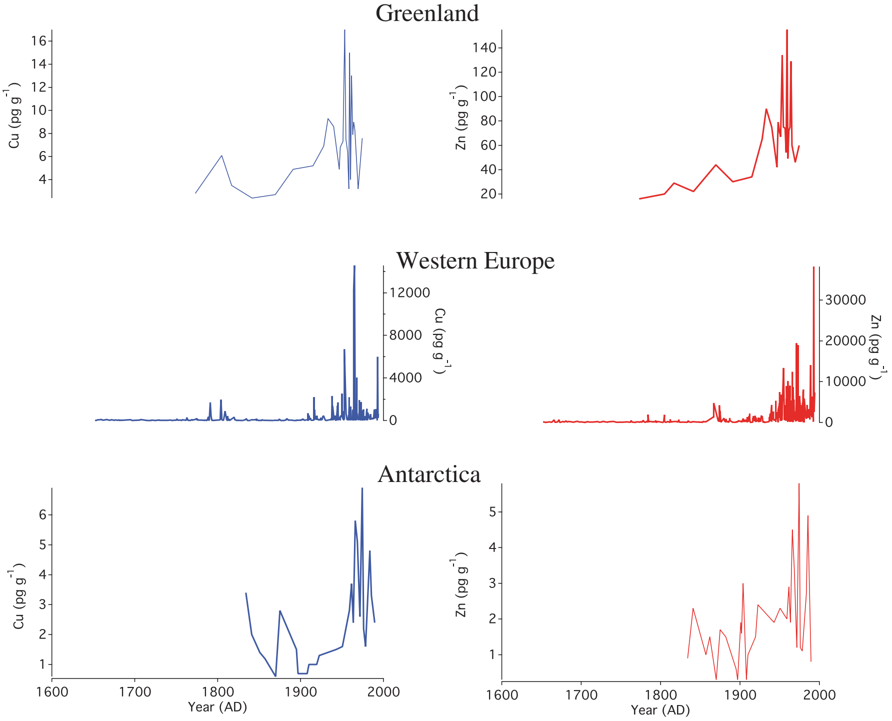


Fig. 4 Cu (*left column*) and Zn (*right column*) concentrations in a Greenland ice core (from Candelone et al. 1995), in a Western Alps ice core (from Barbante et al. 2004) and in Antarctic firn (from Planchon et al. 2002a)

of refuse (Nriagu and Pacyna 1988). In contrast, a significant decrease in Cu concentration was not found (Candelone et al. 1995), probably due to its still relatively important natural emission sources of windborne mineral dust.

The advent of the continuous flow analysis technique coupled to ICP-SFMS allowed more detailed investigation of the history of trace element pollution in the Northern Hemisphere. Cd and thallium (Tl) which were determined in Greenland snow and ice showed that atmospheric deposition for these elements was high by the early 1900s, with a tenfold increase from preindustrial levels (McConnell and Edwards 2008). The levels found at the beginning of the last century were 2–5 times higher than during recent decades. This early increase occurred after 1860 AD and was attributed to coal burning in North America and Europe. In this study the different signature of sources of trace elements emissions over time, from coal-dominated industrial (1860–1940 AD) to oil-dominated industrial (1940–2003 AD) was also distinguished. A Tl peak, indicating a marked enrichment at the beginning of the last century, was also recorded in a Swiss peat bog (Shotyk and Krachler 2004).

In the Canadian High Arctic Tl, and silver (Ag) were determined in snow and ice collected from Devon Island indicating a predominant recent anthropogenic contribution for these metals (Krachler et al. 2008b). In this core also antimony (Sb) was studied showing concentrations increasing 6–8 times during the last century and peaking during the 1950–1960 AD time period, reflecting contamination from industrialization, the economic growth that followed World War II, as well as the introduction of flue gas filter technologies (Krachler et al. 2008a, 2005). The modern Sb EFc (referenced to scandium) was ~25 and may have resulted from Asian production of Sb sulfides such as stibnite (Sb_2S_3) and as a by-product of Pb and Cu smelting. Starting perhaps several thousands of years ago, the Devon Island ice core suggests a 5-fold enrichment above the natural background for Sb, arsenic (As) and bismuth (Bi), which was attributed to mining and smelting emissions as a co-product of ancient Pb sulphide ores (Krachler et al. 2009). As noted before, Pb emissions from mining activities during the Greek and Roman periods were detected in Greenland (Hong 1994, Rosman 1998). Additional evidence of large scale Sb contamination during the Roman and also the Medieval Period was provided through analyses of peat samples from various bogs in Europe (Shotyk et al. 2005a, and references therein).

In the western European Alps Cd, Cu and Zn were determined in snow and ice from Dome de Goûter, Mt. Blanc (Van de Velde et al. 2000b). Concentrations were constant until the end of the nineteenth century and then they increased 10, 15 and 30 times for Cu, Cd and Zn, respectively, until the 1970s. During the following two decades Cd and Zn concentrations decreased while Cu continued to increase. Cobalt (Co), chromium (Cr), molybdenum (Mo), and Sb were also determined in this core. Concentrations in recent firn were found to be generally higher than in ice dated from before the middle of the nineteenth century. Mo displays the strongest increase (16 times), followed by Sb (5), Co (2–3) and Cr (2–3) (Van de Velde et al. 1999). In this latter study it was suggested that enrichments in Co, Mo, and Sb were due to contributions from oil and coal combustion while Cr originated from Fe, steel, and Fe-alloy industries. In this core from Mt. Blanc a significant increase factor (3) was found also for U in post-World War II layers and was attributed to tropospheric transport of dust emitted during extensive mining and milling operations, mainly in the former German Democratic Republic (Barbante et al. 2001a).

In the western Alps trace elements were also determined in another ice core extracted from the glacier saddle of Colle Gnifetti, Monte Rosa at 4450 m of elevation, and with a time scale spanning from 1650 to 1994 AD. Higher concentrations were found during the second half of the twentieth century than in the seventeenth and eighteenth centuries. The highest increase were observed for Cd (36 times), Zn (19), Bi (15), Cu (11), and nickel (Ni; 9), suggesting a significant input of these trace elements to the central European atmosphere (Fig. 4 displays trends for Cu and Zn) (Barbante et al. 2004). Consistent with the ice core results, Cu, Zn and Cd were also found to increase until about 1960 AD in sediment cores from Lake Zurich (Switzerland) (von Gunten et al. 1997). However, Cu and Cd decreased sharply afterwards in the sediment records, in accordance with the trend registered in the Mt. Blanc ice core. In the eastern European Alps only a few trace element data are available from a snow pit dug on Mt. Ortles in 2009 at 3830 m of elevation. These suggest a pollution source in the adjacent Po' Valley in Italy (Gabrieli et al. 2011a).

The first trace element data from the high altitudes of Central Asia were extracted from a firn/ice core drilled at an elevation of 7010 m near the top of Muztagh Ata glacier, east Pamirs, which was dated from the mid-1950s to 2000 AD. Increases in concentrations were observed for Sb (three times) and perhaps Bi (two) from the mid-1960s to the beginning of the 1990s (Li et al. 2006). In another study in Central Asia, trace elements were quantified in an ice core recovered from the Miaoergou glacier in the eastern Tien Shan, spanning the period 1953–2004 AD. Also in this case only slight enhancements in concentrations were observed for Cd (2.7), Sb (1.8), Bi (1.5), Tl (1.2), and tin (Sn) (1.6) during the 1953–2004 AD time period, perhaps due to enhanced anthropogenic emissions from activities such as metal smelting, mining, stationary fossil fuel combustion, and combustion of gasoline in Eurasia, particularly Xinjiang in northwestern China, Russia, and Kazakhstan (Liu et al. 2011).

In the high-altitude Himalayan glaciers trace elements from 1650 to 2002 AD were determined in a Mount Everest ice core drilled at 6518 m elevation. Bi, U, and cesium (Cs) concentrations and EFc's were found to have increased since the 1950s. The likely sources for the enrichment of Bi included mining, metal smelting, oil and coal combustion, as opposed to mining and refinement as the sources for U and Cs (Kaspari et al. 2009). As, Mo, Sn, and Sb were determined over the period from 1205 to 2002 AD in another high-altitude ice core from Mt. Everest. Compared to the pre-1900 period, increases in concentrations and EFc were observed after the 1970s, with the highest increase in EFc for Sn (2.6) and the lowest for As (1.4) in the 1995–2002 AD period (Hong et al. 2009). The increases in these elements were attributed to increased anthropogenic emissions from stationary fossil fuel combustion and nonferrous metals production, likely in India.

Few trace element data are available from tropical high altitude glaciers in the Southern Hemisphere. The 137 m ice core drilled at the summit of Nevado Illimani (6350 m) in the eastern Bolivian Andes was analyzed for various trace elements from the section dated from 1919 to 1999 AD. Significant increases were observed for the concentrations of several species such as Cu (2–6 times), As (2), Zn (2–4), Cd (2–4), Co (2–15), Ni (2–10) and Cr (2–5) (Correia et al. 2003). Other ice core sections from a snow/ice core drilled at an altitude of 6542 m on the Sajama ice cap in Bolivia were also analyzed for various trace elements. In this case increasing trends were observed for Cu, Zn, As, Ag, Cd and Bi during the nineteenth and twentieth centuries (Hong et al. 2004). In this period an increase of EFc values was found for As (5), Bi (7), Cu (2), Zn (4), Ag (5) and Cd (5). The notable excesses in Cu, Zn, Ag and Cd were attributed to metal production activities, especially in Peru, Chile and Bolivia where a continuous increase in production occurred during the twentieth century.

In the most remote sites of the Southern Hemisphere, recent enrichments of trace elements in Antarctic snow and ice were detected with more difficulty than in the Arctic due to the lower concentrations and the greater isolation of Antarctica from emission sources in the Southern Hemisphere. Measured concentrations of Cd, Cu and Zn in snow from Adelie Land in East Antarctica were initially found not to have significantly increased during the time period 1940–1980 AD (Görlach and Boutron

1992). In a core from Law Dome in East Antarctica, enrichments of Cu concentrations during the twentieth century were observed to be greater by a factor of 1.5 than during earlier centuries, consistent with increasing anthropogenic emissions for Cu over that period (Vallelonga et al. 2004). In another study conducted on samples collected from a deep snow pit dug in Coatsland in West Antarctica, Cu showed a 2-fold increase (from ~2 to ~4 pg g^{-1}) during the period from 1923 to 1986 AD (Wolff et al. 1999). This increase of Cu in Antarctic snow was suggested to originate from South American smelters emissions that are advected relatively far to the south compared to other Southern Hemisphere emissions. Analysis of samples from the same snow pit also found pronounced enhancements after the mid 1940s for Cr (2–4), Zn (2–4), Cu (~4), Ag (~7), Bi (~10) and U (~5) (Planchon et al. 2002a) (Cu and Zn are displayed in Fig. 4). The enrichments were attributed to emissions from human activities in Southern America, Southern Africa and Australia, especially from non-ferrous metal mining and smelting in Chile, Peru, Zaire, Zambia and Australia. Interestingly an enrichment peak in Cr, Bi and perhaps U was found in this Antarctic snow pit at the beginning of the twentieth century, similar to the corresponding trace element enrichment found in the Arctic at about the same time (McConnell and Edwards 2008).

Organic Compounds

Environmental monitoring of organic pollutants in snow and ice started only recently and has led to regional studies of pesticide exposure (Ruggirello et al. 2010) as well as the investigations of other types of human related activity, such changes in fuel use (Gabrieli et al. 2010). The delay in the relatively recent development of these studies was also due to the challenging techniques required to determine organic compounds in the environment. Some of them, such as polycyclic aromatic hydrocarbons (PAHs) and persistent organic pollutants (POPs), require pre-concentration on compound-specific solid phase extraction columns coupled to separation devices such as high pressure liquid chromatographs or gas chromatographs. In addition, the sensitivity required to detect and quantify very low concentrations of organic compounds in polar ice and snow could be achieved with the latest generation of mass spectrometers, such as ion trap or triple-quadrupole mass spectrometers (Gambaro et al. 2008).

The first category of organic pollutants detected in ice cores was PAHs, a class of relatively non-reactive organic compounds. PAHs are by-products of the incomplete combustion of various fossil fuels, including fuel oil, gasoline and coal, as well as biomass burning. PAHs are of interest because they are a threat to human health: they have been identified to have carcinogenic and mutagenic properties and have been listed by the US Environmental Protection Agency (USEPA) as a "priority pollutant". PAHs were first studied in ice cores in the 1990s in central Greenland where Kawamura et al. (1994) reported a 400-year ice-core record that demonstrated a 50-fold increase from pre-1800 background concentrations (2.3 pg g^{-1})

to late twentieth century values (103 pg g^{-1}). Jaffrezo et al. (1994) investigated 13 PAHs in a Summit snow pit corresponding to 4 years of deposition. They reported average total PAHs concentrations of 1360 fg g^{-1} and observed a distinct seasonal cycle of summer minima, elevated winter concentrations and spring peaks. These observations were reproduced and refined by Masclet et al. (1986) with a second Summit snow pit record covering the period from 1993 to 1996 AD. They found that total PAHs concentrations correlated well with black carbon concentrations (with an average PAHs/carbon ratio of 0.1 %). Concentrations of fluoranthene and pyrene, indicators of coal and fuel-oil combustion sources, were found to be well correlated with sulfate, a byproduct of coal combustion. High concentrations of retene, an indicator of boreal forest fires, were not always coincident with high ammonium concentrations.

Gabrieli et al. (2010) presented a record of PAHs concentrations over the past 300 years in the Alpine ice core from Colle Gnifetti on Mt. Rosa which demonstrated the overwhelming increase of PAHs in Europe since the nineteenth century. Total concentrations increased from 2 pg g^{-1} before 1875 AD to peak values of 32 pg g^{-1} between 1945 and 1955 AD, followed by decreasing levels since the 1970s. A different industrial development history for Asia is reflected by the PAHs record from the East Rongbuk glacier in the Himalayas (Wang et al. 2008b), where fluxes increased continuously to 8 ng cm^{-2} y^{-1} in the late 1990s. This history suggests a predominantly Indian source for the emissions transported to the Himalayas, with PAHs co-deposited with excess sulfates. Accordingly, a lake sediment record from the Northeastern Tibetan Plateau (Wang et al. 2010b) shows total PAH fluxes at about 0.3 ng cm^{-2} y^{-1} in 1860 AD, and increasing greatly after 1960 AD to approximately 14 ng cm^{-2} y^{-1}, reflecting the somewhat earlier development of industry in China (Fig. 5). In this latter case, fluxes of the 16 USEPA-listed priority PAHs similarly varied from 0.2 ng cm^{-2} y^{-1} in 1860 AD to 11 ng cm^{-2} y^{-1} after 1960 AD.

A second category of organic pollutants that has been studied in ice cores involve POPs, which is an umbrella term that refers to bio-accumulative, long-lived organic compounds that present a public or environmental health threat, such as polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs, including aldrin, DDT, and dieldrin). Since the 1970s many of these compounds have been regulated or banned in some way, and the Stockholm Convention on POPs in 2004 enforced the prohibition of the production and use of 16 of these compounds in 151 countries. Glaciers have great potential for the study of POPs because they act as "cold condensers", i.e., concentrating POPs by removing them from the atmosphere (Daly and Wania 2004). Unfortunately, the very glaciers that accumulate POPs are the same ones that provide drinking and irrigation water to highly populated areas and are now rapidly melting due to climate change. Schmid et al. (2010) conducted a compelling study of the release of POPs into downstream freshwater systems decades after being first used as pesticides.

In a series of papers (Maggi et al. 2006; Villa et al. 2001, 2003), Villa and colleagues reported historical profiles of PCBs since the 1950s from the Lys Col, next to Mt. Rosa in the Western Alps. They found that hexachlorocyclohexane (HCH) concentrations peaked at 20 pg g^{-1} in the 1970s and then decreased and stabilized

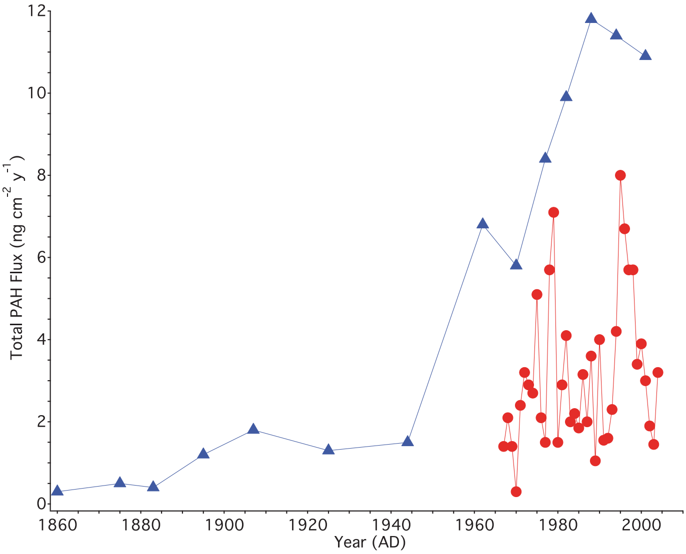


Fig. 5 Total PAH fluxes determined from an ice core from the Dasuopu glacier in the central Himalayas (*circles*, from Wang et al. 2008b) and from a sediment core from Qinghui Lake on the Tibetan Plateau (*triangles*; from Wang et al. 2010b)

at 0.5 pg g^{-1} after 1980 AD. In contrast, DDT concentrations steadily increased from 1 pg g^{-1} in 1965 AD to 10 pg g^{-1} in 1996 AD; this trend was attributed to a local factory that produced DDT as a precursor to difocol pesticide. These findings were confirmed by similar DDT trends in the sediments of nearby Lake Maggiore (Guzzella et al. 1997). First Hermanson et al (2005) and then Ruggirello et al. (2010) provided a comprehensive evaluation of current and past pesticide concentrations in snow and ice from Svalbard, a remote polar island which has no history of pesticide use. The latter demonstrated the persistent and extensive distribution of POPs like HCH, chlordane, DDE (a DDT byproduct) and dieldrin, most of which had decreasing flux trends. Chlordane fluxes decreased from ~15 pg cm^{-2} y^{-1} in 1990 AD to ~5 pg cm^{-2} y^{-1} in 2000 AD and dieldrin had steadily decreased from 55 pg cm^{-2} y^{-1} in 1950 AD to 5 pg cm^{-2} y^{-1} after 1995 AD.

Studies of North American glaciers reveal a similar history of accumulation of POPs in ice long after being banned. Donald et al. (1999) reported concentrations of DDT, chlordane and dieldrin in a temperate glacier in western Canada, observing that peak values (2.6 pg g^{-1} for DDT, 0.05 pg g^{-1} for dieldrin, 0.07 pg g^{-1} for chlordane) occurred in the 1980s and 1990s, a decade or more after being phased out in the US. While evaluating the release of PCBs from a snowpack in Banff National Park, Blais et al. (2001) found that at least 10% of the summer glacial melt contained PCBs which had been deposited between 1950 AD and 1970 AD. Comprehensive studies of POPs in lake sediments, soils and aerosols have also been conducted in North American watersheds (e.g. Hornbuckle et al. 2006), generally demonstrating post-1970s peaks in POPs concentrations and, more recently, slowly declining concentrations. However, at the Agassiz Ice Cap (Ellesmere Island, Canadian Arctic) no evidence of a consistent long-term trend PCB deposition was found for the period 1963–1993 (Gregor et al. 1995).

Extensive studies of POPs have also been conducted in Himalayan glaciers (Wang et al. 2010a, 2010b, 2008b), in which it was shown that DDT concentrations peaked at about 2 pg g^{-1} in the 1970s and then decreased sharply to 0.2 pg g^{-1} after being banned in India in 1989 AD. HCH concentrations similarly peaked at about 6 pg g^{-1} in the early 1970s but dropped to about 1 pg g^{-1} after 1980 AD. These trends further confirmed the dominant Indian source of pollutants to the East Rongbuk Glacier. A study of POPs in the Dasuopu Glacier demonstrated a strong winter enhancement of those PAHs related to the use of heating fuel, with total concentrations below 26 pg g^{-1} and DDT concentrations at about 0.2 pg g^{-1}. Concentrations of all PAHs in the Dasuopu Glacier have been steadily decreasing from their highest values at ~2000 AD (Wang et al. 2008a).

Studies of organic pollutants in Antarctica have been limited. Fuoco et al. (2012) recently reported PAHs and PCBs levels in snow and ice from Talos Dome in coastal East Antarctica. They found a sharp increase in PCBs since 1930 AD with occasional spikes related to volcanic eruptions. PAH concentrations increased by 50% and PCBs by 200% after 1930 AD. Kang et al. (2012) studied OCP deposition in surface snow over a traverse from the coast to Dome Fuji in central East Antarctica. Although they did not sample older snow or ice, they observed that Antarctic concentrations of HCH were 2 to 20 times lower than concentrations found in glaciers in Norway and Svalbard.

An emerging new field of research concerns brominated flame retardants (BFRs). These are a class of compounds used to slow the diffusion of flame in residential and commercial indoor fabric, foam, and electronic products in the industrialized world. An atmospheric BFR deposition history was identified in an ice core extracted in the Svalbard including including hexabromocyclododecane (HBCD), 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE), decabromodiphenyl ethane (DBDPE), pentabromoethylbenzene (PBEB), and 15 polybrominateddiphenyl ether congeners (PBDE). It was found that the greatest inputs were HBCD and BDE-209, 910, and 320 pg cm^{-2} $year^{-1}$ from 1995 to 2005 (Hermanson et al. 2010). Finally, polybrominated diphenyl ethers (PBDEs) and Perfluoroalkyl substances (PFASs) were detected in a 1997–2007 AD shallow firn core from Colle Gnifetti in the Alps (Kirchgeorg et al. 2013).

Black Carbon

Several findings and developments have recently been reported regarding the environmental impacts of another important organic compound. Elemental carbon (EC) or black carbon (BC) (see Rose and Ruppel, this volume), which is commonly called soot, is primarily emitted from the combustion of biomass and coal, thus making it a proxy related to both natural combustion processes and industrial development (Ramanathan and Carmichael 2008). An important consideration regarding the emission of BC is its highly refractory nature; it is a strong absorber of solar energy and thus has a very strong radiative forcing effect (McConnell 2010). Because the accumulation of BC on glacier ice reduces the albedo while BC in the atmosphere may also amplify the current warming trends at high altitudes (Ramanathan and Carmichael 2008), reduction of anthropogenic emissions can be an effective measure for inhibiting melt. The study of BC has been accelerated by the development of the Single Particle Soot Photometer, an instrument that is field-portable, has sufficient sensitivity to study BC in aerosols as well as in polar ice, and can be coupled to continuous flow analysis systems commonly used for analysis of ice cores at high resolution. Highly-resolved records of BC deposition describing the industrial development of the Northern Hemisphere have been produced from Greenland ice. There was a seven-fold increase in BC concentrations from 1.7 ng g^{-1} before 1850 AD (the start of the industrial era) to peak concentrations of about 12 ng g^{-1} in 1910 AD, with lower concentrations of 2.3 ng g^{-1} since 1955 AD (McConnell et al. 2007). Kaspari et al. (2011) reported a three-fold increase in BC concentrations in the East Rongbuk Glacier, from background levels of 0.2 ng g^{-1} from 1860 to 1975 AD up to 0.7 ng g^{-1} between 1975 and 2000 AD. In the Alps BC concentrations were determined in an ice core from Colle Gnifetti and were found to vary between 7 and 128 ng g^{-1} increasing by a mean factor of 3.7 between preindustrial (1755–1890 AD) and modern times (1950–1975 AD) (Lavanchy et al. 1999). These results were essentially confirmed by further analyses from another Colle Gnifetti core, although with lower maximum concentrations (20 ng g^{-1}), during modern times (Thevenon et al. 2009). These studies are also consistent with EC analyses (in a range of 6–50 ng g^{-1}) performed in the alpine core from Fiescherhorn glacier (Switzerland) (Jenk et al. 2006). A recent study of BC deposition at two Antarctic sites from 1850 to 2000 AD indicates that any anthropogenic contribution to Antarctic BC fluxes is minimal (Bisiaux et al. 2012). These results may be due to a hemispheric gradient in anthropogenic biomass burning emissions, with greater emissions in the Northern Hemisphere than in the Southern Hemisphere.

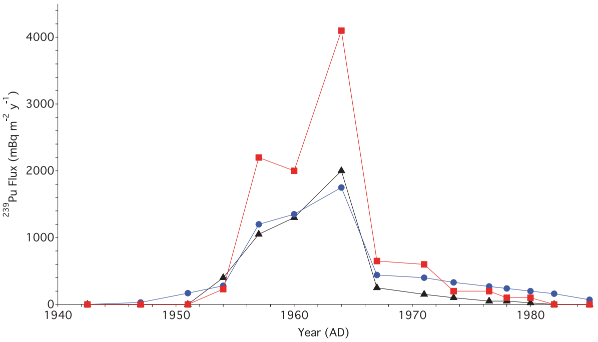
Radionuclides

After the detonation of the first atomic bombs, radionuclides started to be deposited and can be detected in ice strata dated to 1945 AD (Kudo et al. 1998). The intentional release or accidental loss of radioactive materials to the environment has been closely monitored (Carter and Moghissi 1977). The earliest atomic bombs operated on the same principle as fission nuclear reactors. After 1952 AD, thermonuclear weapons were developed, involving combined fission-fusion reactions and resulting in much greater energy yields and radionuclide production. Atmospheric testing of nuclear weapons was not regulated until the signing of the 1963 AD “Limited Test Ban Treaty”, after which an additional 64 above-ground tests were conducted until 1980 AD, when all such tests were banned (Norris and Arkin 1988). The most serious cases of accidental release of radionuclides involve nuclear power plant accidents, such as Chernobyl (Ukraine 1986 AD) and Fukushima (Japan 2011 AD). The presence of radioactive material in snow and ice is quantified either by β-radioactivity or specific detonation byproducts including tritium (^{3}H) and isotopes of chlorine (^{36}Cl), iodium (^{129}I), cesium (^{137}Cs) and plutonium (^{239}Pu). In this section we explore three applications of glaciological studies of radionuclides: the reconstruction of past atmospheric bomb tests; the use of well-dated atomic bomb horizons in the ice layers for developing core chronologies; and the study of atmospheric chemistry and dynamics.

The study of radionuclides in ice and snow has enabled an accurate reconstruction of the regional and global extent of nuclear weapons' testing as well as accidental radioactivity releases. Picciotto and Wilgain (1963) were the first to identify a 5–10-fold increase in β-activity in Greenland as a result of the first above-ground thermonuclear bomb tests from 1952 to 1955 AD. Later studies continued to monitor the evolution of radionuclide deposition in Greenland as well as to extend the research to Antarctica (Crozaz 1969). In particular, monitoring focused on ^{3}H, which has both natural and anthropogenic production sources. In addition to being formed by nuclear weapon detonations, ^{3}H (half-life 4500 days) is formed in the upper atmosphere from interaction with cosmic radiation and is rapidly incorporated into water molecules to form tritiated water (HTO). As such, HTO becomes diffused in the hydrological cycle, being precipitated as rain or snow, and eventually is incorporated into the considerably larger oceanic reservoir. A number of investigators (Jouzel et al. 1979; Koide et al. 1982; Merlivat et al. 1973) reported concentrations of ^{3}H in Greenland and Antarctica, focusing on the two bomb peaks in the late 1950s and early 1960s. ^{3}H concentrations corresponding to the 1963 AD bomb peak were approximately 500 times greater than background levels in Greenland (Koide et al. 1982) and approximately 100 times greater in Antarctica (Fourré et al. 2006). Fourré et al. (2006) demonstrated that ^{3}H concentrations in Greenland snow and ice have consistently decreased since the 1960s, as would be expected from natural decay and dilution into the oceans, whereas levels remained higher than background in central Antarctica due to the more frequent incursion of stratospheric air through the more persistent polar vortex. ^{3}H levels in central Antarctica were 2–3 times greater compared to lower-altitude coastal zones.

By the late 1970s, detection of radioactivity peaks from nuclear bomb tests had become a common stratigraphic dating tool for ice core studies (Hammer et al. 1978) and is still routinely employed (Eichler et al. 2000; Kehrwald et al. 2008; Knusel et al. 2003) also at high resolution such as in the case of tritium determined in the alpine core from Fiescherhorn glacier (Schwikowski et al. 1999). Gabrieli et al. (2011b) reported a high-resolution record of ^{239}Pu concentrations in the Alpine Colle Gnifetti ice core from Mt. Rosa, demonstrating that Pu concentrations remain approximately twice that of pre-1952 AD concentrations during the 1970s and return to background levels by 1980 AD (Fig. 6). Histories of radionuclide deposition have also been reported from other mountain glaciers at middle and low latitudes around the world, including Huascarán in the Andes of Peru (Thompson et al. 1995a), Guliya in the Kunlan Shan of China (Thompson et al. 1995b), Miaoergou

Fig. 6 Averaged ^{239}Pu fluxes determined in ice core records from the European Alps. (*circles*: Colle Gnifetti, Monte Rosa, from Gabrieli et al. 2011); *triangles*: Col du Dome, Mont Blanc, from Warneke et al. 2002) and Siberian Altai mountains (*squares*, from Olivier et al. 2004)



Glacier in the Tien Shan of China (Liu et al. 2011) and Belukha in the Siberian Altai (Olivier et al. 2004). These studies consistently demonstrate two radioactivity peaks: the first, relatively low and wide, in the mid- to late 1950s (β, ^{3}H, ^{36}Cl, ^{137}Cs, ^{239}Pu) and the second, relatively high and narrow between 1962 and 1964 AD (β, ^{3}H, ^{137}Cs, ^{239}Pu).

The explosion at the Chernobyl nuclear power plant in April, 1986 AD led to a resurgence of interest in detection of the released radionuclides. Particularly high levels of activity were recorded in the Alps (10–20 Bq kg^{-1}) and in Svalbard (1–9 Bq kg^{-1}) whereas radioactivity levels in Northern Greenland and North America were consistently below 1 Bq kg^{-1} (Pourchet et al. 1988). The fact that nuclear disasters, such as that at Chernobyl, are essentially discrete, well-recorded atmospheric releases of radionuclides has resulting in such events being utilized for glaciological studies. Vincent et al. (1997) measured ^{137}Cs in ice and snow at various locations over the Dome du Goûter on Mt. Blanc in the Western Alps and demonstrated the effect of wind scouring on surface accumulation across the dome. ^{137}Cs concentrations were found to vary from 10 Bq m^{-2} at the dome summit to 25 Bq m^{-2} at a drilling site 30 m away, and up to 3000 Bq m^{-2} at a second drilling site over 100 m distant. This phenomenon was only observed for the thin layer of accumulation associated with the Chernobyl disaster. For the 1950s and 1960s bomb peaks, the deposition of radionuclides was more extensive over time and hence less subject to surface scouring, so all three sites at the Dome du Goûter had similar ^{137}Cs concentrations of 2000–3000 Bq m^{-2}.

The emission, distribution and deposition of radionuclides to ice sheets and glaciers have also been employed to investigate atmospheric circulation and aerosol deposition processes. Heikkilä et al. (2009) compiled ^{36}Cl flux histories from a global suite of eight ice cores, demonstrating the existence of a broad peak from 1955 to 1964 AD. They employed this network of ice core-based ^{36}Cl deposition to validate an advanced climate model of global stratospheric and tropospheric aerosol and precipitation transport, called ECHAM5-HAM. The history of ^{36}Cl emission is unique because this species results from neutron activation of ^{35}Cl in sea salts, and hence was exclusively produced by nuclear bomb testing on Pacific Ocean atolls or islands. The largest tests occurred in 1954 AD (producing 112 kg ^{36}Cl) with smaller tests in 1958 AD (producing 71 kg ^{36}Cl) and 1962 AD (producing 54 kg ^{36}Cl).

Similarly, releases of ^{129}I due to nuclear bomb tests, accidents and reprocessing (the extraction of fissionable Pu from spent nuclear fuel material) have been detected in an ice core (Reithmeier et al. 2006) and allowed the improvement of models of atmospheric chemistry and circulation (Reithmeier et al. 2010). The March 2011 AD Fukushima nuclear power plant disaster has already become a topic of study (Hsu et al. 2012), and is likely to be included as a chronological tiepoint in future glaciological studies.

Conclusions and Perspectives

We have shown how ice and firn cores provide a broad suite of information on the occurrence of anthropogenic contaminants in the past and present atmosphere. The advent of highly sensitive analytical techniques based on mass spectrometry allows the detection of anthropogenic impacts of these contaminants on firn and ice extracted from the remotest glaciers and ice sheets of the planet. The Arctic and Antarctic firn and ice records have provided a global perspective of the contamination from toxic elements such as Pb, Cu, Cd, Zn and various radionuclides. Other contaminants such as Hg, PGEs, BC and organic species such as, POPs and PAHs need to be further investigated to better understand their diffusion to the remotest locations of the Earth.

Knowledge of the dispersion of some anthropogenic toxic species has proven to be extremely important for policy makers as the attempt to take action to preserve terrestrial and aquatic ecosystems and protect human health. During the last few decades it has become apparent how studies on toxic contaminants in ice cores have the capability to influence political decisions to mitigate the diffusion of such species. For instance, knowledge of the global impact of atmospheric Pb emissions was an instrumental contribution to the decision to ban leaded gasoline. Subsequently, ice core analyses documented the effectiveness of this decision as Pb concentrations in polar snow were found to slowly decrease by the 1980s.

In this context, starting with the 1980s other inorganic (Zn, Cd) and organic (PCBs and POPs) species were observed to decrease in Arctic firn thanks to the technological advances forced by policies focused on reducing the impact of these toxic species in the atmosphere. Nevertheless, massive regional industrialization such as that occurring in Asia today is resulting in new and potent sources of anthropogenic contaminants into the atmosphere. The few mid and low latitude ice core records in existence do not provide coherent indications of the regional trends of atmospheric contamination. In this context, policymakers, governmental agencies, and public resource administrators require novel and more precise insights into short-term regional changes in the composition of the atmosphere. Studies on *fluxes* of targeted species to ice sheets and high altitude glaciers may provide a guide for prioritizing which anthropogenic emissions need to be regulated at regional levels. Ice cores still appear to be not only suitable but also convenient archives to conduct diffuse monitoring operations, typically lasting decades.

We note that most of the ice and firn records report only concentration data. While often the largest part of the concentration variability is influenced by the atmospheric input of the studied species, still a significant part of the variability is influenced by changes in snow accumulation rate. In cases of dry deposition of contaminants, snow accumulation significantly modulates the concentration of the species in the ice. In this context, in order to refine the modeling of transport and deposition of these species, it is also important to evaluate carefully the accumulation rate in order to assess fluxes (concentration × water equivalent accumulation rate). Nevertheless, we acknowledge that snow accumulation rate cannot always be obtained precisely from ice cores, especially when the seasonality of the signal is not pronounced and ice thinning deviates from conventional linear models at greater depths in the glaciers and ice sheets.

Another emerging difficulty to monitoring modern changes in regional atmospheric contamination by means of ice and firn cores is linked to the increasing widespread post-depositional effects due to the ongoing rapid climate change that is causing significant surface snow ablation and obliteration of the signal through melt water percolation. Modern ice core and firn records will need to be extracted at the highest latitudes and even higher elevations to guarantee that an accurate environmental signal is preserved. Especially at low latitudes, global climatic change is already limiting the paleoenvironmental potential of locations that were entirely suitable drilling sites until only a few decades ago.

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Use of Catalogued Long-term Biological Collections and Samples for Determining Changes in Contaminant Exposure to Organisms

Linda M. Campbell and Paul E. Drevnick

Abstract For decades, biological materials have been collected and held in museum collections, natural history collections (NHC), herbaria and environmental specimen banks (ESB). Those biological materials and accompanying data represent a potentially important source of retrospective analyses of contaminants and other chemical tracers. In ideal situations, those can provide valuable insights into changes in contaminant accumulation and concentrations over time and space. This chapter explores the benefits of such curated and catalogued specimens for contaminant research, as well as limitations and key considerations which must be kept in mind when using such samples. Three case studies examining temporal trends in contaminants using long-term biological collections are also presented.

Keywords Museum · Contaminants · Mercury · Organochlorines · Birds · Fish · Retrospective analyses

Introduction

Museum and herbarium specimens of animals and plants stored worldwide in natural history collections (NHC), as well as catalogued samples from environmental specimen banks (ESB), can be valuable for documenting long-term changes in biotic accumulation of contaminants. Those sources of biological tissues often complement long-term contaminant monitoring programs, such as the long-running Sportfish Monitoring Program by the Ontario Ministry of Environment (Province of Ontario 2013), which typically analyzed organisms, such as fish, at the time of

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sampling, but do not store samples because of logistical constraints. Monitoring programs can be used to carry out retrospective analyses of *data* (e.g., French et al. 2006; Gandhi et al. 2014); however, they do not allow for retrospective analyses of *samples* for other emerging contaminants or chemical tracers. Both monitoring programs and retrospective analyses of catalogued samples provide valuable insights and have their respective advantages and disadvantages (Gewurtz et al. 2011), although only catalogued archive samples make it possible to reassess emerging chemicals and legacy contaminants using improved analytical technology.

While typically not collected for chemical analyses, animal, plant and other biological specimens held in NHCs, ESBs, biological collections in museums and herbaria represent a valuable repository of catalogued samples collected during periods when scientists were not as aware about environmental contaminants (Table 1). Those specimens, which can date back to the mid-1800s or even earlier, can be useful indicators of environmental contamination during a period of increasing industrialization prior to the 1970s. As a result, those catalogued tissues provide baseline data on contaminant concentrations for comparing against those of modern organisms. NHC specimens are diverse, ranging from whole organisms to various types of tissues, all carefully preserved and catalogued as per standard curation practices for that type of collection. Analyses of NHC specimens are often highly appealing to environmental scientists, as inclusion of those samples in studies can make it possible to extend temporal analyses of tissue contaminant concentrations over decades (e.g. Frederick et al. 2004), even centuries in some cases (e.g., Outridge et al. 2009). However, the issues of contamination, preservation and chemical stability due to storage need to be taken into consideration. Museum and herbaria specimens were often not collected for the specific purpose of chemical analyses, so interpretations of such data are not always straightforward (e.g., Renauld et al. 1995; Hogstad et al. 2003).

In contrast, biological tissue archives and ESBs especially set up for the purpose of chemical monitoring and appropriate long-term storage of samples for chemical analyses have typically been established for only a few decades at most. Typically, selected tissues are isolated, processed in clean laboratories, and frozen with rigorous quality control. There are at least 23 ESB in 15 countries at the time of this writing, with more being developed (Day et al. 2014). Long-term specimen archives were established by many national and regional governments when society became concerned about increasing environmental contaminants and environmental health, usually around the 1970s (e.g., Kolossa-Gehring et al. 2012). Countries such as Germany, Sweden, Japan, United States of America, and Canada have established long-term archives typically centered around specific types of tissues such as marine mammals (Becker et al. 1997; Miyazaki 1994), aquatic organism tissues (McGoldrick et al. 2010), terrestrial and avian wildlife (Braune et al. 2010). A few countries also maintain multi-matrix (e.g. many types of samples from animal, plant and non-living material) ESB, including Germany (Kolossa-Gehring et al. 2012) and Sweden (Odsjö 2006), which produce useful information on the national state of environment.

Table 1 Typical tissue and sample type analysed for contaminants and chemical tracers from catalogued archives held in Natural History Collections and Environmental Specimen Banks

Birds	Fish	Mammals	Reptiles	Invertebrates	Plants
• Feathers • Egg contents • Egg shells • Toe pads	• Whole fish (preserved) • Whole fish (homogenized) • Muscle • Scales • Otoliths	• Fur, hair & baleen • Keratin structures (nails, claws) • Ossified tissues: Bone, teeth, tusks & other ossified tissues • Blubber • Organs	• Scales • Skin • Shell (Turtles) • Muscle	• Whole body • Shell-removed • Muscle (e.g. from legs or tails)	• Flowering parts. • Roots • Tree cores • Tree bark • Whole moss & lichen. • Seaweed and other algae.

Increasingly, researchers are recognizing the high value of museum and herbaria NHC to obtain data on biological tissue contaminant concentrations prior to the 1970s. This chapter will provide a critical examination of both museum and herbaria NHC and long-term monitoring specimen banks for contaminant research, and discuss the benefits of using those resources for such research. We will first detail the types of tissues and specimen collections that have been used for contaminant analyses. Then we will outline challenges and key limitations to keep in mind when interpreting data obtained from such collections. Finally, we provide three case studies that successfully used long-term specimen collections to extend analyses of contaminants beyond what was feasible for modern sampling. All specimen collections share one thing in common: specimens tend to be catalogued and indexed in a common institutional database for reference. Therefore, from here on, we will use “catalogued” as a key descriptor to refer to specimen and tissue samples from any kind of long-term collection.

The Uses of Catalogued Tissues and Specimens for Contaminant Research Museums and herbaria around the world contain biological specimens, often collected for taxonomic and systematic research, and maintained by professional curators over time using standard NHC protocols. Collections can include both local organisms acquired as part of most museums’ and herbaria’s mandates to increase knowledge of natural history in their region, and those from international locations associated with specific research projects undertaken by curatorial staff. Many museums and herbaria are long-established, with the oldest items in their catalogued collections dating back approximately to the same era as for their establishment—although many biological materials can date back centuries especially if collected as a part of anthropological or archeological research. Over the past few decades. As support for taxonomic and systematic research declined, but funding has increased for other areas of biological research (Pyke and Ehrlich 2010), thereby increasing attention in the value of museum and herbaria collections as repositories of biological tissues for analyses in the opening decades of the twentieth century (Suarez and Tsutsui 2004; Lavoie 2013).

The use of NHC specimens for contaminant analyses is not a recent phenomenon, with many pioneering studies taking place around the time of increased concern about environmental contaminants in the 1960s and the 1970s. Those studies tended to focus on birds and mammals whose external tissue structures (feathers, fur, teeth) were easily accessed and subsampled without extensive structural damage to the museum specimen. Many bird and mammal specimens are stored as skins, gently stuffed with cotton wool, so there are typically no internal organs available for analyses. Skins are typically treated with fungicides and pesticides to prevent insect and fungus loss, which are important considerations for any researcher wishing to undertake contaminant analyses of such specimens.

In the 1960s, the increasing use of DDT and its observed impacts on bird populations were becoming increasingly apparent. As a result, it was important to establish a baseline for comparison with modern bird samples. Several scientists undertook analyses of catalogued bird egg and bird feathers, as well as analyzing a database of eggshell thicknesses going back to the 1880s. They were able to demonstrate significant and positive relationships between increasing DDT concentrations, the decline of bird populations and the thinning of eggshells over time (Ratcliffe 1967; Hickey and Anderson 1968; Peakall 1974). Likewise, a Swedish study of preserved bird specimens demonstrated a consistent pattern of increasing mercury over time between 1940 and 1950, likely associated with industrial development (Berg et al. 1966). Scientists in Japan attempted to use bat specimens from a museum Chiroptera collection in Tokyo to establish a pre-application baseline prior to the use of organomercuric fungicides for agriculture in the region (Miura et al. 1978). Such research has continued with a steady series of publications since that period, which have investigated specific concerns that can only be understood using catalogued biological collections. Those include spatiotemporal patterns of contaminants throughout a large region (e.g., marine mammals of the Arctic; Dietz et al. 2009; birds of Michigan; Head et al. 2011) or to undertake retrospective analyses of specific contaminants known to influence population health for a vulnerable species (e.g. endangered Florida panthers *Puma concolor coryi*; Newman et al. 2004).

Correspondingly, in line with the bird and mammal research, there was a similar movement towards analyses of chemically wet-preserved fish from museum ichthyological collections in the early 1970s (e.g., Miller et al. 1972; Evans et al. 1972; Barber et al. 1972). Whole fish are typically fixed in formalin for a short period before transferred to ethanol or another alcohol preparation for long-term storage in glass or metal for larger fish. However, serious doubt was cast upon the use of wet-preserved fish collections for retroactive contaminant analyses (Gibbs et al. 1974; Renauld et al. 1995). Around this time, long-term aquatic freshwater and marine specimen banks and monitoring programs were established in the 1970s and 1980s, ensuring a better quality of sample and analyses for fish contaminant research. Subsequently, very little was published on preserved fish until the early 2000s when there was a resurgence of interest and a better capacity to clean and identify specific compounds and congeners of interest separate from the total contaminant burden. Currently, most modern studies focus on mercury, specifically methylmercury, in preserved fish, with the theory that most methylmercury measured in fish tissues would be of biological origin via accumulation, not via external contamination which is assumed to be mostly inorganic mercury (e.g., Drevnick et al. 2007; Hill et al. 2010; Kraepiel et al. 2003; Poulopoulos 2013). Exploratory investigations have been carried out to assess the potential of using wet-preserved fish tissues analyses of other elements as well (Renauld et al. 1995; Poulopoulos 2013).

Plants, mosses, algae and other primary producer materials from any herbarium, museum or specimen bank appear to be less cited in the literature compared to animal tissue studies. Herbaria typically store pressed plant material with identifying diagnostic structures attached to a flat labelled whiteboard, while mosses, lichen and fungi are air-dried and stored in a labelled paper envelope or container. Mercury and arsenic contamination of herbaria from older preservation methods remain a major concern for many herbaria worldwide (Oyrazun et al. 2007), making for another complicating consideration for researchers. In ecological studies, moss and lichen samples from herbaria are more frequently considered (e.g., Herpin et al. 1997; Minganti et al. 2014) relative to other types of primary producer specimens, likely due to their utility as atmospheric biomonitors of contaminants (Augusto et al. 2013; Foan et al. 2010; Wolterbeek 2002), and their storage method minimizing contamination. Tree ring cores for dendrochronological and dendrochemical research have been used increasingly for metal and contaminant analyses (Siwik et al. 2010; Watmough and Hutchinson 1996), which also brings in the potential for analyses of older wood material in museums and herbaria for multi-decadal and multi-century contaminant analyses (Padilla and Anderson 2002). All considerations and challenges associated with sampling animal specimens in catalogued collections at museums also apply to plant and primary producer materials in herbaria and archeological collections.

Specimen archives and ESBs, by their nature, are maintained for high quality samples and data. As a result, there is extensive standardized documentation of specimens (size, location of sampling, names of samplers, time of sampling, etc.), quality control used for sample processing and storage as well as quality control for analytical results (Day et al. 2014). Therefore, data obtained from ESBs tend to be of the highest quality, and are typically more consistent and more robust than those from NHC specimens. Furthermore, properly prepared and frozen or dried catalogued tissues tend to be the least altered (McFarland et al. 1995), so thus can be analysed for a wider range of contaminants such as organic compounds relative to wet-preserved museum samples. Those ESB samples also tend have larger volume, so larger number of subsamples can be analysed. As a result, opportunities exist for retrospective analyses of tissues from key regions, especially as new chemicals become a concern (e.g., brominated flame retardants in Japanese marine mammals; Tanabe and Ramu 2012), or if new contaminants need to be tracked retrospectively (e.g., Borgmann and Whittle 1992). However, limitations and significant challenges exist for specimen banks especially in regards to long-term operation, national priorities, funding levels and access to limited samples (Braune et al. 2010).

Sources and Considerations for Catalogued Tissues Natural history museums, herbaria and other museum institutions holding NHC and biological materials often have multiple foci. Those can include the need for educating the public about regional flora and fauna, national and international collection interests of curators and research staff, and the institutional priorities as decided by its board and senior staff. In addition, collections can have inherent biases due to the goals during the sampling itself, such as obtaining type specimens and voucher specimens, which are essential for species description as per international taxonomy and species description standards. Therefore, obtaining sufficient samples from such collections for spatiotemporal continuity and robust experimental designs appropriate for contaminant research may not always be possible. The spatial, temporal and taxonomical content of catalogued collections can be diverse and wide-ranging, sometimes shifting over time with changing institutional priorities, making it difficult to design a research project without a thorough investigation of multiple catalogues. In fact, many researchers often find that they must consult the catalogues and visit many museums and herbaria in order to collect a sufficient number of specimens for any single site and temporal period (e.g., Poulopoulos 2013). As a result, the types of tissues sampled tend to be restricted to a short list (Table 1), with feathers, fur, nails and muscle being the most common types of tissues used for analyses.

Most museums and herbaria are members of consortia, both national and international, which allow them to share their electronic catalogues and access to paper catalogues. Graham et al. (2004) tabulated a list of national and international NHC databases with corresponding websites, most of which are still current. It must be kept in mind that many museums and herbaria are also in the process of converting paper records and specimen labels into electronic databases, so many databases may still be incomplete. Often it is necessary for researchers to work closely with curators to track down and document specimens of interest during a research visit. Researchers wishing to investigate collections for potential samples can query databases listing the catalogued specimens and any ancillary information associated with those specimens. Two such international consortia compiling national databases around the world are the Global Biodiversity Information Facility (GBIF, URL: http://www.gbif.org/) and the more recent Scientific Collections International (SciColl, URL: http://www.scicoll.org/content/about-scicoll). Even so, not all institutions with NHC have contributed databases, and it is wise to individually contact curators and archivists in the region, especially to track down specimens of interest from smaller museums, universities and private collections (Casas-Marce et al. 2012).

It is important to understand that, for many NHC, conserving the structural integrity of each specimen is of paramount concern for curators and archivists for taxonomic and systematic purposes. This is often in direct conflict with environmental chemical research, because for many types of chemical analyses, the removal of a small tissue sample and destructive analytical techniques are required. Non-invasive techniques, which do not rely on destructive methods, such as x-ray fluorescence (XRF) and micro-XRF using synchrotron technology (Janssens et al. 2000), are usually preferred by curators and archivists whenever possible especially for rarer samples. Recent improvements in analytical techniques and corresponding lower detection limits have meant that increasingly small sample masses are now feasible for analyses which make it easier to take smaller tissue samples. Those technological improvements have helped with gaining access to high-value collections while ensuring minimal destruction. However, in recent times, due to the increasing focus on usefulness of museum and herbaria collections for long-term trend analyses of contaminants, chemical signatures, and genetic material, many curators have established policies for collections under their responsibility to facilitate "responsible destructive sampling" when there is scientific merit. Those policies can include retaining duplicate imperfect specimens and simplifying paperwork (Lister et al. 2011). A mutually beneficial relationship between the researcher and the curator is advised, including help with database entry, maintaining sample provenance in publications, updating and correcting data and respecting the sample integrity as per collection priorities at all times.

Another high priority for curators and archivists is maintaining provenance of specimens and documenting how collections are used to aid education and research, especially if tissue must be removed from the specimen. This includes tracking the various uses of catalogued collections and any subsequent data derived from specimens. This additional information and meta-data will enhance the value of the specimens and the museum's role in research. As a result, it is highly recommended that all researchers include a list of specimen codes associated with each sampled specimen in their published output, such as an appendix in a thesis, online supplementary material accompanying a published journal article, or cited in any output with a freely available online document with permanent URL via a university or research website repository. These steps enhance the chain of provenance and the curators' ability to maintain meta-data related to each specimen and correct auxiliary data.

ESBs tend to be more focused on national priorities with particular taxon groups, regions, and/or times being targeted for intensive collecting and cataloguing. Sampling for specimen banks is frequently done specifically for environmental monitoring of contaminants and other chemical tracers, meaning that temporal continuity for selected sampling locations may be better established relative to samples obtained from many NHCs. Requests to access specimens in an ESB will usually be screened by a scientific committee who will consider several parameters, including scientific merit, whether the information can be obtained via other avenues, whether there is sufficient tissue remaining, and the requirement for all publications using ESB specimens acknowledge the source of tissues. Through the standardized banking of specimen tissues, important questions that can only be answered through retrospective analyses (Braune et al. 2010), as well as evaluating compliance with environmental regulations over time (Day et al. 2014), are made possible.

While the quality of samples and data from ESB may be more consistent, working with ESB samples has inherent challenges. Nearly all ESBs were established in the 1970s or later, meaning that samples in catalogued ESB collections may not date back to earlier years prior to the period of increasing industrial contamination. This is in contrast to many NHC that often contain specimens collected earlier, often to the early 1900s or even the 1800s in some cases. Furthermore, despite consistent sampling, ESB archives may not necessarily have the range of species and sampling locations required for a large spatiotemporal analytical project, a food web study, or large-scale biodiversity patterns. However, a robust study designed to maximize the value of samples collected within ESB's constraints can be valuable, not only scientifically, but also for policy and legislation formulation.

Data Interpretation and Cautions

Once samples are obtained from long-term catalogued collections and analysed, the data will need to be interpreted and presented. There are several inherent challenges that must be taken into consideration when presenting results. Those challenges include preservation methodology, storage of specimens, sampling bias, spatiotemporal patchiness of collections, and ethical considerations. A major challenge of using catalogued specimens is that the results may not be directly comparable to freshly collected modern samples, or there is no experimental confirmation that such specimens can be comparable over time. All catalogued samples in long-term collections and specimen banks have been preserved by different means, e.g. chemical preservation (wet, dry), drying or freezing (Table 2). Each preservation method will affect the chemical structure and ratios of elements in different ways.

Of greatest concern for contaminant and trace element analyses of NHC specimens is chemical fixation and wet preservation of samples. The wet-chemical preservation process introduces more chemicals to the specimen, intended to preserve its structural integrity, but can significantly affect the chemical composition of its tissues. Formalin, which consists of about 37 % formaldehyde in water with methanol, combines with nitrogen in proteins to form methylene bridge crosslinks in tissues (Kiernan 2000). The formation of crosslinks results in a hardening of tissues and preservation of tissue structures, hence the "fixation" step. Once fixation is done, the specimen will often then be immersed in ethanol or another alcohol for long-term preservation. There have been several experimental studies suggesting that tissues undergoing formalin fixation and ethanol preservation will have consistent and predictable changes in stable isotopes of C and N, which can then be adjusted to comparable modern values (Rennie et al. 2012; Schmidt 2009). Studies of preservative effects on mercury, trace elements, and contaminants in tissues, however, still are scarce despite the fast-growing number of publications using wet-preserved samples for trace elements. Hill et al. (2010) and Poulopoulos (2013) both carried out experiments indicating that mercury concentrations in wet-preserved tissues undergo consistent and predictable changes, which suggest that NHC ichthyological collections and other wet-preserved organisms may be used for mercury research. Furthermore, Poulopoulos (2013) assessed the effects of preservative on various trace metals in fish muscle over time using inductively coupled plasma—mass spectrometry (ICP MS), and found that most trace elements followed a similar temporal trend in fish muscle after preservation, and provided several recommendations for appropriate protocols for sampling and interpreting subsequent data from museum collections. Because ethanol can extract fatty tissues and organic chemicals from tissues, it is not highly recommended that NHC wet-preserved tissues are analysed for fatty acid or lipid-soluble organic contaminants without extensive prior laboratory experimentation as per Poulopoulos (2013) and Rennie (2012).

Dry preservation of biological specimens can be undertaken in several ways. First the specimen is skinned, and either the skin (with feathers, fur or other structures attached) or the skin with skull is dried around a cotton wool support. To prevent insect and rodent damage, the skin can be preserved with toxic powders (arsenic mercuric compounds, pesticides) or with borax (Schieweck et al. 2007). As a result, skins prepared prior to the 1960s may often have arsenic or mercury contamination (Hogstad et al. 2003), which needs to be carefully cleaned prior to trace metal analyses. Prepared skins are then kept in sealed drawers to minimize exposure to light, UV, insects and other pests. Skins are often prepared by removing internal organs and bones, then adding a preservative or pesticide to prevent damage to the skin over time before mounting over a cotton wool form (Hogstad et al. 2003). As a result, it is frequently recommended that feather, fur and external structures, such

Table 2 Most common preservative and storage methods to ensure longevity of catalogued specimens in Natural History Collections and Environmental Specimen Banks, and the associated advantages and disadvantages of each method

Preservative & fixative methods	Most common examples:	Taxa	Tissue types	Purpose	Advantages	Disadvantages	Cautions
Wet Chemical	• Formalin (fixative) • Ethanol • Isopropanol • Other alcohol formulations • Lugol's preservative (potassium iodine)	• Fish • Invertebrates • Phytoplankton	• Typically whole body • Can subsample whole-body for specific tissues such as muscle and inert tissues (scales, nails)	• To preserve taxonomic structures, inexpensive medium- to long-term storage.	• Very long-term storage if chemical refreshed occasionally, fixed tissue structures for taxonomy. • Relatively inexpensive compared to freezing.	• Loss of colour, distortion of shape and tissue due to chemical action. • Can affect chemical signatures and contaminant patterns.	• Interpretation of ecotracer and contaminant signatures must take into account "preservative effect", which can be significant for many elements. • Ethanol source can influence δ^{13}C value (e.g., corn, sugar beet, sugar cane) • Not all contaminants can be analysed, such as certain organochlorines.
Dry Chemical	• Arsenic • Mercuric powders • Organic pesticides • Mothballs	• Bird • Mammal • Fish • Reptile • Plant • Insects	• Skins with feather & fur. • Taxidermy mounts • Herbarium archives	• Preserved skins easier to store, retains characteristics of feather & fur structures. • Taxidermy mounts for display.	• Keeps insects, fungi and other organisms away from specimen	• Toxicity to handlers • Masks true contaminant concentrations in organism. • Need advanced washing and compound-specific or congener-specific analytical techniques.	• Arsenic, mercury and organic pesticides can mask contaminant concentrations in organism, need advanced washing and special analytical techniques, which does not work for all species (e.g.

Table 2 (continued)

							Hogstad et al., 2003) • Can use methylmercury, known isotope ratios / types of contaminants, and other indicators.
Dried or dry conditions with no chemical preservation	• Dehumidifiers • Desiccant cabinets with desiccant chemicals • Silica gel • Calcium sulfate	• Fish • Bird • Mammal • Reptile • Insects	• Muscle. • Ossified structures (bone, teeth) • Feathers	• Long-term storage of samples for analyses. • (note: mothballs often used in storage)	• Dried specimens can still be easily sampled and analysed for most contaminants and chemical tracers.	• Requires extensive preparation of most organism (e.g. removal of organs) resulting in loss of tissues potentially useful for analyses. • Mold and other pests can still result, altering specimen's chemical composition.	• Degradation of contaminant concentrations with time unknown.
Frozen	• Homogenized or subsampled tissues. • Frequently at one of the two temperatures: • -20°C • -80 °C	• All taxa	• Whole body • Muscle • Blood • Urine • Organs • Egg contents	• Long-term storage of samples for analyses.	• Long-term storage, least alteration of tissues in regards to chemical and contaminant signatures. • Samples stored at -	• Expensive, requires significant investment in infrastructure, operating and maintenance. • Lower temperatures (e.g. -20oC) and repeated freezing & thawing of	• Access to samples can be highly restricted if held by ESBs. • Many species homogenized whole or specific tissues homogenized, meaning that tissue-specific analyses or taxonomic-

Table 2 (continued)

	80ºC or properly dried samples are preferred.. • High quality data and laboratory results.	samples may lead to uncertainty of sample integrity. • Loss of organ and cellular structure due to homogenizing typical for most specimen archive standard protocols.	specific analyses are not always possible.

as toe pads be sampled rather than the skin itself (Hogstad et al. 2003). Camphor (mothballs) or other pest deterrents may be kept in the drawers, possibly introducing additional contaminants to the samples.

Dried specimens are usually desiccated via air drying, drying in an oven, or by freeze-drying. Many types of samples such as moss, lichen, fur and feather samples are then stored dried with no further preservative, often over desiccant crystals, considerably simplifying the collection of trace analysis samples. Dried samples kept in desiccant conditions are highly stable (McFarland et al. 1995). However, a major issue is that most dried samples in NHC were not originally collected, prepared, mounted or stored with trace contaminant analyses in mind so they likely have been exposed to cross-contamination from other specimens or always-present dust (e.g., Oyarzun et al. 2007), which adds to the challenge of interpreting data derived from such samples. Extra cleaning and sampling considerations must be factored in to improve the quality of dried samples for contaminant and trace element analyses (Sigrun-Dahlin et al. 2012).

Biologically "inert" structures, i.e., ossified structures (bones, teeth), cartilage, and keratin, are typically air dried and not chemically preserved, and are thus amenable for contaminants research. External structures, such as baleen (Hobson et al. 2004) and teeth (Farmer et al. 2006), provide useable material for contaminant and trace element analyses with some cleaning of the specimen. Bones may be boiled or immersed in ammonia in a "degreasing" step, dried and mounted (Neves et al. 1995). As a result, analyses of archived skeletal materials, especially those that have been mounted, may provide challenges that have not yet been experimentally verified in the literature.

Frozen specimens are more commonly associated with ESB collections, and can be stored in ordinary −20°C freezers, −40°C cold rooms or ultra-low −80°C for genetic, fatty acid and other types of specialized analyses (Braune et al. 2010). Like dried specimens, frozen specimens may be among the most straightforward to analyze, although long-term storage effects are of concern with literature reviews showing mixed results for stability of organic contaminants and trace elements (McFarland et al. 1995; Day et al. 2014).

How a sample is stored and the length of storage are important considerations, depending on the analysis in question. Chemical changes, UV, degradation, and decomposition are all factors to keep in mind. Ethanol can extract organic material, and as a result, organic contaminants and carbon isotopes can be affected by length of storage. For dry samples, humidity and ultra-violet light are key factors in degradation of contaminant and chemical tracer concentrations and as such, storage type, and length are important factors to consider (McFarland et al. 1995. Most detailed methodology publications related to the effect of storage on samples are from medical and clinical studies (e.g., Cuhadar et al. 2013). In general, refrigeration has been shown to be sufficient to preserve trace elements in urine for ICP-MS analyses over a month (Bornhorst et al. 2005). Dried and freeze-dried samples also have been shown to conserve trace elements and mercury for several months to few years (McFarland et al. 1995). Likewise, organochlorine compounds tend to remain consistently stable in frozen samples at −80°C over several years and in freeze-dried samples (McFarland et al. 1995), although there are some exceptions to this in the literature. One common constant by all authors is that the storage technique needs to be tested on the particular tissue type and contaminant of concern before commencing to use that technique.

Each collection has its own priorities, and therefore sampling bias will be a big factor in using long-term catalogued collection material for research. Often it is challenging to create a robust research design for a project prior to approaching curators and archivists as the number of species, size ranges or time periods may simply not be available. Researchers must be prepared to derive an experimental design based on what is present already in collections and acknowledge that spatiotemporal patchiness and paucity of key samples may be present. Furthermore, as space becomes more restricted over time, curators will be required to discard samples while conserving type and voucher specimens, so there may be a bias towards older original specimens in some collections due to this priority on taxonomically important specimens. There is also bias towards smaller representatives of many species due to storage issues: for example, many small fish can be stored in a single jar or many smaller birds and mammals can be stored in a small drawer—while only a few larger individuals can be stored in larger containers or on shelves making it difficult to get an appropriate size range for each species.

Tissue availability is another challenge. Curators may restrict sampling only to particular types of tissues or structures, which can make it logistically difficult to extrapolate data from one type of tissue to what is used for modern research techniques. Researchers may need to be prepared to use modern laboratory and field studies comparing contaminants in different types of tissues for a single individual when preparing to standardize data across tissues and time periods.

Ancillary data are essential—analyzing a sample without knowing location, species, or time of collection will result in poor data. Both ESB and NHM catalogued collections will have specimen labels and data detailing the date, species collected and in most cases, the name of the collector. Older specimens may only have ancillary data on a paper label with faded handwriting, or have incomplete information prior to establishment of standard protocols on accepting and maintaining collections, making it challenging to compile all information for each specimen.

Can we compare wet-preserved fish tissues from the early twentieth century to those of modern freshly-caught fish? Adjusting for probable changes in contaminant concentrations due to preservation, storage and tissue type all adds more uncertainty to the data. Currently, there is more focus on stable isotope data for archived and fresh samples, although researchers have started to investigate potential impacts of wet-preservation methods on mercury and metals (Hill et al. 2010; Poulopoulos 2013). Drying and storage length of dried tissues do not appear to have been investigated in the peer-review literature at this date, but it is very probable that changes occur over time. Freezing at temperatures below −80°C and repeated freezing-thawing of samples for subsampling is an issue as it can lead to decreased stability of the sample with significant differences in contaminant concentrations (Krystek and Ritsema 2005; Hale and Greaves 1992; Cuhadar et al. 2013). As a result, it is frequently recommended that the storage technique be consistent throughout the archival lifespan of the catalogued specimen, and storage conditions should be kept constant.

Case Studies

To illustrate the successes and challenges of using catalogued specimens for contaminants research, we will present three case studies, the first two of which involved analyses of mercury in preserved animal tissues. Perhaps more than other contaminants, mercury has been measured in tissues from catalogued specimens for many studies conducted to infer pollution source and/or extend temporal trends. Dietz et al. (2009) provided a review of such studies that used bird and mammal specimens collected in the Arctic. Although we focus on mercury, similar successes and challenges are possible for other contaminants. The DDT studies presented in the introduction are a prime example of a major success of using museum specimens to understand a pollution problem. The third case study in this section focuses on organochlorine contamination in Lake Ontario.

Isle Royale—a Comparison of Multiple Records of Mercury Pollution

Isle Royale is an archipelago in Lake Superior that supports an ecosystem sensitive to atmospherically-deposited contaminants. The archipelago is protected from most human influences by its relative isolation within a Great Lake and by multiple designations as a national park, a wilderness area, and an international biosphere reserve. It was a surprising discovery in the 1970s that concentrations of organochlorine contaminants (Swain 1978) and mercury (Kelly et al. 1975) were higher in fish in “inland” lakes of Isle Royale than in surrounding waters of the Great Lakes, where discharges of untreated industrial and municipal wastewater were common. Among ecosystems, the relationship between contaminant loading and accumulation in biota is often not straightforward. Contaminant concentrations in Isle Royale fish were/are comparatively elevated because of food web dynamics that favor biomagnification (organochlorines) or water chemistry that enhances bioavailability (mercury) (Swackhamer and Hornbuckle 2004). For organochlorines, production bans cut off contamination at the source, and rates of atmospheric deposition (Baker and Hites 2000) and concentrations in fish (MDEQ 2014) declined at Isle Royale. For mercury, a naturally occurring element, human activities worldwide have released geological stores (mineral deposits and fossil fuels) resulting in a 3–5-fold enhancement (global average) in atmospheric deposition (Engstrom et al. 2014). In the Great Lakes region, controls on mercury emissions have gradually decreased rates of atmospheric deposition since the mid-1980s; however, mercury concentrations in fish have been uncoupled from deposition for 80+ years, determined by investigations of mercury cycling at Isle Royale that featured the use of catalogued tissues.

The magnitude and rate of change of atmospheric mercury deposition to Isle Royale is largely known from lake sediment cores. Lake sediments are the most reliable archive of atmospheric mercury deposition (Biester et al. 2007), although because lakes also receive inputs of mercury from their watersheds, the relationship between atmospheric mercury deposition and sedimentary mercury accumulation is not always straightforward. Sediment cores collected from five lakes at Isle Royale show a cohesive 3-fold increase in mercury accumulation rates, beginning c. 1890 and continuing to the present (Drevnick et al. 2007) (Fig. 1a). The unabated increase is at odds with a region-wide analysis that found sedimentary Hg accumulation rates peaked in the mid-1980s, followed by a 20 % decline (Drevnick et al. 2012).

A dataset of mercury in teeth from moose (*Alces alces*) (Vucetich et al. 2009) provides an important check on the lacustrine record. As part of a long-running study of predator-prey interactions at Isle Royale, teeth have been collected from moose carcasses since the early 1950s. The counting of cementum lines (layers of bonelike connective tissue covering the root of a tooth) was used to determine birth and death years of individuals, and teeth were "stored dry in paper bags inside wooden cabinets, and were never exposed to potential sources of contamination." Vucetich et al. (2009) measured mercury, as well as lanthanum and strontium to correct for any accumulation of mercury of geogenic origin, in adult and calf moose teeth and reported an abrupt 65 % decline in Hg concentration between 1980 and 1986. The authors reported no trend in Hg concentration before or after this period, but a re-analysis of data from calves (which were defined as < 1 year old and thus had a narrow window of exposure) suggests a more gradual decline (of similar overall magnitude) from 1983 to the present (Fig. 1b). Ungulates accumulate mercury almost entirely from the plants they consume (Gnamus et al. 2000), and moose diet (plant selection, feeding location) has not changed in coincidence with the trend in tooth mercury. Having ruled out other contributing factors to the decline, Vucetich et al. (2009) concluded that the cause must be a drop in atmospheric mercury pollution. This conclusion agrees with the region-wide analysis, i.e., that mercury deposition is declining.

The discrepancy between the sediment and moose teeth records helps to constrain rates of atmospheric mercury deposition. Wet and dry mercury deposition rates were measured at Isle Royale during periods of 1997 and 1998 (U.S. NPS 2014), but only show a snapshot view. Using the model of Swain et al. (1992), the sediment record can be used to model total (wet + dry) mercury deposition long term (Fig. 1c), with a present estimate of 11.3 $\mu g/m^2/yr$. Aligning estimates for total mercury deposition with the broken-stick regression line for Hg/La in moose teeth shows the records were in strong agreement during the period 1958–1983, but diverge thereafter. Which record is correct? Data from measured rates of wet mercury deposition from a site in adjacent northeastern Minnesota fits in the wedge between the two records. An unknown is dry mercury deposition, which at Isle Royale may amount to 40 % of wet mercury deposition (U.S. NPS 2014), allowing us to conclude that total mercury deposition remains in the wedge (of Fig. 1c) and,

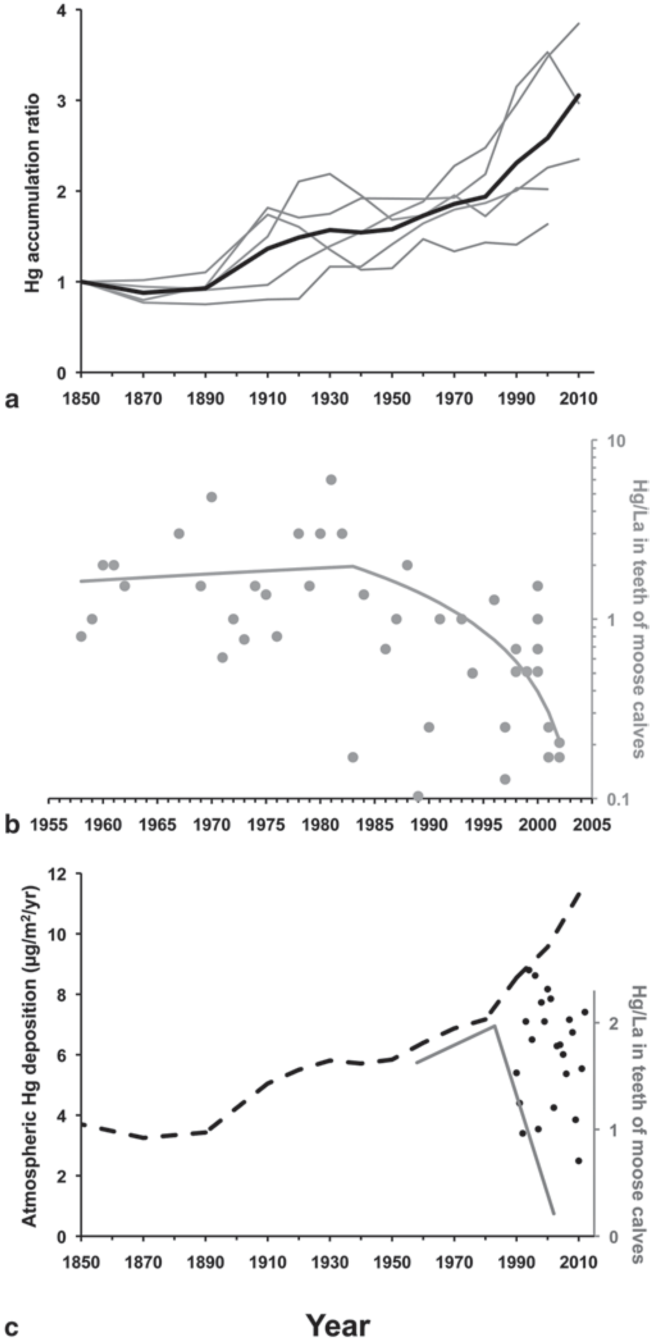

Fig. 1 **a** represents sedimentary mercury accumulation rate for a given period compared to a background (1850) rate. The *thin*, *gray* lines are for cores collected from five lakes at Isle Royale. Lakes include Intermediate, Richie, Sargent, Siskiwit, and Whittlesey. The thick, *black* line repre-

importantly, appears to have declined. Using data from the sediment cores for modeling atmospheric mercury deposition resulted in overestimation of actual rates. The sediment data may be affected by increased output of mercury from watersheds, either from a change in the retention of "new" mercury (recently-deposited) or from output of "old" mercury (from a legacy of past deposition).

Mercury concentrations in fish tell another story, beginning with a wealth of catalogued fish samples. In 1929, Walter Norman Koelz of the University of Michigan Museum of Zoology (UMMZ) led a sampling expedition to the inland lakes of Isle Royale and collected nearly 15,000 fish for the museum's research collection. The fish were preserved in formalin and transferred for storage in ethanol, both solutions free of added mercury (Kelly et al. 1975). To fairly compare mercury concentrations in these specimens to fresh fish, it is necessary to correct for an approximate 30 % weight loss in ethanol. Kelly et al. (1975) and Drevnick et al. (2007) have used these specimens for mercury-related research, and a sample of the data is shown in Fig. 2. From 1929 to 1971, the median mercury concentration (expressed in wet weight) in axial muscle of walleyes (*Sander vitreus*) increased from 0.2 to 0.7 µg/g (a 3.5-fold increase). For comparison, during that same time period sedimentary mercury accumulation increased 1.2 fold. The additional increase in fish mercury compared to mercury loading to lakes (also observed in adjacent northeastern Minnesota by Swain and Helwig 1989) is hypothesized to have resulted from sulfate in acid rain that stimulated ecosystem production of methylmercury, the form of mercury that accumulates in fish. Methylmercury is not preserved in sediment and thus does not provide a record of methylmercury production; however, products of sulfate reduction (the process that results in the production of methylmercury) can be stored in sediment. There is a strong correlation among lakes and time between concentrations of chromium reducible sulfur (an operational term that represents products of sulfate reduction) and concentrations of mercury in fish. With mercury loading to lakes continuing unabated (as evidenced from the sediment data), declines in mercury concentrations in walleye, northern pike (*Esox lucius*), and other fish species since the mid-1980s appear to be solely attributed to controls on sulfate deposition (Drevnick et al. 2007).

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sents the mean. The data show sedimentary mercury accumulation rate is increasing to the present. Data from Drevnick et al. (2007). **b** represents mercury/lanthanum data from moose calves at Isle Royale (Vucetich et al. 2009). The regression line is from a "broken stick" model with the following equation: Hg/La = −25.2 + 0.0137(year)—0.106(year-1983). The model shows no significant trend pre 1983 ($p = 0.61$), but a significant decline since 1983 ($p = 0.038$). **c** has three components. The dashed, *black* line shows the modeled atmospheric Hg deposition, based on the sediment record. The model is from Swain et al. (1992): sedimentary mercury accumulation = 3.7 + 0.83(watershed area/ lake area), where the intercept (3.7) represents atmospheric mercury deposition to a lake with no watershed. For this analysis, estimates of atmospheric mercury deposition were made by multiplying the mercury accumulation ratio (see Fig. 1a) by 3.7, assuming there has been no change in watershed retention of atmospherically deposited mercury. The gray line is the broken stick regression line from the moose data; the line appears different from Fig. 1b because of a change is scale. The *black* circles show measured wet mercury deposition from site MN 18 of the National Atmospheric Deposition Program (NADP). Data were retrieved from Glass and Sorensen (1999) and the NADP website (http://nadp.sws.uiuc.edu/)

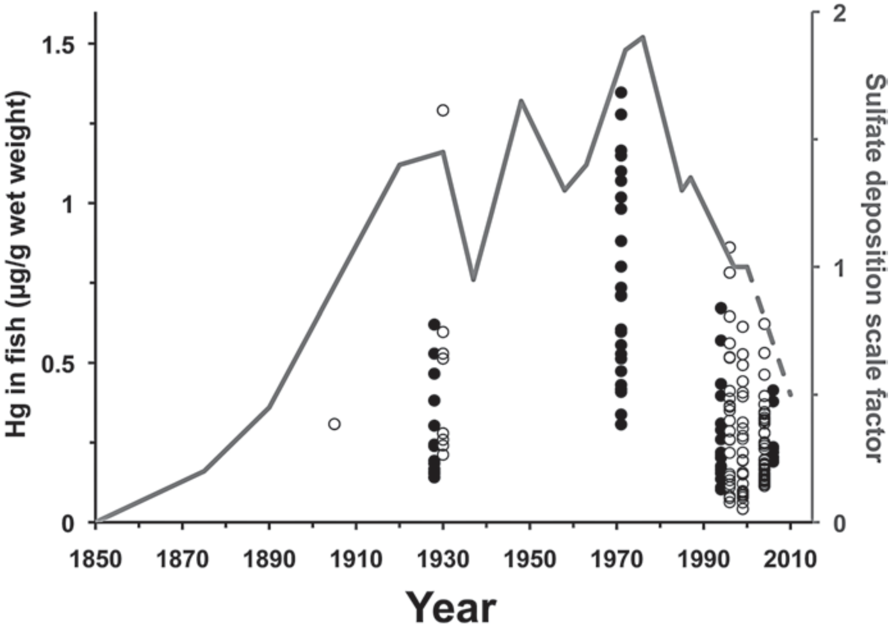

Fig. 2 has two components. The circles represent concentrations of mercury in skin-on axial muscle from fish from lakes of Isle Royale: *black* for walleye from Chickenbone, Dustin, and Whittlesey and *white* for northern pike from Eva, Richie, and Sargent. Data sources include Kelly et al. (1975), Kallemeyn (2000), Gorski et al. (2003), and Drevnick et al. (2007). Data points early in the record (1905, 1929) are from catalogued fish samples at the University of Michigan Museum of Zoology. The *gray* line shows the history of sulfate deposition in the Great Lakes region, as estimated by Aherne et al. (2003). The solid line indicates estimates are based on empirical observations. Dashed line is a model forecast. The scale factor is unitless; a factor of 1.0 is equivalent to a deposition rate of 13.2 kg S/ha/yr (measured rate in 1997)

In total, the use of catalogued tissues for mercury research at Isle Royale allowed insight that otherwise was not possible. The record from moose teeth indicates rates of atmospheric mercury deposition are declining. Mercury concentrations in fish are also declining because rates of atmospheric sulfate deposition are declining. Management of atmospheric mercury and sulfur emissions, largely via regulations on coal combustion for electricity generation, are making significant progress towards recovery of lake ecosystems from mercury contamination at Isle Royale and likely elsewhere in the Great Lakes region.

Mercury in Tuna, Revisited

Miller et al. (1972) tested the seemingly straightforward hypothesis that there is no difference in mercury concentration in tuna between museum specimens (dating from 1878–1909) and samples caught “recently” (1970–1971). Results of mercury analyses, 0.38 ± 0.14 μg/g in museum specimens ($n = 7$) and 0.29 ± 0.14 μg/g in recent samples ($n = 5$) (both expressed as wet weight), did not allow the authors to reject their null hypothesis. Rather, the results were used as evidence to support the ideas that mercury pollution since 1900 could only result in a negligible increase in mercury concentration in open ocean waters and that mercury in wide-ranging ocean fish is of natural origin (Hammond 1971). The first of these ideas was based on faulty data; before the advent of clean sampling techniques, it was accepted that the mercury concentrations of open ocean waters ranged in the low parts-per-billion, whereas we now know that a typical mercury concentration is ~200 parts-per-quadrillion (Lamborg et al. 2012). Current models of global mercury cycling unanimously agree upon an increase in mercury concentration in ocean water since preindustrial times (Black et al. 2012). Validation of this increase, however, requires an independent record of oceanic mercury, and a common approach has been to measure temporal changes in biota. For this purpose, museum collections have repeatedly been revisited for bird feathers, and recently Vo et al. (2011) reported a post-1940 increase in mercury concentrations in feathers from black-footed albatross (*Phoebastria nigripes*) while accounting for changes in mercury exposure from diet or food web shifts, with analyses of carbon and nitrogen stable isotopes. Finding a similar increase in fish has proven elusive. Kraepiel et al. (2003) compared mercury concentrations in yellowfin tuna (*Thunnus albacares*) caught off Hawaii in 1971 and 1998, found no recent increase, and (to come full circle with Miller et al. 1972) concluded that methylmercury (the form of mercury that accumulates in fish) forms from mercury naturally present in deep waters, sediments, or possibly hydrothermal vents. This idea has been challenged by three independent lines of data (see Blum et al. 2013, Lamborg et al. 2006, and Sunderland et al. 2009), but nonetheless was key in a court ruling that exempted tuna companies from warning consumers of a reproductive toxin (methylmercury) in their products (State of California v. Tri-Union Seafoods, 171 Cal. App. 4th 1549, 90 Cal. Rptr. 3d 644 2009). The court stated that "virtually all methylmercury [in tuna] is naturally occurring."

Why is there confusion about mercury in tuna? At center is a dispute about the risk of mercury in fish to human consumers, between tuna companies (consumer freedom) and governmental health agencies (consumer protection). What level of mercury is toxic to humans? Toxicity values (e.g., reference dose) are debatable because of the many potential studies that can be considered as the base of the calculations and because of uncertainty factors that modify the final product. However, unbiased science should be able to inform the public about the mercury content in tuna. Success in that task has been questionable, though. With all of the tuna caught annually, it should be straightforward to design monitoring programs to answer the appropriate questions. The U.S. Food and Drug Administration, for example, has a monitoring program in place and allows the public to see the data (U.S. FDA 2014), but information is not provided that would allow for an analysis to determine whether mercury concentrations are changing with time.

To determine whether mercury concentrations in tuna are changing with time, it is necessary to examine the data in context, especially with fish age and size. As fish grow older and larger, their mercury concentration increases because methylmercury is readily accumulated (via the diet) but difficult to eliminate. Further, as fish grow larger they may switch to diet items that have higher mercury content. It is common practice to standardize mercury concentrations to a specific length or weight, so for a given species datasets can be fairly compared across space and time.

Miller et al. (1972) gave very limited information about the ages and sizes of the museum specimens in their study ("each slightly under 0.6 m in length") and no information about the age or size of the recent samples, which reinforces the need for all researchers using museum collections to indicate specimen numbers as part of their metadata. Placing the data in context (Fig. 3) reveals some surprises. For albacore tuna (*Thunnus alalunga*), the mercury concentration of a specimen caught off the California coast in 1880 is a statistical outlier when compared to a larger dataset for individuals from California, Oregon, and Washington (Morrissey et al. 2004). The data point is biased high (i.e., high mercury for given length), which could be a real phenomenon or may be an artifact of museum preservation. The authors addressed the issue of mercury in preservative and could not "rigorously exclude" the possibility, but it does not appear to be an issue in any of their data. Rather, if the data point is corrected for 30% lipid loss (Kelly et al. 1975), which has the effect of concentrating mercury in the remaining tissue, the mercury concentration would fall into place in the length-mercury relationship. It is unclear, however, what is an appropriate correction factor for tuna, and Gibbs et al. (1974) warned that, until preservation effects are understood, comparisons between museum specimens and unpreserved samples "must be considered unreliable." For skipjack tuna (*Katsuwonus pelamis*) and Atlantic bluefin tuna (*Thunnus thynnus*), the data from Miller et al. (1972) fit neatly with larger datasets. Although, if lipid loss is important in the museum specimens, the data points for these two species would be biased low, opening up the possibility that mercury concentrations have increased since the late nineteenth century and early twentieth century. In fresh tuna, Balshaw et al. (2008) determined that mercury and lipid content in muscle tissue are inversely related, with mercury decreasing at a rate of −0.0046 µg/g (wet weight) per percent lipid. For Atlantic bluefin tuna, the one museum specimen (caught off the Massachusetts coast in 1886) is at the far left side of a length distribution that is considerably larger than shown; Fig. 3C only shows age-1 fish (Mather and Schuck 1960). Mercury concentrations at this young age are low and highly variably (Cumont et al. 1975) and therefore rather insensitive to use for detecting temporal change.

The study by Miller et al. (1972) was an early attempt at a difficult and contentious issue. Other problems with the study include small sample sizes (a common drawback of contaminants research involving museum specimens) and the failure to account for changes in trophic position. The shortening of food webs, shown to occur in ocean fisheries since *c.* 1950 (Pauly et al. 1998), reduces the biomagnification of mercury (Cabana and Rasmussen 1994). This oversight is excusable because in 1972 a simple method to determine trophic position (i.e., analyses of carbon and nitrogen stable isotopes) had not yet been discovered. Going forward, there are no excuses for poor collection or representation of data. Mercury contamination of ocean fish is a serious global health issue, now being tackled by the UN Minamata Convention on Mercury that must be guided by valid data (Selin 2014).

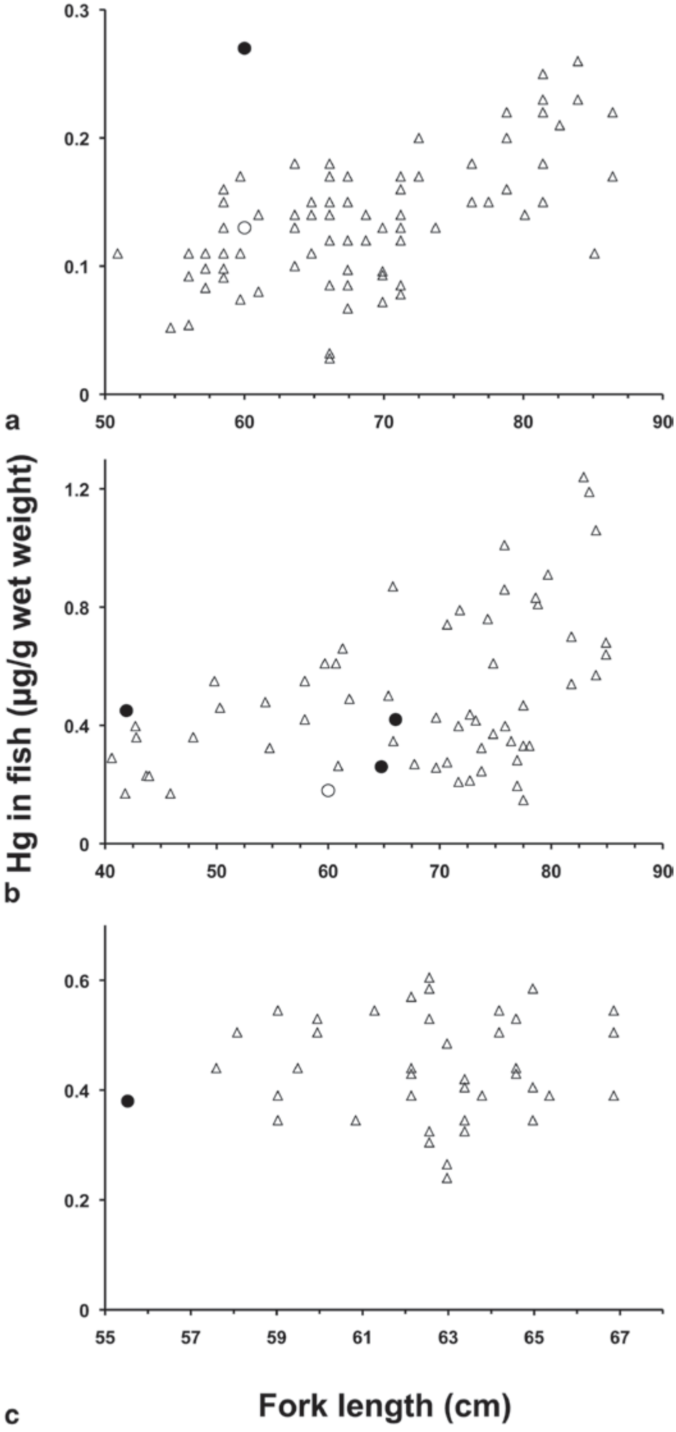

Fig. 3 Mercury concentrations in muscle tissue of tuna from Miller et al. (1972) (circles), placed in the context of larger datasets (triangles). Solid circles represent museum specimens dating from

Chlorinated Hydrocarbons in Gull Eggs from Scotch Bonnet Island, Lake Ontario

Herring gull (*Larus argentatus*) eggs from Scotch Bonnet Island, collected annually since 1971 and archived in the Canadian Wildlife Service Specimen Bank, have been instrumental in understanding biotic exposure and effects from organochlorine contaminants in Lake Ontario. Fresh eggs have been analyzed at regular intervals, but because of changes in analytical methodology during the course of the program, early data are not directly comparable to more recent data. A re-analysis of eggs from the specimen bank has remedied this problem (Norstrom and Hebert 2006). Concentrations of individual organochlorine contaminants were at their highest at the beginning of the record, and controls on production and/or release have resulted in steady decreases in 2,3,7,8-TCDD (dioxin) (see Fig. 2 in Norstrom and Hebert 2006), chlorobenzenes, chlorostyrenes, and dieldrin. From the mid-1960s to the mid-1970s, reproductive success of herring gulls on Scotch Bonnet Island was poor, averaging 0.1 chicks per nesting pair. Poor reproductive success was due to egg disappearance—from inattentive parenting—and embryo mortality (Peakall and Fox 1987). With significant declines in organochlorine exposure by the late 1970s, the average number of chicks per nesting pair increased to > 1, similar to herring gulls in other Great Lakes and strongly suggested that exposure caused effects.

Cook et al. (2003) used the herring gull egg record from Scotch Bonnet Island and nearby sediment core records to model lake trout (*Salvelinus namaycush*) fry mortality in Lake Ontario. Lake trout were extirpated from Lake Ontario *c.* 1960 and attempts to re-establish the population via stocking failed because of sac fry mortality. 2,3,7,8-TCDD and similarly structured chemicals (e.g., PCBs) bind to the aryl hydrocarbon receptor, which (when bound) activates phase I and phase II metabolism—processes that are intended to detoxify and eliminate xenobiotics, but can instead result in activation (increased toxicity). Such is the case for these chemicals. Lake trout sac fry exposed to 2,3,7,8-TCDD show overt toxicity that results in death (King-Heiden et al. 2012). Cook et al. (2003) compiled a 60-year record of toxicity equivalent concentrations (TEC) for 2,3,7,8-TCDD and other organochlorines that bind the aryl hydrocarbon receptor, from sediment core records (prior to 1971) and herring gull egg record (1971 onward), with appropriate conversion factors and assuming these records ran in parallel with lake trout exposure. TECs from 1940 to 1980 were sufficiently high to result in 100 % mortality to lake trout fry, hence the extirpation of lake trout from the lake post 1980, with significant declines in contaminant concentrations, stocking programs have had success, and a viable lake trout population now again inhabits Lake Ontario.

1878–1909; open circles represent samples caught "recently" (1970–1971). Kris Murphy, Division of Fishes, Smithsonian Institution, re-measured lengths of the museum specimens and has added this information to the museum's electronic catalog, accessible at < http://collections.mnh.si.edu/search/fishes/>. For all data from "recently" caught specimens from Miller et al. (1972), a fork length of 60 cm was assumed (see text). Panel A shows data for albacore tuna from the U.S. Pacific coast (CA, OR, WA), with the larger dataset from Morrissey et al. (2004). Panel B shows data for skipjack tuna from the Indian and North Pacific oceans, with the larger dataset from Choy et al. (2009) and Kojadinovic et al. (2006). Panel C shows data for Atlantic bluefin tuna from the North Atlantic Ocean, excluding the Mediterranean Sea, with the larger dataset from Cumont et al. 1975

Recommendations and Conclusions

Success in using catalogued specimens for contaminants research requires finding samples that have the potential to provide information to answer the research question (source, temporal trends, effects) and then ensuring that the samples provide results that reflect reality. Validation must involve either in-house experiments, e.g., as performed by Hill et al. (2010) and Poulopoulos (2013) to understand the impacts of preservation on contaminant concentration, or referring to the work of others. A valid comparison of catalogued sample data to results from modern samples also requires understanding (and adjusting for) changes in the ecosystem, as done by Vo et al. (2011) with the ancillary analysis of carbon and nitrogen stable isotopes to account for changes in mercury exposure in albatross from shifts in the food web. When reporting data from catalogued specimens, it is advised to list the sources (e.g., museums) where the samples were obtained and also the identification code for each sample, in supplementary materials if necessary. This information is important for curators and archivists and also allows others the potential to repeat the work—a requirement of peer-reviewed science. The information given in Miller et al. (1972), for example, allowed us to revisit the samples for the case study on mercury in tuna.

NHC and ESB catalogued specimens offer a powerful medium for making or extending (when monitoring data are available) timelines of biotic exposure to contaminants. Curators and archivists are increasingly becoming aware of the additional value of NHC specimens as a repository of long-term contaminant and chemical tracer information, which are resulting in changing collection policies and management. Preservation and storage remains a challenge especially with the high cost of low-temperature storage, although great strides have been made in quantifying the effects of long-term preservation and storage on chemical signatures in biological tissues over recent years. Provenance remains a significant priority especially for curators of key collections, so it is necessary for researchers to co-operate with curators and ensure the traceability of their sample analyses (through lists of specimen codes and sources) in their publications and the metadata accompanying all databases. Catalogued specimens have already provided significant insights into long-term trends of environmental contaminants in biological tissues, and with better sampling protocols, metadata management and storage techniques, this potential will continue to grow in the near future.

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Tracking Contaminant Transport From Biovectors

Roland Kallenborn and Jules M. Blais

Abstract We investigated contaminant transport and accumulation into ecosystems via migrating and invasive organisms. This review examines contaminant bioaccumulation and biomagnification in the context of physico-chemical properties of pollutants, the ecology, life cycles, and behavioural aspects of the carrier organisms (i.e. biovectors). Lake sediment profiles can provide an important historical archive for biovectors, such as the accumulation of metals and persistent organic pollutants, because these sediment profiles may be influenced by biological inputs (including fish carcases, animal waste, and other biological materials). Future research priorities are recommended based on the knowledge gaps identified. This chapter aims to provide science-based information for environmental scientists and regulators for the development of new coordinated research strategies, monitoring and research programs as well as international regulations for the mitigation of hazardous effects of anthropogenic pollutants.

Keywords Biological transport · Contaminants · Invasion · Nomadism · Persistent organic pollutants · Radio isotopes · Long-range transport · Vertebrates · Insects · Plankton · Trophic levels · Marine environments · Climate change · Transformation · Metabolism · Ecotoxicology · Risk assessment · Behaviour

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Introduction

Individual or population migration is a behavioural strategy to improve survivorship and reproductive success. In this context, animal populations actively seek advantages and/or avoid seasonal disadvantages by moving into different locations, often in large numbers. Better access to food resources or avoiding harsh winter climates are typical motivations to migrate long distances into more favourable habitats for resting and reproduction (Elewa 2005). Migration of organisms is considered a behavioural "*mechanism for avoiding unfavourable environments by moving to expectedly more auspicious locations at different times. In other terms, migration may represent an often regular, even seasonal movement of organisms and/or populations from place to place to favourable locations owing to the change in the environmental conditions or locations chosen for the benefit of specific often population related purposes (i.e. reproduction, overwintering)*" (Elewa 2005). The term "migration" is usually characterized by regular or annual seasonality. Infrequent or sporadic "migration" patterns are usually described as nomadism or invasive movements (e.g. migratory locusts = *Locusta migratoria* L., Lemming = *Lemmus lemmus* L.).

The term biovector usually refers to organisms (or groups of organisms) as carriers for substances (pollutants, bioactive chemicals and/or nutrients) as well as biological agents (including viruses, bacteria) transporting and subsequently releasing their burden as a part of complex distribution process. Already in medieval times, rat (*Rattus norvegicus* L.) invasions were associated with epidemic dispersion of infectious diseases (i.e. plague) with disastrous consequences for the infected human populations (Harrison 1946; Lloyd 1908).

In the context of environmental pollution, biovector transport typically refers to the directional distribution of contaminants following emission, accumulation, transport, and deposition or transfer into the receiving ecosystems (Blais et al. 2007). Biovector transport is today considered an important part of directional transfer usually following bioaccumulation and bioconcentration (for lipophilic substances like persistent organic pollutants = POPs) and intensified by population migration and movement patterns of the effected species, followed by transfer or deposition to a receptor ecosystem.

The extension and size of migrating populations may vary considerably depending on local, behavioural, environmental and species-specific internal physiological conditions (e.g., age, gender, etc.). Invasions, however, are obviously triggered by external habitat-related factors such as changing environmental conditions, population size (rapid increase and growth), access to food and competitive ecological structures in the food web (e.g. predator—prey relationships, competitive species etc.). In the event of a predator—prey balance becoming disrupted and the predatory pressure becomes too high, the affected species/populations will respond with invasion of new habitats in order to improve their fitness (i.e., access to food, reproduction, etc.) and/or reducing the predatory pressure on the population.

In addition, seasonal vertical movements of marine invertebrates (e.g., *Calanus* spp. in Arctic waters) have been identified as an additional migration type with considerable impact on the local and regional ecosystem structure and food webs (Perticarrari et al. 2004; Frangoulis et al. 2005; Berge et al. 2009).

Since environmental conditions continuously change, even on a regional scale (i.e. desertification, global climate change, changes in vegetation profiles), species and populations tend to respond by moving into new, although previously not favourable, habitats (Lejeusne et al. 2010; Lee et al. 2008; Hershner and Havens 2008; Hellmann et al. 2008; Dangles et al. 2008). However, this strategy will add considerable ecological stress to the current ecosystem structures and will consequently lead to unbalanced non steady-state situations with consequences for indigenous species in the affected ecosystems (Engel et al. 2011; Cooling et al. 2012; Burton et al. 2010; Bierwagen et al. 2008).

In the context of environmental pollutants research, this review will consider both regularly occurring migration patterns (migratory species) as well as invasion events as potential distribution pathways for anthropogenic pollutants to ecosystems and food webs. Traditionally, research on biovectors as potential transport pathways for anthropogenic pollutants has been largely neglected in environmental contaminant research.

In contrast to abiotic distribution processes, biovectors are not only considered as directional transport pathways, but they also focus and bioconcentrate pollutants by direct bioconcentration to organisms from a broadly distributed, but very dilute, chemical reservoir in water, soil, or air. The delivery of these contaminants may be magnified when populations migrate in large numbers and release or transfer these bioaccumulated contaminants to a receptor food web following the death of the carrier organisms (in the case of semelparous and anadromous salmon, for example), consumption by predators, or release by animal waste.

A few paleo-environmental studies have identified a clear linkage between contaminant distribution and migration of vertebrate species (Blais et al. 2005, 2007; Evenset et al. 2007a; Michelutti et al. 2009a, Huang et al. 2013), and in the past few years, there has been much attention given to this topic, as we elaborate below.

Regional and global distribution processes of pollutants are an important aspect of interdisciplinary environmental research (Wania and Mackay 1996; Kallenborn et al. 2007; Heidam et al. 2004; Armitage et al. 2011). It is becoming increasingly recognized that migration of populations may play an important role in the distribution of anthropogenic pollutants in the environment (Blais et al. 2005, 2007; Michelutti et al. 2009a; Evenset et al. 2007a; Corsolini et al. 2011; Heidam et al. 2004). Due to global climate change, increased occurrences of invasive behaviour as well as changes in migration pathways have been registered in many regions (Zhang et al. 2011, 2012a, b; Wright et al. 2010; Winder et al. 2011; Willis et al. 2010; Theoharides and Dukes 2007; Taylor et al. 2012; Sorte et al. 2010; Song et al. 2012; Shao 2009; Ruxton and Schaefer 2012; Robinet and Roques 2010; Pyke et al. 2008). It is therefore important to evaluate migration and invasive behaviour of populations as a potential early warning signal for effects on ecosystems caused by recent global climate change (Kallenborn et al. 2012).

Prerequisites for Pollutant Transport in Biological Systems

Several factors in addition to behavioural and species-dependent physiological processes affect the biovector mediated distribution of anthropogenic pollutants. Also the inherent physico-chemical properties of the chemicals and the pathway of uncontrolled pollutants released into the environment are of importance for the comprehensive assessment of the transport potential (Wania and Dugani 2003; Shen et al. 2005; Praetorius et al. 2012; Klasmeier et al. 2006; Hung et al. 2010; Fenner et al. 2005; Breivik and Wania 2003; Beyer et al. 2003; Armitage et al. 2011; Matthies et al. 2009; Juraske et al. 2007). Important scientific parameters for the characterisation of physico-chemical properties are listed in Table 1.

In order to be integrated effectively into biological tissues, the contaminants have to resist environmental degradation and transformation (persistence) and be bioaccumulative (enrichment into biological tissues like biological fluids, lipids, peptides and proteins). Usually these basic properties meet the requirements of the United Nations Environmental Programmes (UNEP) Stockholm Convention for the international regulation of POPs (persistent organic pollutants), where POPs are defined as a sub-group of PBT compounds (P = Persistent, B = Bioaccumulative, T = Toxic). In the case of persistent pollutants (e.g., POPs), which accumulate in tissues of migratory and/or invasive species, the evidence of effective biovector transport as a pathway for anthropogenic POPs distribution is obvious, since only anthropogenic sources are identified for this type of pollutant (Cowan-Ellsberry et al. 2009). However, trace metals may originate from a combination of natural and anthropogenic sources (i.e. Hg, Pb, Cd), therefore the anthropogenic origin should be assessed (Yang et al. 2007; Wren et al. 1994; Willey et al. 2006; Weinbruch et al.

Table 1 Important selected parameters for the definition of the environmental properties of anthropogenic pollutants

Parameter	Property	Description
Boiling point	Volatility	Temperature when the substance is transferred from the water into the gas phase
Log K_{OW}	Lipophilicity/ Hydrophobicity	The decadic logarithm of the Octanol-Water partitioning coefficient describes the distribution of a substance between octanol (simulating Lipid properties) and water
$\tau_{½}$ = Half-Life time	Environmental Stability	Described the time span until a compound is decomposed to 50 % of its original concentration under natural/standardised conditions
Henry`s constant	Environmental Mobility	Defines the linear relationship between the partial pressure and the distribution of a gaseous compound between the gaseous and the liquid phase in a closed system
LD_{50} = Lethal dose	Toxicity	Described the applied dose of a compound at which an experimental population is reduced to 50 % of the original size

2012; Walna and Siepak 2012; Oliveira et al. 2011; Shevchenko et al. 2003; Sanchez-Hernandez 2000; Odland and Nieboer 2012; Ebrahimpour et al. 2011; Dutkiewicz and Swiatczak 1993; Dragovic and Mihailovic 2009; Doong et al. 2008; Braune et al. 1999; Berg et al. 2004; Barrie et al. 1992; Bargagli 2000).

In addition to physico-chemical properties, established migration patterns of the carrier species are of equal importance for the complete evaluation of biovectors for contaminant distribution in the environment (Elewa 2005). Well-known examples are birds and marine mammals (including whales and seals) with well-established annual or multi-annual migration cycles covering large distances, which, for selected species, even cross hemispheric borders (Elewa 2005).

High POPs in top predator birds (i.e., birds of prey) in Europe and North-America have been linked to the massive population declines in the 1960s and 1970s (Clark et al. 2001; Chen et al. 2009; Byczkowski 1977; Arai and Takeda 2012; Hamlin and Guillette 2010; Haegele and Tucker 1974; Guillette 2006; Gomara et al. 2007; Davison and Sell 1972). Specifically, the chlorinated pesticide dichlorodiphenyltrichloroethane (*p, p*`-DDT, IUPAC name: 1,1,1-trichloro-2,2-di(4-chlorophenyl) ethane) and its transformation products were associated with egg shell thinning in top predator birds (Clark et al. 2001; Ware 1975; Scott et al. 1975; Ratcliffe 1973; Mellink et al. 2009; Mateo et al. 2000; Lundholm and Bartonek 1992; Lundholm 1982, 1980; Lindvall and Low 1980; Kolaja 1977; Johnson et al. 1975). Especially migratory top-predator birds like the Peregrine Falcon (*Falco peregrinus*), Merlin (*Falco columbarius*), the European White-tailed Sea Eagle (*Haliaethus albicilla*) as well as *Ciconiformes* species (e.g. *Ciconia ciconia L*.,) were affected by extremely high *p, p*`-DDT and *p, p*`-dichlorodiphenyldichlorethylene (*p, p*`-DDE, IUPAC name: 1,1-*bis*-(4-chlorophenyl)-2,2-dichloroethene) burdens (Zabik and Dugan 1971; Yang et al. 2007; Wright et al. 1972; Wiktelius and Edwards 1997; Wiemeyer and Porter 1970; Ware 1975; Vieira et al. 2001; van Drooge et al. 2008; Thomas et al. 1992b; St Omer 1970; Scharenberg and Struwe-Juhl 2006; Scharenberg and Looft 2004; Reidinger and Crabtree 1974; Ratcliffe 1973, 1967; Olafsdottir et al. 1995; Nakamaru et al. 2003; Movalli et al. 2008; Moriarty 1972; Mora 2008; Mora et al. 2002; Merino et al. 2007; Mbongwe et al. 2003; Mateo et al. 2000; Krantz et al. 1970; Kenntner et al. 2003; Johnston 1975; Hela et al. 2006; Corsolini et al. 2011; Behrooz et al. 2009).

Even migrating *Passeriformes* species were reported with elevated POPs (Ormerod and Tyler 1992; Dauwe et al. 2003; Mora 2008). Due to the previously documented effects of DDTs, it is safe to conclude that migrating bird species have been regularly exposed to high pesticide burdens in their southern resting regions, accumulated the contaminants in the body tissues and transported them into their breeding regions where the contaminants may have accumulated and transferred effectively along the regional food webs.

Thus, species dependent behavioural strategies in combination with favourable physical-chemical properties of the respective contaminants are the prerequisites for an effective distribution of biovectors to the overall global distribution processes of pollutants. However, based upon logistical restrictions, research priorities and technological challenges, it is difficult to estimate the contribution of biovector

Table 2 Examples for biovector mediated pollutant transport

Marine Species	Systematic name/ order	Contaminant group	Comment	Reference
Glaucous gull	*Larus hyperboreus*	POPs, Trace metals incl. Hg		196, 198, 200-202, 232
Herring gull	*Larus argentatus*	POPs		232
Arctic char	*Salvelinus alpinus*	POPs, trace metals incl. Hg	Anadromous	233
Atlantic salmon	*Salmo salar*	POPs	Anadromous	
Beluga	*Delphinapterus leucas*	POPs		171–173, 181
Seals	*Pinnipedia*	Hg/POPs7 trace metals incl. Hg		160-170
Polar Bear	*Ursus maritimus*	Hg, POPs, trace metals incl. Hg		182, 183,
Atlantic cod	*Gadus morhua*	POPs		139–142, 148
Sockeye salmon	*Oncorhynchus nerka*	POPs		184
Chinook Salmon	*Oncorhynchus tshawytscha*	POPs		186–188, 196
Terrestrial and freshwater species	*Scientific name/ Order*	*Contaminant group*	*Comment*	*Reference*
Reindeer/Caribou	*Rangifer rangifer*	radioisotopes, metals		223,226–231
Passerine species	*Passeriformes*	POPs		116,117,108
Birds of prey	*Falconiformes*	POPs		72-80, 103–114
Arctic char	*Salvelinus alpinus*	POPs, trace metals incl. Hg	Land-locked	
Water snake	*Nerodia sipedon*	POPs		203
Jackrabbit	*Lepus californicus*	Radioisotopes		122
Threadfin shad	*Dorosoma petenense*	Trace metals incl. Hg		239

based pollutant transport to the overall long-range transport, which includes among other pathways, transport via atmosphere, oceans, rivers and ice (Vetter et al. 1996; Miljevic and Golobocanin 2007). Due to its restricted transport capacity, the bulk movement of persistent contaminants from biovectors is small compared to transport by air and ocean currents (Macdonald et al. 2005; Klasmeier et al. 2006), though the high transfer efficiency of contaminants from biovector to receptor ecosystem may result in significant contamination from some migratory species (Evenset et al. 2007a; Blais et al. 2007).

Evidence of biovector contaminant transport has been documented in terrestrial and marine environments. Terrestrial (fresh water fish, passerine bird species, birds of prey) and marine species (amphipods, fish, cetaceans, seals, and marine birds) have been identified as biovectors (Table 2). Here we provide a review of the current scientific literature on biovectors, recommend strategies for future research on the environmental consequences of biovector contaminant transport, and show how environmental archives such as lake sediments have contributed to this understanding.

Biovectors for Persistent Organic Pollutants (POPs)

Concerns about the potential role of biovector-mediated transport for POP distributions in environmental systems were raised as early as 1962 when Rachel Carson (1962) elaborated on the potential environmental hazards associated with uncontrolled release of organic agricultural chemicals and subsequent accumulation in higher organisms (bioaccumulation).

Human Consumers as Recipients of Biovector Transported Pollutants

An immediate consequence of biovector-mediated pollutant transport is the direct uptake and bioaccumulation of POPs into species (marine and terrestrial) exploited for human consumption. Among others (including marine mammals exploited as traditional food source in many regions of the Earth), selected marine fish species, commercial objects for the modern fishing industry for many centuries, may serve as examples.

The Atlantic cod (*Gadus morhua* L.) was subjected to commercial high volume fishing for centuries. Uncontrolled fishing led to overfishing and extreme reduction (<95 % compared to registrations before the 1900s) of the North Atlantic cod population in many regions including the Eastern Canadian populations, North Sea, Baltic and Irish Sea populations. Currently Atlantic cod is harvested under strict national regulations in the North-Eastern Atlantic, along the Norwegian coast, the Barents Sea and along the Greenland coast (Mieszkowska et al. 2009; Hutchinson 2008; Nielsen et al. 2001).

In early spring every year, cod eggs are released during spawning in shallow coastal waters (<30 m depth) and are thereafter drifting into to the deep North-Atlantic Ocean. The larvae develop in the open waters until maturity (2–4 years) before moving back to the spawning grounds every year. Regular migration routes of immature Atlantic cod are rarely reported. However, mature Greenland cod have been reported to migrate more than 1000 km in large schools and north-eastern Atlantic cod may move up to 800–900 km between winter feeding grounds and spawning areas. The migration patterns are illustrated in Fig. 1. The carnivorous Atlantic cod has an average life span of 15–20 years and is mainly feeding on crustaceans and other fish species. The ethology and physiology of the Atlantic cod is well studied and documented. Relevant information may be found in textbooks and scientific papers (Olsen et al. 2012; Stenseth et al. 2006; Jorgensen et al. 2008).

With an average content of 1.5 % dry weight (d.w.) triacylglycerol (TAG) and around 8 % d.w. phospholipids (Fraser et al. 1988), the cod eggs may serve as a

Fig. 1 Migration range and distribution patterns for North Atlantic cod, Polar cod (*Boreogadus saida*), Herring (*Harengus harengus*) and Capelin (*Mallotus villosus*) according to (Stenevik and Sundby 2007)

preferred excretion pathway for the contaminated mother fish (as documented for other species), exposing the developing larvae with considerable lipophilic POPs already in this early life stage. However, there are presently no scientific studies on mother- offspring contaminant relationships reported for Atlantic cod confirming this hypothesis. Nevertheless the migrating mature long-lived Atlantic cod is known to accumulate very high levels from prey species taken along the migratory pathways from and into the spawning grounds of lipophilic POPs in their fatty tissues and particularly in the liver tissues (Jenssen et al. 2007; Sinkkonen et al. 2004; Hellou et al. 1993, 1994). Ultimately large schools of mature Atlantic cod are moving towards their traditional spawning grounds where they are harvested annually (under well-defined regulatory conditions) from large coastal fishery boat fleets. During the annual cod fishing season, large amounts of bycatch are released by the

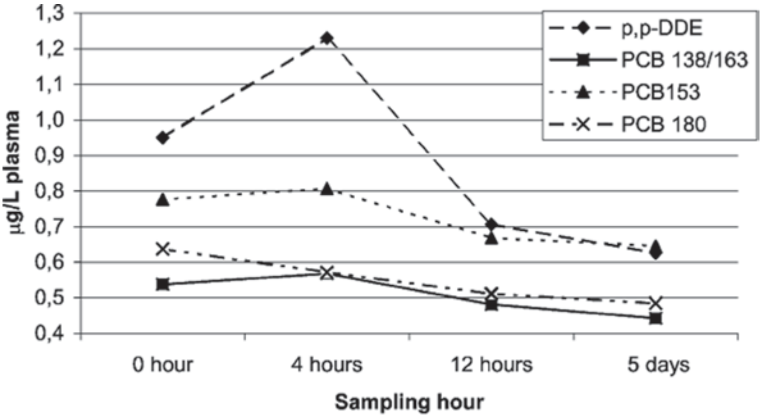

Fig. 2 Elevated plasma POP levels in human consumers after Cod liver consumption according to Sandanger et al. (2003)

fishing fleets into the ocean, and thus may contribute additionally to potential accumulation of pollutants in the local marine sediments (Hall et al. 2000).

The lipid-rich cod livers are today also used as a source for cod-liver oil. Cod liver oil is appreciated as both a healthy food supplement (vitamin D and ω-3 fatty acid source) as well as a basic ingredient for numerous cosmetic and medical products. High POP contamination levels of commercial cod liver oils have been documented for decades (Fraser et al. 1988; Montano et al. 2011; Smutna et al. 2009; Rawn et al. 2009; Jacobs et al. 2004; Sandanger et al. 2003a). Due to this high contamination (Fig. 2), cod liver oil products have to undergo extensive cleaning procedures before being sold on the market as consumer products.

In some northern regions, the liver tissue of the Atlantic cod is appreciated as a delicacy. In combination with roe and local vegetables, the cod liver is served boiled as a local dish ("mølje") on the tables of the North Norwegian households during and after annual spring fishing along the North Norwegian coastal spawning grounds (Sandanger et al. 2006). This seasonal exposure to POPs by human consumers can be very high, but is dependent on the consumption frequency and the amount of liver consumed (Sandanger et al. 2003b, 2006; Brustad et al. 2004). POPs in blood of human consumers can increase rapidly for selected compounds after consumption (Fig. 2).

Although exposure to POPs by consumers may sometimes even exceed the official thresholds for the tolerable intake, according to current understanding, the health benefits (Vitamin D resource, ω-3 FA access, etc.) still exceed the risks posed by the pollutants. Therefore, the responsible authorities still refrain to issue advisories for the consumption for this local food in northern Norway. Other heavily exploited fish species like tuna (Storelli et al. 2008), herring (Mackenzie et al. 2004) and sea bass (Fernandes et al. 2009) with relatively high pollutant levels may also be considered examples for similar uptake routes via biovectors into human consumers.

Comparable pathways are also identified in circum Arctic countries (all eight Arctic nations) where the i.e. indigenous Inuit people in the western Arctic (Alaska, Greenland and Eastern Canada), many living according to their traditional lifestyle, conduct seasonal hunting on various marine mammal species along the Alaskan, North Canadian and Greenlandic coasts. The subcutaneous fat tissue from seals (blubber) is appreciated as an important nutritious food source. However, this lipid-rich (>70 % d.w. lipid content) blubber tissue is now also a highly effective storage medium for POPs, which accumulate in these tissues during the entire life-span of the usually quite long-lived seal (Sobek et al. 2010; Letcher et al. 2010; Kucklick et al. 2002, 2006; Fisk et al. 2001; Hansen 2000, 1998). Consequently, high concentrations were found in Inuit traditional country foods (Dallaire et al. 2009; Van Oostdam et al. 2004; Carlsson et al. 2014). As a part of the circum-Arctic Monitoring and Assessment Programme (AMAP), and the Canadian Northern Contaminants Programme (NCP), the levels and effects of pollutant exposure in the indigenous peoples of the North are being constantly investigated and evaluated (Arnot et al. 2011; Brown and Wania 2008; Deutch and Hansen 2000; Deutch et al. 2007; Hansen 1998, 2000; Donaldson et al. 2010; Bonefeld-Jorgensen 2004, 2010).

The consumption of whale meat, including narwhal (*Monodon monoceros*) and beluga (*Delphinapterus leucas*), is an integral part of the traditional diet for indigenous Arctic populations (Carlsson et al. 2014). These Odontocete whales are long-lived species with regional migration patterns (belugas often move in family groups) mostly along coastal migration routes to/from overwintering areas to their summer habitats (Dietz et al. 2008; Solovyev et al. 2012; Bailleul et al. 2012). However, many whale species found in Northern waters are also known to migrate extreme distances, crossing over hemispheric borders. These organisms and populations will therefore bioaccumulate pollutant signatures from both hemispheres of the globe. Whales (odontocetes as well as baleen whales) are usually long-lived species with strong bioaccumulation potential for persistent pollutants (including POPs), depending on their trophic position in their respective food webs. Especially odontocete whale species (as marine top predators) are identified as carriers of considerable pollutant burdens (Litz et al. 2007; Bossi et al. 2005; Weisbrod et al. 2000; Bard 1999; Dekock et al. 1994; Borrell 1993; Aguilar and Borrell 1991). Therefore, consumption of whale meat will lead to increased POP related exposure risks for human consumers. The age-adjusted time trends for POPs in Belugas are illustrated in Fig. 3.

POP distribution profiles over time have been investigated in relevant species as well as in ecosystems and habitats affiliated with migrating species (Riget et al. 2010; Evans et al. 2005; Riget et al. 2004; Muir et al. 1999). In particular, POPs in seabirds (individuals and archived egg samples) are actively utilised as archives for temporal trend studies (Mallory and Braune 2012; Bustnes et al. 2010; Hebert et al. 2009; Helgason et al. 2008a; Gamberg et al. 2005; Herzke et al. 2002; Muir et al. 1999). The long-lived and migrating Northern Fulmar (*Fulmarus glacialis*) has also been the focus of recent studies on biovector-mediated transport of pollutants in Northern regions (Guzzo et al. 2014; Foster et al. 2010, 2011a).

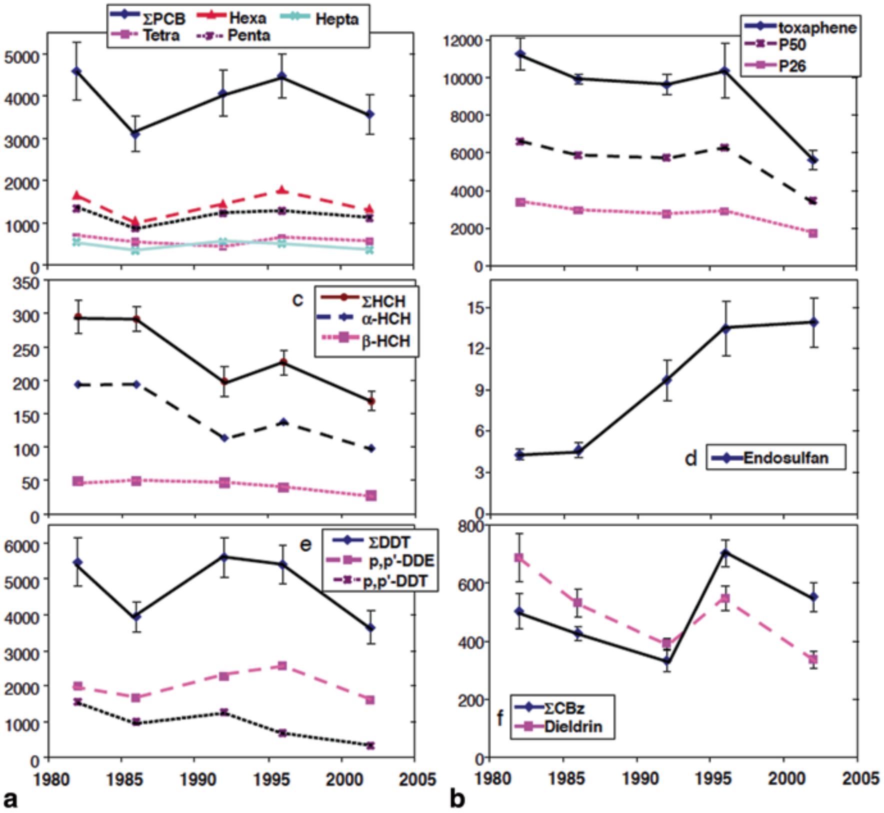

Fig. 3 Temporal trends of age adjusted concentrations of selected POPs in Canadian Belugas *(Delphinapterus leucas*) according to Braune et al. (Braune et al. 2005). Concentrations in ng/g (lw = lipid weight basis)

The Polar Bear as Indicator of Arctic Change

Due to environmental changes currently observed in Arctic regions, the polar bear (*Ursus maritimus*) populations are relying more on scavenging large whale carcasses compared to earlier observations where hunting of seals (i.e., ringed seals, harp seals) were the major food source for the circum-Arctic populations. This changing foraging strategy is documented and reported for the populations of the Beaufort Sea coast, Alaska (Bentzen et al. 2008), and Svalbard, Norway (Derocher et al. 2002). As described for the Svalbard polar bear population, scavenging on large whale carcasses of sperm whale (*Physeter macrocephalus*), bowhead (*Balaena mysticetus*) and beluga have the potential for increased exposure risk for POPs in these polar bears.

Anadromous Fish Species as POP Biovectors

Anadromous fish species (mainly salmonids) are actively using both freshwater- and marine environments as their living habitats. The annual migration of these fish species between the marine feeding grounds and the freshwater spawning areas is usually associated with considerable physiological adaptation (smoltification) in order to adapt to the respective water conditions (mainly salinity differences). High POPs in these organisms under considerable physiological stress may negatively influence this delicate smoltification process (Jorgensen et al. 2004, 2006) with considerable effects on their fitness.

During the annual spawning season in spring, anadromous fish species are migrating in large schools from their marine feeding grounds into their natal freshwater spawning locations. Many of these species, including Arctic char (*Salvelinus alpinus*), Atlantic salmon (*Salmo salar*), Sockeye (*Oncorhynchus nerka)* and Chinook (*Oncorhynchus tshawytscha*) are known to carry considerable POP burdens (Jorgensen et al. 2006; Berntssen et al. 2011; Bustnes et al. 2012; Cullon et al. 2009; Janetski et al. 2012) since they are top predators in their respective food webs. They are considered important transport vehicles for persistent pollutants (including POPs) from the marine- into the freshwater ecosystems. However, these migrating fish are usually subject to extensive fishing pressure and considered a delicacy by humans as well as for a variety of top-predator animals (i.e. bears and raptor bird species) feeding on the abundant fish in their respective freshwater habitats (Gende et al. 2001; Ruggerone et al. 2000; Quinn and Buck 2000; Scheel and Hough 1997; Hewson 1995). The pollutant burden carried by the individual salmonid fish, and thus, the migrating population, can be very high (Bustnes et al. 2012). In addition, this behavioural migratory pattern results in an effective bioconcentration effect for the respective persistent, bioaccumulative pollutant, where the pollutants previously distributed and diluted in a large marine system are effectively biomagnified in the anadromous fish and subsequently released and/or transferred in high quantities to the receptor food webs. The biovector's pollutant burden is, thus, directly introduced into a much smaller local freshwater/terrestrial ecosystem. This contaminant load is finally accumulated into the predating and/or scavenging animals (Gregory-Eaves et al. 2007; Janetski et al. 2012) with potential consequences for individual and population fitness.

One of the consequences leading to an effective and massive release and bioconcentration of biovector-transported pollutants in the receiving environment is the massive die-off of Sockeye salmon (and others) after spawning. This event will ultimately lead to a near 100 % release of the transported pollutants into the receiving freshwater system during a relatively short time period every year (Krümmel et al. 2003, 2005). This seasonal release of POPs is also well documented in the receiving sediment layers of the effected freshwater ecosystems. POP distributions in sediment cores from sediments exposed to deposition from die-off of salmonid fish after spawning can be utilised as archives for temporal distribution studies (Krümmel et al. 2005, 2009).

Sea Birds as Pollutant Carriers

Another transfer pathway for biovector-mediated transport of POPs from marine feeding grounds into freshwater environments has been described for Arctic seabirds (Evenset et al. 2007a; Evenset et al. 2004; Blais et al. 2005; Michelutti et al. 2009a; Choy et al. 2010a).

As a recent Canadian study revealed, seabirds are playing a key role in providing small, isolated freshwater ecosystems in the High Arctic with important nutrients for keeping the biological system in a natural equilibrium (Blais et al. 2007; Brimble et al. 2009; Michelutti et al. 2009a)

Pelagic seabirds are also identified as effective carriers for POPs, accumulating high concentrations in their lipid-rich tissues. During the hatching season, many seabird species gather in enormous colonies on cliffs and other coastal habitats in the North. During hatching and recreation, the birds release large amounts of contaminated guano (excrements) to the soil or directly into freshwater lake systems, depositing POPs continuously into the aquatic and terrestrial environments. This pollution source is consequently resulting in elevated POPs in aquatic sediments and foodwebs (Blais 2005; Blais et al. 2005, 2007; Michelutti et al. 2009a, b; Choy et al. 2010a; Evenset et al. 2004, 2005, 2007a; Kallenborn et al. 2007, Huang et al. 2013). A schematic pathway of this pollutant transfer from the marine into the fresh water ecosystems is depicted in Fig. 4.

Water Snakes as Pollutant Carriers

In addition to migration (individuals and large population groups), an invasive behaviour may also result in changes of pollutant uptake and distribution patterns. For example, POPs in Lake Erie water snakes (*Nerodia sipedon*) seem to be directly influenced by the invasive appearance of a new potential prey species; the round goby (*Apolonia melanostomus*). The snakes obviously changed their diet (>95 gobi) as a result of this community shift in the aquatic environment. Due to this diet change, the POP burden and distribution patterns in water snakes changed, which impressively demonstrated the intricate linkage between food web structure and contaminant uptake and distribution (Fernie et al. 2008).

Biovectors for Trace Metals and Radioactive Materials

Terrestrial Environment Pathways

One of the earliest examples provided for the potential role of biovectors in the distribution of anthropogenic pollutants was presented for ^{137}Cs. The role of

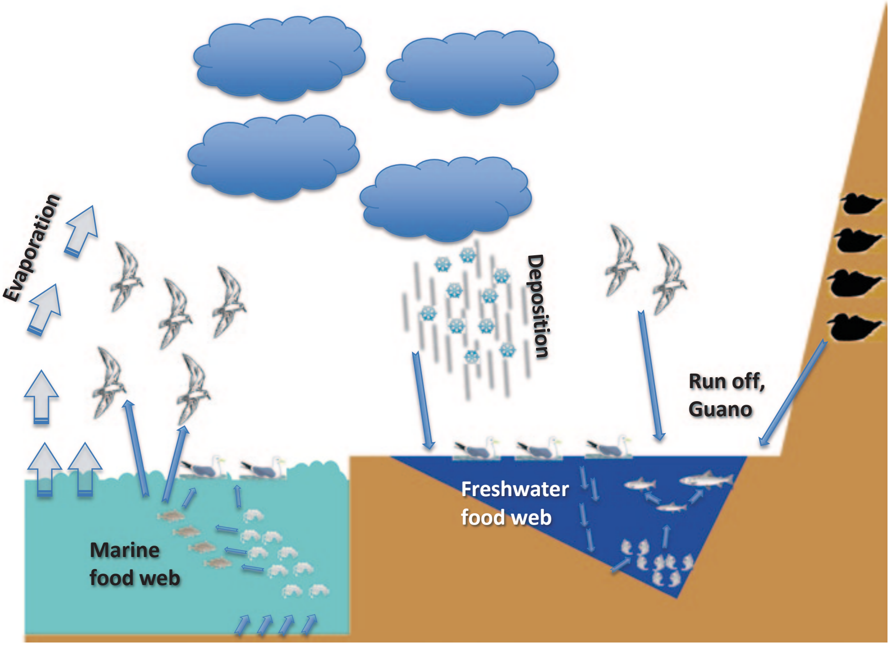

Fig. 4 Illustration of the effective pollutant transfer and up-concentration from the marine to a freshwater environment

jackrabbits (*Lepus californicus*) for the distribution of radioactive ^{137}Cs was investigated (O'Farrell and Gilbert 1975) in a natural habitat in the Western USA where rabbits deposited and concentrated ^{137}Cs.

In contrast to the main focus on marine environments for the previously discussed examples on organic pollutants, radioactive materials as well as trace metals were often found at higher levels in terrestrial environments relative to marine ecosystems. Thus, migration patterns of terrestrial organisms are usually the focus of research on biovector mediated distribution patterns for this type of pollution.

However, reports on biovector mediated transport for radioactive materials are sparse compared to the POPs. Indications, however, for this type of distribution process can be found indirectly by searching and carefully examining the currently available literature on radioactive contamination in biota (Macdonald et al. 2007; Amundsen 1995; Aarkrog 1994; Smith et al. 2011; Gwynn 2010; Dahlgaard et al. 2004; Jones et al. 2003; Strand et al. 1999; Brown et al. 1999; Kryshev et al. 1998; Salbu et al. 1997; Florou and Chaloulou 1997; Ostapenyan and Umnov 1996; Gaso et al. 1995; Matishov et al. 1994; Baysal and Tuncer 1994; Penttila et al. 1993; Blaylock 1974; Fukai 1966).

One of the prominent examples for biovector-mediated transport and accumulation of anthropogenic radioactive materials is linked to the radioactive fall-out after the Chernobyl accident (Amundsen 1995; Johansson et al. 1995; Aarkrog 1994; Deruig and Vanderstruijs 1992; Bretten et al. 1992). Contaminated particulate material (i.e. ^{137}Cs, ^{99}I, ^{90}Sr) was transported via the atmosphere into the northern Scandinavian regions and deposited on the ground. Subsequently, by feeding on contaminated lichens and mushrooms, the radioactive fall-out was directly transferred and bioconcentrated into the local reindeers (mainly in Norway and Sweden). Consequently, elevated radioactivity (i.e. ^{137}Cs, ^{99}I) was measured during monitoring campaigns in northern Norway and Sweden in reindeers (Forberg et al. 1992; Johansson et al. 1995) leading to temporary restrictions and regulations for human consumption of reindeer meat products in these regions. The reindeer obviously accumulated the radioactive material, and due to their annual migration between winter and summer feeding grounds, redistributed this contamination in the region. In addition, this elevated contamination had consequences for human consumption of reindeer meat products in the regions for many years after the accident occurred. More information on distribution and effects of radioactive materials in the environment can be found in the scientific literature (Howard 2000; Kryshev et al. 1998; Strand et al. 2002; Aarkrog et al. 2000; Amundsen 1995; Thomas et al. 1992a; Miettine.Jk 1971)

Marine Environment Pathways and Linkage into the Fresh Water

Distribution and effects of anthropogenic trace metals (including Hg = mercury) have been the focus of the environmental sciences for decades. However, the role of animal migration patterns on the distribution and bioconcentration of trace metals is currently not well understood. A recent study discussed the role of seabirds as biovectors for trace metals and evaluated the role of trophic level in this process based on sedimentary deposits (Michelutti et al. 2010).

Anadromous fish species are also found to be a suitable transport medium for Hg. The transport of marine Hg into freshwater environments via Arctic char was described in a recent study (Swanson and Kidd 2010). This pathway (transport via anadromous fish) is considered an important transfer pathway for Hg and other metals into pristine and remote fresh water environments.

Similarly, seabird-mediated transfer of Hg from marine to coastal terrestrial environments close to large bird colonies was shown at Cape Vera, Devon Island, Canada (Choy et al. 2010b). Mercury (Hg), currently one of most investigated trace metals in environmental contaminant research, seems to follow similar pathways as described for POPs (Sigler et al. 2003; Braune et al. 2005; He et al. 2005; Dietz et al. 2006; Swanson et al. 2006; Helgason et al. 2008b). The potential impact of an invasive planktivorous fish species on distribution and uptake processes of Hg was reported for a fresh water lake environment in a 20-year long-term study (Eagles-Smith et al. 2008). The population dynamics of the investigated invasive species (threadfin shad = *Dorosoma petenense*) had distinct consequences for the predatory species (bass etc.) in the investigated ecosystem. Elevated Hg levels were found in the pelagic species whereas no differences in Hg were identified in the benthic fish species of the freshwater system. The changes of Hg levels in the changing food web are illustrated in Fig. 5.

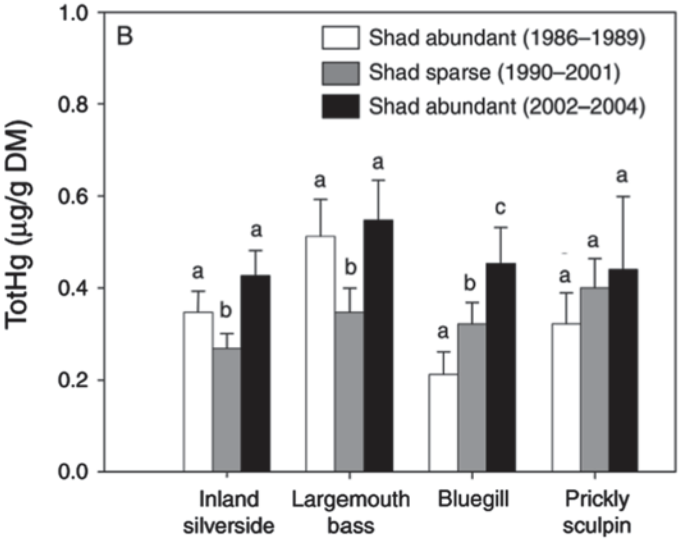

Fig. 5 Total mercury concentrations (TotHg) in major species of the changing freshwater food web (Clear Lake, Cal.) according to (Eagles-Smith et al. 2008). Concentrations are given in g/g DM (=Dry matter)

For long-lived species such as odontocete species (beluga whales) as well as other marine mammals (e.g., walrus), teeth tend to accumulate mercury. This feature has been successfully utilised for temporal trend studies on whale carcasses collected in the Canadian Arctic dating back into preindustrial times (Outridge et al. 2002). Teeth from other species have also been utilised as archives for the investigation of long-term temporal trends of contaminants (Dietz et al. 2009; Outridge et al. 2005, 2009; Vucetich et al. 2009; Kinghorn et al. 2008).

As already shown for persistent organic pollutants, the nutrient and pollutant input from breeding seabird colonies on receiving sediments in freshwater environments has also frequently been utilised for the investigation of trace metal temporal trends (Blais et al. 2005). In combination with stable isotope investigations, this type of trend investigation has the potential to reveal the intricate food web based interactions in fragile freshwater environments (Choy et al. 2010a; Michelutti et al. 2009a; Michelutti et al. 2010). Long-term trend investigations in sediments using ornithogenic trace metals are reported in the scientific literature (e.g. Sun et al. 2006; Blais et al. 2007; Brimble et al. 2009; Huang et al. 2013), as we elaborate below.

Biovectors as Archive for Temporal Trend Investigations

Studies have revealed how biovector transport can concentrate contaminants (via bioaccumulation and congragation) in local receptor ecosystems (Krümmel et al. 2003; Evenset et al. 2007a) even with potential risk to human consumers (Carlsson et al. 2014). For remote ecosystems, such as the polar regions, continuous long-term monitoring of contaminants in biota (i.e. egg samples and other tissues) reveal temporal trends (van den Brink et al. 2011; Xu et al. 2013; Vorkamp et al. 2004; Vetter et al. 2003; Elliott et al. 1998; Bignert et al. 1998; Riget et al. 2011). Although the accumulation and long range transport of contaminants is well established, the importance of bioaccumulation into organisms, and direct release from biovectors into the receptor ecosystems is not an integrated part of these classical monitoring activities. Therefore only when the species-specific release of pollutants is established, can biovector related trend information be derived.

The above is a new and important research area, and the relevance of biovectors as archives for retrospective trend analysis of pollutant levels is demonstrated by several studies. For example, Sun et al. (2006) showed that seal hair collected from a lake sediment core in Antarctica can be used for long term trend analysis (estimated time span over 2000 years) on metal concentrations after carefully dating the sediment core archiving the seal hairs. In addition, long-term POP trends from Penguins on King Georg island (Antarctica) were investigated on adjacent lake sediments (Sun et al. 2005). Total mercury concentrations were measured and the time trends reflected the periods with extensive human usage of Hg for gold and silver mining activities, especially in the southern hemisphere. Another recent study exploited sediment cores in the vicinity of penguin colonies for time trend investigations of metal concentrations (Guerra et al. 2011). The authors acknowledged the contribution of the nearby colony to the overall metal loading of the sediment, but concluded that local geological contribution, as well as natural processes to the metal burden found in the sediments. The anthropogenic contribution seemed to be of minor importance.

A recent study (Nie et al. 2012) confirmed that seal and penguin droppings are considered a major contribution of Hg in sediment cores from the Ross Sea region (Antarctica). The biological origin of the Hg was also confirmed by elevated phosphorus (as an indicator bio-element) in the respective cores. The authors concluded that Hg enrichment in the sediment profiles from the Ross Sea region were caused by biovectors such as penguins and seals resting/breeding in this region.

Several Arctic studies on long-lived seabird populations also revealed the potential of receiving lake/pond sediments as archives for temporal trend studies. In combination with co-factors such as nutrient levels, stable isotope distributions ($^{13}N/^{14}N$; $^{12}C/^{13}C$ etc), pollution trend studies were able to reveal the complex food web based interactions in freshwater environments influenced by biovectors (e.g., Brimble et al. 2009; Choy et al. 2010a, b; Foster et al. 2011a, b; Michelutti et al. 2009b, 2010)

Contaminant profile investigations in natural archives for urban and rural bird species have also revealed temporal trends (Nocera et al. 2012). A population of chimney swifts (*Chaetura pelagica*) where birds were breeding in an urban location in Ontario Canada from 1944–1992 (for 48 years), was used in a pollution trend study. The deposits of guano and egested insects at the base of a chimney were dated and investigated for the temporal trend of *p, p*`-DDT and its metabolites. Based upon the archived insect remains and associated contaminant data, the authors argued that, besides the continuously increasing contaminant burden in the birds, DDT applications during this time period considerably reduced the Coleoptera populations and thus likely caused negative nutritional consequences for swifts and other aerial insectivores.

Also, droppings at resting places of bats can be used as archives for pollutant temporal trend investigations. For example, Clark et al. (1995) collected bat guano cores, primarily from Mexican free-tailed bats (*Tadarida brasiliensis*), to investigate organochlorine pesticides from several caves. The main transformation product of *p, p*`-DDT, *p, p*`-DDE, was found to be the most prominent organochlorine contaminant in all samples. The authors concluded that the chemical residues were a direct result of the continuous use of DDT over decades in the respective regions.

Biovector Transport of Pollutants and Climate Change

Global climate change is a major research focus in many scientific disciplines in the environmental and earth sciences. The currently available scientific predictions also foresee direct and indirect influences of a changing regional and global climate on migratory pathways and also invasive strategies in ecosystems (Adger et al. 2002; Ahola et al. 2007; Barbet-Massin et al. 2009; Barrett 2012; Both et al. 2006; Brander 2010). As described earlier, one of the basic features of migration and invasive behaviour is the active search or directed movements of individuals and/or populations for finding suitable/favourable living conditions. This would also include favourable climates for feeding and reproduction.

Pollutant distribution pathways in ecosystems are expected to be directly and indirectly influenced by regional and global climate change, including the pathways of biovector-mediated pollutant distribution (Armitage et al. 2011; Kallenborn et al. 2012). Climate-related changes in migration patterns have been observed for many species that are known to be significant pollutant carriers. For example, the annual migration pattern of the Atlantic cod (*Gadus morhua*) to and from traditional spawning grounds is currently changing (Brander 2010; Beaugrand et al. 2008). This shift is illustrated in Fig. 6, where the catch rates for cod is shown for 2012 in the Barents Sea, clearly demonstrating that the cod stocks are moving into the central and northern Barents Sea.

Due to a shift of the temperature regime in North Atlantic surface waters, the North Atlantic cod populations currently find suitable spawning conditions north of their previous spawning areas in the Western Barents Sea. Currently the abundance of mature Atlantic cod stocks is continuously rising in fishing areas of the North-Western Barents Sea. Only about 10 years ago, this area was considered marginal for the cod fishery (Brander 2010; Mieszkowska et al. 2009; Dempsey and Fisher 2005).

The Arctic region is currently experiencing unprecedented changes in ecosystem structures due to climate change. The complexity of these changes is comprehensively described in a recent report provided to the Arctic Council of Ministers in 2011 (Olsen et al. 2011; AMAP. 2012). As a result of these environmental changes,

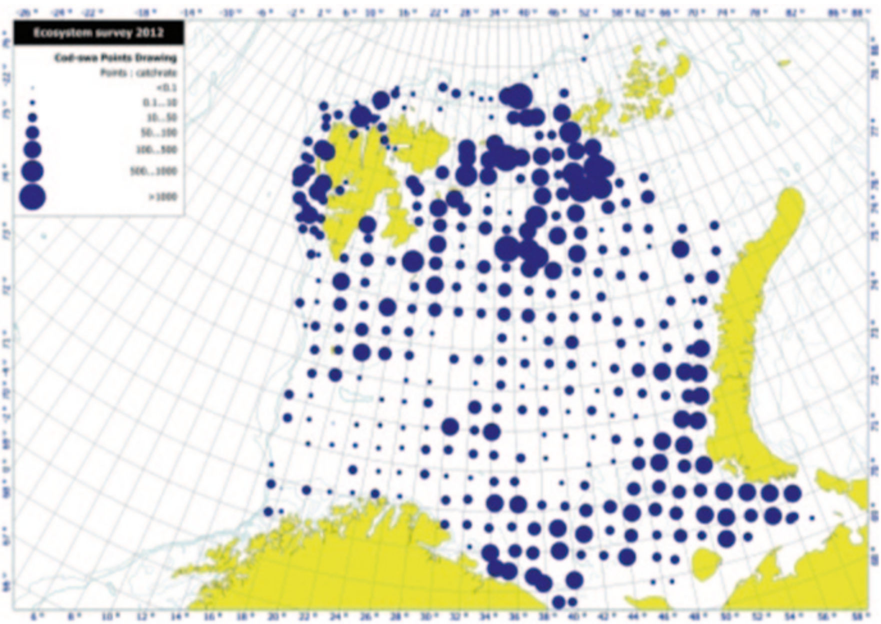

Fig. 6 Presentation of the recent 2012 catch rates for the Atlantic cod fishing in the Barents Sea. (Figure: Courtesy of the Institute of Marine Research (IMR), Bergen, Norway)

new species are currently invading the Arctic marine ecosystem with the potential to compete with indigenous species. The reestablishment of the blue mussel (*Mytilus edulis*) in the North-Eastern Barents Sea is an example of the quick response of molluscs on a rapidly changing climate regime in the Arctic environment (Berge et al. 2005). The distribution of molluscs in the Arctic marine environment is today considered an important footprint and sentinel for climate change processes (Wassmann et al. 2011). Due to the continuously progressing reduction of summer ice coverage, and the associated ecological changes in the central Arctic specifically, the composition of the lower pelagic and benthic trophic levels in the Arctic food web is expected to change (Borga et al. 2010; Hallanger et al. 2011). These alterations will have considerable consequences for bioaccumulation and foraging strategies in higher trophic levels up to top predator Arctic species (Kallenborn et al. 2012; Macdonald et al. 2005). For example, when the climate conditions in the central Arctic are changing, the smaller Arctic cod (*Boreogadus saida*) is expected to be replaced by the North Atlantic cod (*Gadus morhua*). Thus, marine top predator mammals (i.e. gulls, seals and whales) will increasingly prey on new species, with considerable consequences for bioaccumulating pollutants (Kallenborn et al. 2012)

The Arctic is today considered a sentinel region for on-going global climate change and similar changes in ecosystem structure are expected to occur in other regions and ecosystems of the world (Macdonald et al. 2005). This also includes invasion strategies and migration patterns (Faaborg et al. 2010; Kennedy and Crozier

2010; Lehikoinen 2011; Leithead et al. 2010; Robson and Barriocanal 2011; Weinstein et al. 2009). However, the scientific linkage between biovector-mediated pollutant transport and migration and invasive species is still not well enough explored in light of current global climate change. In order to identify early changes in biovector-mediated pollutant distribution, comprehensive baseline studies are urgently needed (Kallenborn et al. 2012).

State of the Science and Knowledge Gaps

Based upon the present review, only a small number of studies are currently available on biovector transport of pollutants. A list of identified examples for biovector mediated pollutant transport is given in Table 2.

Many studies focusing on food web structures and bioaccumulation/biomagnification pathways provide indirect evidence on the mechanisms and magnitude of biovector-mediated distribution processes for anthropogenic pollutants. The current literature review revealed a regional focus on Arctic and Northern regions for related studies on pollutant uptake and distribution via biota along and across regional food webs (Table 2). Similar mechanisms are expected to occur also in other regions of the world.

Biovectors are today considered a minor and maybe even negligible pollutant transport pathway when they are discussed in the context of the entire global pollution distribution mechanisms revealed by modern environmental sciences during the past decades (Fang et al. 2011; Hursthouse and Kowalczyk 2009). However, the few examples for biovector-mediated pollutant distribution available in the present scientific literature clearly reveal the potential of these mechanisms for effective and efficient transfer and bioaccumulation in the receptor food webs (including humans). During favourable circumstances, the impact on the local food web may be important on a local scale. This is especially the case when long-lived colony-breeding seabirds may serve as carriers for bioaccumulative anthropogenic pollutants for the transfer into local freshwater ecosystems. Examples have been found in the Arctic (Evenset et al. 2007a; Blais et al. 2005; Blais et al. 2007; Michelutti et al. 2009a, b, Huang et al. 2013). A simple example may illustrate this hypothesis: The Norwegian Arctic island Bjørnøya (Bear island, 74.4 N, 19.0 E) has been in the centre of the scientific interest since high levels of polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) were detected in land-locked Arctic char (*Salvelinus alpinus*) in Lake Ellasjøen during the early 1990s (Evenset et al. 2007b; Evenset et al. 2004). In addition, extremely high POP levels were found in the glaucous gulls from the local bird colony. A distribution profile for selected POPs for the local marine/terrestrial food webs revealed the effectiveness of the pollutant transfer from the marine into the local freshwater environment.

A 3-year atmospheric POP measuring program at Bjørnøya (Bear Island) revealed average concentrations for ΣPCBs of around 30 pg/m^3 (33 congeners analysed according to (Kallenborn et al. 2007a). Between 1200 and 1500 m^3 of air was filtered over glass fibre filters (GFF, for particle phase collection) and polyurethane filters (PUF, for gas phase collection) for quantitative analyses. This corresponds to ca. 45 ng PCB in average accumulated in the air samples collected during the 48h-sampling period at the Bjørnøya meteorological station without considering seasonal or trend-specific patterns. PCBs are deposited directly to the sea surface and accumulated in the marine pelagic and benthic food webs in the marine environment around Bjørnøya. It is assumed that the organic pollutants identified enter the local marine food web after atmospheric long-range transport from middle latitude source regions and subsequent deposition in the Bjørnøya marine environment.

In local glaucous gulls, which have been identified as the main carrier species for the transfer of POPs into the Bjørnøya fresh water environment, concentrations of up to 700 ng/g on a wet weight basis (w.w.) were recorded in blood samples in a long-term monitoring program (Verreault et al. 2010). The glaucous gulls at Bjørnøya can cover ocean areas of thousands of square kilometres every summer season while feeding on marine fish, crustaceans, etc. By assuming an average concentration of around 100 ng/g ww, an average individual bird carries ca. 150 µg PCB in its body (estimated whole body average PCB concentration and average body weight of ca. 1500 g). According to recent information from the Norwegian Polar institute, Tromsø, Norway (13.10.2013: http://www.npolar.no/en/species/glaucous-gull.html), around 1000 pairs (2000 individuals) are annually breeding on Bjørnøya, mainly in the southern part of the island around Lake Ellasjøen. Thus, the glaucous gull population carries ca. 300 mg PCBs during the breeding season to/from Bjørnøya. The glaucous gulls, however, reduce continuously their PCB burden through the release of guano (excrements) in the colonies and into Lake Ellasjøen. The PCB contamination is directly released into the water (bathing) or is draining indirectly into the watershed during rain events etc. Concentrations of around 1000 ng/ww of PCB (33 congeners) were found in intestinal/guano samples from Ellasjøen glaucous gulls (Evenset et al. 2007a). Assuming at least one excretion event per bird per day when bathing in the lake (observations during the breading period: for an average of 100 birds on the water during day time), and neglecting drainage from the bird cliff, around 100 µg PCBs are released daily into the waters of the lake and subsequently accumulated in the short local freshwater food web. Thus, during the breeding season from June to August (ca. 80 days), around 8 mg PCBs (0.008 g, around 2.5 % of the total glaucous gull population burden) are introduced in a nutrient-rich medium and accumulated in the local freshwater environment of Lake Ellasjøen (around 0.7 km^2 surface area). This high PCB exposure leads to very high PCBs reported in the local long-lived land-locked Arctic char population (concentrations up to 700–1000 ng/g wet weight are reported regularly). The reported concentrations are considered among the highest concentrations ever measured in Arctic char from remote Arctic freshwater ecosystems (Evenset et al. 2004a). Detailed information and calculations on the POP pollution budget of the Lake Ellasjøen freshwater environment can be found in the scientific literature (Evenset et al. 2004, 2007a; Herzke et al. 2003).

The rough and qualitative estimation for the biovector-mediated transfer of PCB from the marine to the freshwater Bjørnøya environments is considered a classic example for the effective transfer and bioconcentration of low level concentrations in a diluted marine ocean environment (many thousand square kilometres of feeding areas for the respective bird species) into high concentrations in biota accumulated in local Arctic fresh water environments (less than one square kilometre). Similar pathways may be found in other parts of the world as well as documented on Northern Fulmar populations (e.g. Blais et al. 2005) and on Hg in penguins in the Antarctic environments (Nie et al. 2012)

Compared to other (mainly abiotic) studies regarding pathways for pollutant transport and fate on regional as well as local scales, biovectors are not currently a major focus of environmental sciences. Especially in light of global climate change, where local food webs will change and invasive species will disturb local and regional ecosystems, the role of biovectors in re-distributing persistent anthropogenic pollutants should be further investigated with a focus on the identification of characteristic criteria for specific receptor sites. There is a need to establish scientific baseline information regarding the potential impact of climate change on biovectors and their role on the distribution and accumulation of contaminants. In this context, the following research priorities are suggested for future international research on biovector mediated pollutant transport research:

- Combined modelling and empirical studies for estimation of regional/local biovector mediated pollutant transport
- Research studies related to biovector-mediated pollutant transport and transfer across ecosystems
- Expansion of current transport models including biovector transport processes
- Inclusion of behavioural, ecotoxicological and physiological biology into on-going environmental pollutant research, such as analytical chemistry, ecotoxicology and modelling (e.g. quantitative Structure Activity Relationship modelling = QSAR)) for elucidation of biovector mediated pollutant research
- Evaluation status on the linkage of climate change induced shifts in invasive behaviour and migration patterns of populations and pollutant distribution

Concluding Remarks

Although evidence for the importance of biovector-mediated transport of anthropogenic pollution is presented here, this research area is still only sparsely covered by published scientific studies and reports. This striking lack of scientific information may be partly compensated by evaluating scientific information provided by related research, as documented in the present review. However, in order to provide better scientific evidence for the role and significance of biovector-mediated pollutant transport and distribution, comprehensive, coordinated international research efforts must be conducted on issues associated with this neglected research area. Funding agencies, monitoring programs and national as well as international regulators are therefore encouraged to put this important research topic on their professional agenda with high priority.

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Using Natural Archives to Track Sources and Long-Term Trends of Pollution: Some Final Thoughts and Suggestions for Future Directions

Jules M. Blais, Michael R. Rosen and John P. Smol

Abstract Newly produced, as well as some so-called legacy contaminants, continue to be released into the environment at an accelerated rate. Given the general lack of integrated, direct monitoring programs, the use of natural archival records of contaminants will almost certainly continue to increase. We conclude this volume with a short chapter highlighting some of our final thoughts, with a focus on a call to action to develop and apply methodologies to assess the fidelity of the archival record.

Keywords Contaminants · Natural archives · Reliability · Reproducibility · Future directions

The natural archives examined in this book (e.g. cores from sediment, ice, and peat, archives in sclerontological, and museum specimens) contain a wealth of information on the composition and timing of pollutant trajectories that reach all corners of the globe. As seen throughout this book, this archival information can be used to set baseline or reference conditions, track sources of contaminants, assess long-range transport potential, and determine the magnitude of human impacts on the natural environment. The knowledge gained from these archives can help locally with management decisions for cleanup of specific habitats and ecosystems, and

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can help regionally and globally to assess atmospheric pollutants and their impacts on sensitive ecosystems.

Researchers can be justifiably proud of the considerable progress that has been made in the use of natural archives in tracking contaminant transport. As described in various chapters of this book, the sheer volume and types of contaminants that are being released into the environment can be staggering. However, the environmental issues and uncertainties resulting from this pollution are confounded by a variety of factors, not least of which is the simple fact that comprehensive monitoring programs rarely exist to track these problems, and if contaminant research is undertaken, it is almost always after-the-fact (i.e. after a problem has been identified). Never before have the paleoenvironmental techniques described in this book been more important. Natural archives provide the framework to put current environmental issues into a scientifically realistic spatial and temporal context, and allow researchers to reconstruct important and hitherto missing data. There is much to be proud of when one reviews the recent history of paleoenvironmental research as it relates to contaminants.

Nonetheless, many challenges remain. Essential to the advancement of this research is an appreciation of the external and internal processes that may alter the archival record, leading to differences between the historical sequence of events and the preserved archive itself. This challenge is not peculiar to contaminant research, but is true for all paleoenvironmental methodologies. The influences of hydrology, molecular diffusion and physical mixing were expanded in this book, and must be considered when conducting paleoenvironmental studies. Despite the potential for alterations in archival profiles, this book reviewed the many examples where clear historical records were preserved in archives, but also cautioned where profiles and other records may be problematic.

This concluding chapter is intended to focus on future directions that could be used to further validate the preservation and interpretation of historical events in natural archives. Our examples are mainly taken from studies dealing with sedimentary sequences, but similar approaches can often be adapted to other natural archives.

Comparing Sedimentary Profiles Against Known Histories

One straight-forward way to test the fidelity of archival information is to find examples where sediment core profiles or other archives can be compared to a known history of contaminant emission. Numerous examples are available where the historical rise and fall of chemical release was compared against the archival record to show an excellent agreement between the known history and the archive. One of the most widely-used global contamination signatures is ^{137}Cs from atmospheric nuclear testing in the 1960s. Although not universally stable (Blais et al. 1995; Foster et al. 2006; Kalminder et al. 2012), the 1963 peak concentration is used as a marker bed in most lake sediment chronologies, and at sites near atmospheric testing ranges, such as in Lake Mead (Nevada, USA) individual bomb tests can be distinguished in some cores (Rosen and Van Metre 2010). The 1986 Chernobyl nuclear accident allowed a further marker bed at some sites in Europe and central Asia, although in places downward migration of cesium caused a smearing for the early 1960s peak (Foster et al. 2006). The known rise and peak concentrations and then discontinued use of lead in gasoline and the bans on many organochlorine compounds, including dichlorodiphenyltrichloroethane (DDT) and polychlorinated biphenyl (PCB), has been shown to corroborate with core chronologies in many coring sites (e.g. Blais et al. 1995; Van Metre et al. 1997; Van Metre and Mahler 2005; Thevenon et al. 2013 and those referenced in this volume), which provide numerous compelling examples from around the world. Future work determining the stability of new compounds and comparing the increased use and regional or global discontinued use (or banning) of emerging organic compounds including pharmaceuticals, metals, or possibly nanoparticles that are beginning to be used in products such as sunscreen, would further our knowledge of how these contaminants persist in the environment. Studies of compounds such as polybrominated diphenyl ethers (PDBEs) and widely used pesticides, fragrances, and fumigants, such as atrazine, Galaxolide (HHCB), and dibromochloropropane (DBCP), would contribute further to the use of natural archives in the understanding of global contaminant distribution and potential mobilization under different chemical conditions.

Resampling an Archive Over Time

Several studies have addressed the question of the stability of the chemical record by a comparison of natural archives collected over decades from the same location. An example was provided by Rydberg and Martinez-Cortizas (2014) who compiled seven annually laminated (varved) sediment cores from Lake Nylanssjön (Sweden) collected over a span of 25 years. Varved sediment cores were collected within a 50 x 50 m area in 1979, 1985, 1989, 1993, 1996, 2002, and 2004, and vertically sectioned into annual layers based on varve layering. This analysis showed that year-to-year variability was largely preserved for most elements, with important exceptions for carbon, nitrogen, and bromine, which tended to decrease in sediments during burial. This study provided compelling evidence that several elements were reasonably preserved in sediment horizons over this 25 year period, though microbial respiration was responsible for mineralizing significant quantities of carbon and nitrogen from surface sediments prior to burial. This methodology was used by paleolimnologists from the University of Umeå for a wide variety of paleo-indicators (e.g. Gälamn et al. 2008, 2009; Rydberg et al. 2008).

A similar analysis was performed at Clay Lake (Ontario, Canada) for mercury in sediment cores resulting from 8 years of mercury discharge to the lake from a chlor-alkali plant (Lockhart et al. 2000). Cores were taken from approximately the same location in 1971, 1978, and 1995, and radiometrically dated to determine chronologies of deposition over time. Chemical analysis revealed that the mercury pulse from the chlor-alkali plant was gradually buried in sediment, with the peak mercury concentration remaining relatively constant over this 24 year period, suggesting that post-depositional modification was negligible.

Another reason to resample lakes is to determine if local bans on chemical use are effective. Mahler and Van Metre (2014) resampled Lady Bird Lake in Austin (Texas, USA) in 2012 and 2014, after coal-tar sealants (a source of polycyclic aromatic hydrocarbons (PAHs) used to protect and enhance the appearance of asphalt pavement) were banned in the city of Austin in 2006. They found that PAH concentrations decreased by an average of 58 % following the ban, indicating that coal-tar sealants were the major source of PAHs to this lake and that the ban was effective in reducing PAH input to the watershed.

Further re-sampling of archives is needed to ensure the stability of other commonly studied compounds, in particular studies involving emerging organic compounds that may be poorly bound to organic matter and sediment under anaerobic conditions.

Comparing Archives Against Modelled Deposition Histories

Contaminant histories are usually compared to known events such as nuclear bomb testing or a specific industrial development. However, modeling the expected content of an individual contaminant or group of contaminants is rarely done because of the uncertainties of emission data within a catchment or lack of data on hydrologic inputs to a lake (Rosen, this volume). There have been some studies that have modeled depositional rates in reservoirs (Price et al. 2000) and simple lake systems (Van Metre and Fuller 2009).

As a first step, Price et al. (2000) used a data-based mechanistic (DBM) modelling methodology to study reservoir sedimentation. They developed a lumped-parameter, discrete-time model that directly related daily rainfall to suspended sediment load (SSL) at the reservoir outflow from 2 years of measured data. This was coupled with a component that related the SSL of inflow to the SSL of the outflow. Modeled sediment profiles and measurements from sediment cores showed general agreement that reflected the importance of low reoccurrence, high magnitude events. This type of model could be developed to incorporate contaminant inputs; however, daily data on contaminant inputs are extremely rare.

Modeling atmospheric contaminant contributions to lake sediments has been done extensively for mercury and these techniques have been summarized by Biester et al. (2007). These models suggested that lake cores are better archives of mercury deposition than peat cores, which undergo diagenetic smearing of mercury deposition in the top 10 cm of the peat before burial. Van Metre and Fuller (2009) used a dual core approach to model mercury input to a western United States lake and found that fallout estimates are generally consistent with fallout reported from an ice core from nearby Upper Fremont Glacier (Schuster et al. 2002). Although the model works well for lakes with simple basins, the model may not work for lakes with complex geometries and multiple sediment inputs. However, for lakes with simple basins, this model can provide a quantitative approach for evaluating sediment focusing and estimating fallout from any contaminant that has a known deposition rate. Modeling of atmospheric black carbon also has been done in Europe and this regional model agrees reasonably well with black carbon emission inventories (Ruppel et al. 2013). The model does show that there is a need for closely-spaced spatially distributed data to improve the response of the models to local emissions (Ruppel et al. 2013).

While modeling of some contaminants with known fallout rates has been done, many other contaminants have not been modeled. In addition, most modeling has been done for atmospherically-derived contaminants. Modeling of watershed inputs requires monitoring data within a watershed over relatively long periods of time. These types of data are rarely available, and so the number of lakes where this type of modeling can be done is limited. Modeling rates of watershed inputs are important for making informed management decisions for lakes subjected to contaminant input, therefore, additional contaminant data are needed for these detailed models to proceed.

Porewater Analysis

Sediment porewater analysis is frequently used to determine the potential for redistribution of metals in a sediment column (cf. Outridge and Wang, this volume), and may be used to show the fidelity of the sediment record for some metals (e.g. mercury, Feyte et al. 2012) and the potential for remobilization of others (e.g. arsenic, Andrade et al. 2010). In addition to the wealth of information provided from porewater analysis of metals in sediments, methodologies for porewater analysis are being used increasingly for organic pollutants to test their potential for remobilization in the sediment record. For example, Zastepa (2013) recently showed that porewaters may be analyzed for microcystins and other algal toxins, providing new insights into the post-depositional solubilisation of these substances. Alvarez et al. (2012) measured organic contaminant concentrations in the upper 30 cm of lake sediment porewaters at 10-cm intervals using *in situ* passive samplers and found that concentrations in the upper 10 cm were much higher than at lower depths. This finding indicated that these contaminants may be mobile and exchange with the overlying lake water may occur, possibly causing harm to benthic invertebrates. Further improvements in the application of sediment profiles for use as natural archives will continue to benefit from porewater analysis to compliment solid phase extraction and analysis.

Regional Archives of Contamination

Whether from sediment archives, museum specimens, ice cores, schlerochronologic studies, or other archives, regional or global depositional patterns can be determined for those contaminants that are atmospherically distributed (e.g. mercury or black carbon). Other contaminants, such as DDT, PAHs, or PCBs, which have had substantial regional impacts, can be studied in a systematic national context in some places (e.g. Van metre and Mahler 2005, 2010), but this systematic approach is rare in a global context. Further work is needed on emerging contaminants and in less well-studied areas of the world in order to bring contaminant depositional rates into a more consistent approach. In addition, by having a regional or national coverage of contaminant inputs, assessment of ecosystem responses or impairment can be compared. Although considerable progress has been made over the last decade or so to increase the spatial coverage of natural archival records, most studies are from Europe and North America. A continued effort to increase the geographic coverage of archival records will be critical for effective global assessments and comparisons.

Long-Term Sediment Stability Experiments

One important research direction that we have not yet encountered is the analysis of lake sediment in a controlled laboratory environment under low temperature and low light to determine long-term stability of the chemical constituents in sediment. Much of the work on assessing the fidelity of natural archival records has used indirect measurements, such as most of those listed above, but direct observational studies of chemical records over long (multi-annual, multi-decadal) periods have not been attempted to our knowledge. This endeavor would resolve many of the questions raised about archival fidelity in this book, but would require a commitment of years—decades to resolve. This is an excellent research opportunity for paleolimnologists at the start of their careers!

Concluding Thoughts

As with most syntheses, this volume raises more questions than it answers. Using paleoenvironmental archives is not without its problems, and clearly we believe in addressing these challenges directly. Nor should some of the assumptions that we are forced to make be minimized or ignored. Indeed, they should be identified and addressed using the most up-to-date approaches in an attempt to mitigate shortcomings, or at least to better understand them. Nonetheless, we are buoyed by the remarkable progress which has been made, especially over the last decade, in the use of natural archives to study the fate, transport, and ecological effects of contaminants over long time scales. The development of new approaches and methodologies, some of which were discussed in this book, will surely provide the foundation for continued advancements in this field. One thing certain is that there will be no shortage of new problems that will need to be addressed.

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Erratum to: The Stability of Metal Profiles in Freshwater and Marine Sediments

Peter M. Outridge and Feiyue Wang

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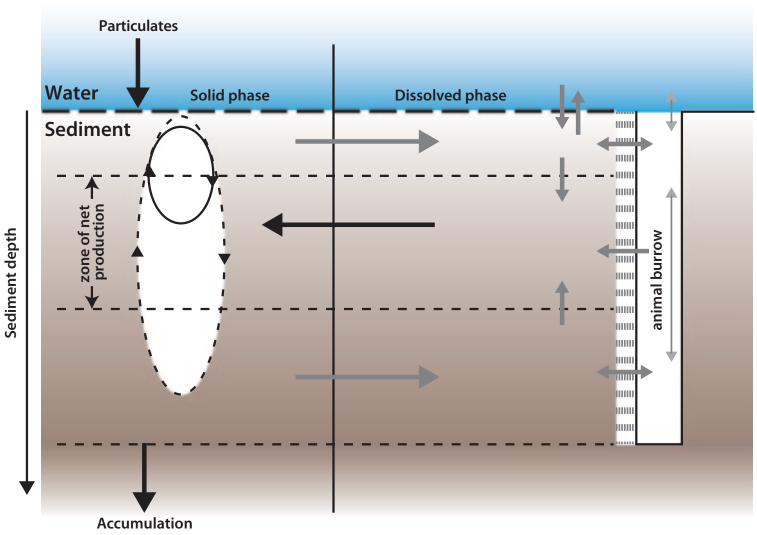
The authors of this chapter would like to apologize for placing the incorrect version of figure 2. The correct version of the figure can be found below:



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