Using Natural Archives to Track Sources and Long-Term Trends of Pollution: Some Final Thoughts and Suggestions for Future Directions

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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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