Volume 239

Pim de Voogt *Editor*

# Reviews of Environmental Contamination and Toxicology

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# Reviews of Environmental Contamination and Toxicology

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# Reviews of Environmental Contamination and Toxicology

Editor
Pim de Voogt



Volume 239

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*Reviews of Environmental Contamination and Toxicology*

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Vancouver Aquarium Marine Science Center
Vancouver, BC, Canada
E-mail: peter.ross@vanaqua.org

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*In Memoriam: Dr. David Martin Whitacre 1943–2015*

*David Whitacre leaves a continuing legacy of promoting science in agriculture to help increase farm production safely while maintaining stewardship of the land itself.*

*David was a native of Lebanon Ohio, born in 1943. He grew up on a farm where he developed a love of restoring old John Deere tractors, with a last count of 24, scattered over Illinois, Ohio, and North Carolina.*

*I first met David and his new wife, Trudy, at Wilmington College, Ohio, while seeking graduate entomology candidates for transfer to The Ohio State University. He completed his M.S. with me just before my move to the University of Arizona in Tucson in 1966. He was offered an assistantship in the Department of Entomology where I had just transferred as department head. He completed his requirements for the Ph.D. in record time. Then interested in pesticide toxicology, he rapidly moved into the industry circuit. He was board certified in General Toxicology in 1982, and he occupied various*

*industry positions including Sr. Vice President of Science for Novartis North America and Vice President of R&D for Sandoz in the United States. He also managed Research for Sandoz Crop Protection in Basle, Switzerland, for 2 years. He retired from Syngenta as VP of Development in 2001.*

*Wanting to split his time between restoring antique John Deere tractors and doing something intellectual, I persuaded him to coauthor* The Pesticide Book *which went thru three more editions. Still enjoying keeping his mind in his profession and being perfectly trained for the job, he became editor of* Reviews *and carried it thru 20 volumes including Volume 210.*

*While being prepared for open-heart surgery, David's heart stopped and couldn't be revived. He died on August 28, 2015, in Greensboro, NC, at the age of 71. He is survived by his wife Trudy of Summerfield, NC; son David Whitacre, research scientist with a PhD in molecular and cellular biology, San Diego, CA; daughter Dr. Elizabeth Whitacre, Emergency Medicine, Albuquerque, NM, and five grandchildren.*

*David was absolutely the best graduate student I ever guided and the most intelligent and fair-minded person I've had the pleasure of knowing.*

George Ware
Professor Emeritus
University of Arizona

# Foreword

International concern in scientific, industrial, and governmental communities over traces of xenobiotics in foods and in both abiotic and biotic environments has justified the present triumvirate of specialized publications in this field: comprehensive reviews, rapidly published research papers and progress reports, and archival documentations These three international publications are integrated and scheduled to provide the coherency essential for nonduplicative and current progress in a field as dynamic and complex as environmental contamination and toxicology. This series is reserved exclusively for the diversified literature on "toxic" chemicals in our food, our feeds, our homes, recreational and working surroundings, our domestic animals, our wildlife, and ourselves. Tremendous efforts worldwide have been mobilized to evaluate the nature, presence, magnitude, fate, and toxicology of the chemicals loosed upon the Earth. Among the sequelae of this broad new emphasis is an undeniable need for an articulated set of authoritative publications, where one can find the latest important world literature produced by these emerging areas of science together with documentation of pertinent ancillary legislation.

Research directors and legislative or administrative advisers do not have the time to scan the escalating number of technical publications that may contain articles important to current responsibility. Rather, these individuals need the background provided by detailed reviews and the assurance that the latest information is made available to them, all with minimal literature searching. Similarly, the scientist assigned or attracted to a new problem is required to glean all literature pertinent to the task, to publish new developments or important new experimental details quickly, to inform others of findings that might alter their own efforts, and eventually to publish all his/her supporting data and conclusions for archival purposes.

In the fields of environmental contamination and toxicology, the sum of these concerns and responsibilities is decisively addressed by the uniform, encompassing, and timely publication format of the Springer triumvirate:

*Reviews of Environmental Contamination and Toxicology* [Vol. 1 through 97 (1962–1986) as Residue Reviews] for detailed review articles concerned with any aspects of chemical contaminants, including pesticides, in the total environment with toxicological considerations and consequences.

*Bulletin of Environmental Contamination and Toxicology* (Vol. 1 in 1966) for rapid publication of short reports of significant advances and discoveries in the fields of air, soil, water, and food contamination and pollution as well as methodology and other disciplines concerned with the introduction, presence, and effects of toxicants in the total environment.

*Archives of Environmental Contamination and Toxicology* (Vol. 1 in 1973) for important complete articles emphasizing and describing original experimental or theoretical research work pertaining to the scientific aspects of chemical contaminants in the environment.

The individual editors of these three publications comprise the joint Coordinating Board of Editors with referral within the board of manuscripts submitted to one publication but deemed by major emphasis or length more suitable for one of the others.

Coordinating Board of Editors

# Preface

The role of *Reviews* is to publish detailed scientific review articles on all aspects of environmental contamination and associated (eco)toxicological consequences. Such articles facilitate the often complex task of accessing and interpreting cogent scientific data within the confines of one or more closely related research fields.

In the 50+ years since *Reviews of Environmental Contamination and Toxicology* (formerly *Residue Reviews)* was first published, the number, scope, and complexity of environmental pollution incidents have grown unabated. During this entire period, the emphasis has been on publishing articles that address the presence and toxicity of environmental contaminants. New research is published each year on a myriad of environmental pollution issues facing people worldwide. This fact, and the routine discovery and reporting of emerging contaminants and new environmental contamination cases, creates an increasingly important function for *Reviews.* The staggering volume of scientific literature demands remedy by which data can be synthesized and made available to readers in an abridged form. *Reviews* addresses this need and provides detailed reviews worldwide to key scientists and science or policy administrators, whether employed by government, universities, nongovernmental organizations, or the private sector.

There is a panoply of environmental issues and concerns on which many scientists have focused their research in past years. The scope of this list is quite broad, encompassing environmental events globally that affect marine and terrestrial ecosystems; biotic and abiotic environments; impacts on plants, humans, and wildlife; and pollutants, both chemical and radioactive; as well as the ravages of environmental disease in virtually all environmental media (soil, water, air). New or enhanced safety and environmental concerns have emerged in the last decade to be added to incidents covered by the media, studied by scientists, and addressed by governmental and private institutions. Among these are events so striking that they are creating a paradigm shift. Two in particular are at the center of ever increasing media as well as scientific attention: bioterrorism and global warming. Unfortunately, these very worrisome issues are now superimposed on the already extensive list of ongoing environmental challenges.

The ultimate role of publishing scientific environmental research is to enhance understanding of the environment in ways that allow the public to be better informed or, in other words, to enable the public to have access to sufficient information. Because the public gets most of its information on science and technology from internet, TV news, and reports, the role for scientists as interpreters and brokers of scientific information to the public will grow rather than diminish. Environmentalism is an important global political force, resulting in the emergence of multinational consortia to control pollution and the evolution of the environmental ethic. Will the new politics of the twenty-first century involve a consortium of technologists and environmentalists, or a progressive confrontation? These matters are of genuine concern to governmental agencies and legislative bodies around the world.

For those who make the decisions about how our planet is managed, there is an ongoing need for continual surveillance and intelligent controls to avoid endangering the environment, public health, and wildlife. Ensuring safety-in-use of the many chemicals involved in our highly industrialized culture is a dynamic challenge, because the old, established materials are continually being displaced by newly developed molecules more acceptable to federal and state regulatory agencies, public health officials, and environmentalists. New legislation that will deal in an appropriate manner with this challenge is currently in the making or has been implemented recently, such as the REACH legislation in Europe. These regulations demand scientifically sound and documented dossiers on new chemicals.

*Reviews* publishes synoptic articles designed to treat the presence, fate, and, if possible, the safety of xenobiotics in any segment of the environment. These reviews can be either general or specific, but properly lie in the domains of analytical chemistry and its methodology, biochemistry, human and animal medicine, legislation, pharmacology, physiology, (eco)toxicology, and regulation. Certain affairs in food technology concerned specifically with pesticide and other food-additive problems may also be appropriate.

Because manuscripts are published in the order in which they are received in final form, it may seem that some important aspects have been neglected at times. However, these apparent omissions are recognized, and pertinent manuscripts are likely in preparation or planned. The field is so very large and the interests in it are so varied that the editor and the editorial board earnestly solicit authors and suggestions of underrepresented topics to make this international book series yet more useful and worthwhile.

Justification for the preparation of any review for this book series is that it deals with some aspect of the many real problems arising from the presence of anthropogenic chemicals in our surroundings. Thus, manuscripts may encompass case studies from any country. Additionally, chemical contamination in any manner of air, water, soil, or plant or animal life is within these objectives and their scope.

Manuscripts are often contributed by invitation. However, nominations for new topics or topics in areas that are rapidly advancing are welcome. Preliminary communication with the Editor-in-Chief is recommended before volunteered review manuscripts are submitted. *Reviews* is registered in WebofScience™.

Inclusion in the Science Citation Index serves to encourage scientists in academia to contribute to the series. The impact factor in recent years has increased from 2.5 in 2009 to almost 4 in 2013. The Editor-in-Chief and the Editorial Board strive for a further increase of the journal impact factor by actively inviting authors to submit manuscripts.

Amsterdam, The Netherlands Pim de Voogt
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# Contents

# Contributors

**Hans Baveco** Environmental Risk Assessment Team, Alterra, Wageningen, The Netherlands

**Paul J. van den Brink** Aquatic Ecology and Water Quality Management Group, Department of Environmental Sciences, Wageningen University, Wageningen, The Netherlands

Environmental Risk Assessment Team, Alterra, Wageningen, The Netherlands

**Theo C. M. Brock** Environmental Risk Assessment Team, Alterra, Wageningen, The Netherlands

**Noël J. Diepens** Aquatic Ecology and Water Quality Management Group, Department of Environmental Sciences, Wageningen University, Wageningen, The Netherlands

**Sandra Ečimovic** Department of Biology, Josip Juraj Strossmayer University of Osijek, Osijek, Croatia

**Martine J. van den Heuvel-Greve** IMARES, Institute for Marine Resources and Ecosystem Studies, Wageningen UR, IJmuiden, The Netherlands

**Albert A. Koelmans** Aquatic Ecology and Water Quality Management Group, Department of Environmental Sciences, Wageningen University, Wageningen, The Netherlands

IMARES, Institute for Marine Resources and Ecosystem Studies, Wageningen UR, IJmuiden, The Netherlands

**Jacek Namieśnik** Department of Analytical Chemistry, Faculty of Chemistry, Gdansk University of Technology, Gdansk, Poland

**Źaneta Polkowska** Department of Analytical Chemistry, Faculty of Chemistry, Gdansk University of Technology, Gdansk, Poland

**Małgorzata Szopińska** Department of Analytical Chemistry, Faculty of Chemistry, Gdansk University of Technology, Gdansk, Poland

**Mirna Velki** Department of Biology, Josip Juraj Strossmayer University of Osijek, Osijek, Croatia

# Prospective Environmental Risk Assessment for Sediment-Bound Organic Chemicals: A Proposal for Tiered Effect Assessment

**Noël J. Diepens, Albert A. Koelmans, Hans Baveco, Paul J. van den Brink, Martine J. van den Heuvel-Greve, and Theo C.M. Brock**

## Contents



N.J. Diepens (✉)
Aquatic Ecology and Water Quality Management Group, Department of Environmental Sciences, Wageningen University, P.O. Box 47, 6700 AA Wageningen, The Netherlands
e-mail: noel.diepens@wur.nl

A.A. Koelmans
Aquatic Ecology and Water Quality Management Group, Department of Environmental Sciences, Wageningen University, P.O. Box 47, 6700 AA Wageningen, The Netherlands

IMARES, Institute for Marine Resources & Ecosystem Studies, Wageningen UR, P.O. Box 68, 1970 AB IJmuiden, The Netherlands

H. Baveco • T.C.M. Brock
Environmental Risk Assessment Team, Alterra, P.O. Box 47, 6700 AA Wageningen, The Netherlands

P.J. van den Brink
Aquatic Ecology and Water Quality Management Group, Department of Environmental Sciences, Wageningen University, P.O. Box 47, 6700 AA Wageningen, The Netherlands

Environmental Risk Assessment Team, Alterra, P.O. Box 47, 6700 AA Wageningen, The Netherlands

M.J. van den Heuvel-Greve
IMARES, Institute for Marine Resources & Ecosystem Studies, Wageningen UR, P.O. Box 68, 1970 AB IJmuiden, The Netherlands



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# 1 Introduction

Aquatic sediments are an important part of the aquatic ecosystem, providing critical ecosystem services and functions (Wall 2004). The sediment compartment acts as a sink for hydrophobic organic chemicals, which can affect the services and functions provided. Therefore, sediment should be considered in prospective environmental risk assessment (ERA) whereas it is currently underrepresented.

Prospective ERA evaluates the future risks of a chemical stressor not yet released into the environment, by comparing outcomes of the exposure and effect assessment. The exposure assessment predicts exposure patterns and concentrations in environmental media such as sediment. The effect assessment describes the relationship between exposure concentration and effects for the assessed endpoints. The effect assessment is often performed in a tiered way, starting with a simple conservative assessment, and includes additional and more complex work only if necessary (Solomon et al. 2008).

Currently, in Europe, a conceptual prospective sediment ERA framework for hydrophobic organic chemicals is under development (ECHA 2014c; EFSA 2015). Such a framework requires clear protection goals, evidence-based concepts for linking exposure and effects, and a transparent tiered-effect assessment procedure for sediment organisms and processes. Furthermore, harmonization of data requirements, test protocols and sediment ERA frameworks between existing regulations/directives would be beneficial (Beketov et al. 2012; Diepens et al. 2014b; ECHA 2014c; EFSA 2015).

The aim of this paper is (1) to present an overview of current approaches for sediment ERA underlying European regulatory frameworks and (2) to provide guidance to establish a harmonised, prospective ERA framework for organic chemicals in sediments of freshwater, estuarine and marine ecosystems. In this paper we focus on prospective sediment ERA approaches in Europe, but we also address useful concepts developed in North America. Furthermore, we focus on the soft bottom sediment benthic community and briefly discuss the use of both artificial and field-collected sediments in conducting sediment toxicity tests for prospective ERA. This issue has been discussed before in Diepens et al. (2014b).

A synthesis of existing approaches and new scientific insights and data is provided, showing how a rational prospective assessment can be performed cost-effectively. After a short introduction in benthic ecology, our analysis starts by defining specific protection goals based on the ecosystem services concept, which in turn is based on the ecological role and functions provided by benthic organisms. We then present and discuss trigger values for sediment testing and data requirements within current European ERA frameworks. Current procedures for exposure and effect assessment, including the use of models, are presented and recommendations are given. Finally, several case studies are provided as ‘proof of concept’ and to illustrate the general features of the framework. The concepts underlying this paper were discussed with representatives of government, industry and academia during a workshop in Wageningen, the Netherlands, in February 2014 (for list of participants see Appendix 1). Discussions, remarks and recommendations from the workshop were used to improve this paper.

## 2 Benthic Ecology

Aquatic sediment is a complex heterogeneous matrix that covers a large part of earth’s surface (freshwater 0.5 %, marine 74 %) (Wall et al. 1997). In this paper, sediment is defined as all unconsolidated material of fine, medium and coarse grain

minerals and organic particles that make up the bottom of aquatic ecosystems (Adams et al. 1992; Palmer et al. 2000). The numerous benthic organisms that inhabit the sediment compartment fulfil a wide variety of crucial ecosystem functions. The benthic food chain and processes in the sediment compartment are not only connected with pelagic organisms and processes, but also with terrestrial soils. Soils, freshwater and marine sediments are closely interlinked as well, e.g. via groundwater systems, and have many functions in common (Wall 2004). Contamination and other anthropogenic pressures can negatively influence critical functions provided by benthic organisms. Protection of benthic organisms is essential for ecosystem functioning and the sustainable use of services provided by nature.

Landscape and local factors such as geology, hydrology, and water chemistry influence the sediment habitat and therewith the diversity and structure of benthic communities (Covich et al. 2004; Wall 2004). In general, sediment can be divided into two types: soft bottom sediments and hard substrates, each containing different benthic organism groups (Gérino et al. 2003). Low flow velocities and fine sediment particles characterize soft bottom sediments. Hard substrates are often found in high-energy areas, such as areas with high flow velocity and wave impact. In this paper we define benthic organisms as follows: organisms that spend their full life cycle, or an important part thereof, living on sediment (epibenthos) or in sediment (endobenthos). For these species, exposure via the sediment compartment may contribute to contaminant-mediated effects. This is not adequately covered by ERA's that are based on exposure in other environmental compartments.

Ecosystem processes performed by benthic organisms cover a wide range of temporal and spatial scales. On the micro scale, populations of microbenthos, which usually have a life cycle of hours to days (including bacteria, fungi, ciliate protozoans, flagellates, and diatoms), perform processes such as nitrogen and phosphate transformation, carbon mineralization and photosynthesis. Meiobenthos populations, which may have a life cycle of days to weeks (including nematodes, harpacticoid copepods, turbellarians, and Gastrotricha), regulate microbenthos populations and are characterized by a variety of feeding strategies (Gray 1981; Wall 2004). Macrobenthos populations, which have a life cycle of months to years (including rooted macrophytes and larger invertebrates such as crustaceans, larvae of dipterans, bivalves, and annelid worms), may act as ecosystem engineers by either mixing or stabilizing sediments. In addition, they produce organic matter (macrophytes in particular) and consume dead organic matter and associated microbenthos (detritivores) or serve as food for other benthic organisms (carnivores). For vertebrates such as fish, amphibians, birds and mammals, macrobenthos may be an important food source and consequently may be subject to exposure via food web transfer. Vertebrates may have a relatively large habitat range, and their life span may cover several years. Classification of benthic organisms based on size is not strictly coupled to taxonomic groups. This is because different species within a taxonomic group, and even different life stages of the same species, may belong to different size classes. For example, Gérino et al. (2003) classified macroinvertebrates in functional groups based on mechanical activities they perform, e.g. bioturbation or feeding strategies. More detailed information on the ecology

of benthic organisms is provided in review papers dealing with benthic bacteria (Nealson 1997), marine fungi (Hyde et al. 1998), marine meiobenthos (McIntyre 1969), micro- and meiobenthos (Fenchel 1978), and freshwater benthic invertebrate species (Covich et al. 1999).

## 3 Ecosystem Functions and Services Provided by Benthic Organisms

An overview of protection goals in EU directives is given by Hommen et al. (2010). Until now, in most documents underlying European regulations and directives, protection goals for benthic organisms have only been defined in general terms, except for pesticides (EFSA 2015). Defining specific protection goals is a crucial starting point in ERA. To operationalize the general protection goals mentioned in legislation, the ecosystem service concept has been proposed (Forbes and Calow 2013; Nienstedt et al. 2012). Ecosystem services are the stocks of natural capital from which humans benefit (Maltby 2013). The concept has been developed primarily as a communication tool to explain societal dependence on nature and as a framework to help decision makers implement policies and measures that support human wellbeing, including sustainable management of the environment. Specific protection goals for water organisms in edge-of-field surface waters subject to pesticide exposure were derived with this method by the European Food Safety Authority (EFSA) (2010b, 2013). In a recent European Chemicals Agency (ECHA) workshop (Helsinki, 2013), it was recognized that this concept could also be applied to derive specific protection goals for benthic ecosystems (ECHA 2014c). Wall (2004) provided an extensive overview of ecosystem functions and services in soils and sediments, whereas Levin et al. (2001) reviewed ecosystem functions provided by benthic communities in estuaries and coastal wetlands. Covich et al. (2004) reviewed the role of biodiversity in the functioning of freshwater and marine benthic ecosystems.

Based on these reviews, and following the approach originally developed by EFSA (2010b), we classified the ecosystem services provided by benthic organisms and ecosystems in freshwater and marine sediment into four groups according to the Millennium Ecosystem Assessment (MEA 2005) (Table 1):

(1) provisioning ecosystem services i.e. products obtained by humans,
(2) regulating ecosystem services i.e. regulating processes beneficial for humans,
(3) cultural ecosystem services, i.e. important conditions for humans related to aesthetic, spiritual, educational and recreational values and benefits, and
(4) supporting ecosystem functions, i.e. ecosystem functions that support ecosystem sustainability and therewith underlie the provisioning, regulating and cultural services.

**Table 1** Estimated importance of ecosystem services provided by freshwater and marine benthic organisms based on a subjective scale from low (1) to high (3), potentially influenced by organic contaminants

| Millennium ecosystem category | Ecosystem services | Freshwater benthic ecosystems | Marine benthic ecosystems | Related soft bottom benthic organisms |
|---|---|---|---|---|
| Provisioning services (Products obtained by humans) | Food | 2 | 3 | Consumable benthic fish, shellfish, and macrophytes |
| | Fibre, construction materials | 2 | 1 | Emergent macrophytes (e.g. thatched roofs) |
| | Genetic resources | 3 | 3 | All species harvested by man |
| | Natural medicines and biochemical substances | 1 | 2 | Potentially all species |
| | Ornamental resources | 2 | 2 | Aquaria and garden pond macrophytes, invertebrates and vertebrates |
| | Fuels and energy | 3 | 2 | Peat, mangrove wood |
| | Biological products | 2 | 2 | Invertebrates for fish bait (e.g. *Nereis* sp., *Arenicola marina*, *Lumbriculus variegatus*) |
| Regulating processes beneficial for humans | Pest and disease regulation | 1 | 1 | Benthic fish and invertebrates (e.g. that control aquatic species that act as host for parasites and diseases) |
| | Sediment bioremediation | 3 | 3 | Bacteria, fungi, microfauna, macrophytes, bioturbating invertebrates and vertebrates |
| | Water purification | 3 | 3 | Bacteria, fungi, microfauna, macrophytes, bioturbating invertebrates and vertebrates |
| | Climate regulation | 2 | 2 | Bacteria (e.g. methane production) |
| | Shore, bank, and sediment stabilization | 3 | 3 | Macrophytes, biofilms (microbes and algae), sediment-stabilizing invertebrates |
| | Hydrological regulation | 2 | 2 | Macrophytes |
| | Pollination | 2 | 1 | Aquatic and semi-aquatic insects that pollinate vascular plants and that have benthic larval stages (e.g. Ephydridae) |
| | Air quality regulation | 2 | 2 | Rooted macrophytes and benthic algae |
| | Invasion resistance | 2 | 2 | All native benthic organisms having similar niche as invasive species |

(continued)

**Table 1** (continued)

| Millennium ecosystem category | Ecosystem services | Freshwater benthic ecosystems | Marine benthic ecosystems | Related soft bottom benthic organisms |
|---|---|---|---|---|
| Cultural services | Education and inspiration | 3 | 3 | All benthic organisms |
| | Aesthetic values | 2 | 2 | Benthic red list species |
| | Recreation and ecotourism | 3 | 3 | Rooted macrophytes, benthic fish, |
| | Spiritual and religious value | 2 | 2 | Potentially all species (including benthos) |
| | Cultural heritage | 2 | 1 | All characteristic benthic organisms of man-made aquatic ecosystems (e.g. channels, ditches, peat excavations) |
| Supporting functions (to facilitate other ES) | Sediment formation and structuring | 3 | 3 | Macrophytes, bioturbating invertebrates and vertebrates, bacteria and fungi |
| | Photosynthesis | 3 | 3 | Rooted macrophytes, benthic algae, photosynthesising bacteria in biofilms |
| | Primary and secondary food production | 3 | 3 | Benthic organisms |
| | Nutrient cycling | 3 | 3 | Benthic organisms |
| | Decomposition and mineralization | 3 | 3 | Benthic detritiores and microbes |
| | Food web control mechanisms | 3 | 3 | Benthic vertebrates, invertebrates and microbes (including pathogens) |
| | Provision of habitat and shelter | 3 | 3 | Rooted macrophytes, biofilms |

For each service, the most important benthic organism groups are identified

For each service provided by benthic organisms, we assessed the relative importance on this service on a subjective scale from low (1) to high (3). Moreover, we identified the ecosystem service providing units (SPUs), also referred to as key drivers by EFSA (2010b) and Nienstedt et al. (2012). SPUs are the main taxonomic groups of organisms providing each service (Table 1).

Freshwater and marine benthic ecosystems may provide similar ecosystem services (Table 1) and overall, similar taxonomic and/or functional groups of

benthic organisms provide these services. However, certain taxonomic groups are largely restricted to either freshwater sediments (e.g. insects) or marine sediments (e.g. Echinodermata). Important SPUs include microorganisms, benthic algae, benthic invertebrates, sediment rooted macrophytes, and benthic vertebrates.

## *3.1 Dealing with Vulnerable Key Species*

Current approaches in prospective risk assessment aim to provide sufficient protection to a wide array of aquatic and benthic non-target species (see e.g. EFSA 2013, 2015). Vulnerable key species are of particular importance. When selecting indicator species for testing, it should be considered whether the lower-tier approaches (those based on standard test species and the application of an assessment factor) sufficiently protect these vulnerable benthic taxa. Vulnerable key species are species that fulfil a highly important role in the ecosystem, have a high risk of exposure (e.g. low avoidance potential), are very sensitive to chemical stress due to specific traits (e.g. poor detoxification mechanism, feeding habit, low elimination rate) and have a low recovery potential (e.g. low recolonisation potential, long generation times). These characteristics make it difficult to culture and test these species in the laboratory. Moreover, it is difficult to identify the most vulnerable key species of each SPU group and type of ecosystem, as many species have a high plasticity, fulfil a variety of functions and might change function depending on their life stage and/or type of ecosystem where they dwell. Furthermore, the vulnerability concept of benthic species and the impact of organic contaminants have not received much attention in the scientific literature. Two approaches to determine vulnerable key benthic species are possible. First, biological traits might be used to identify these species. A good example of such a trait-based approach to identify vulnerable aquatic invertebrates is provided by Rico and Van den Brink (2015). Trait-based approaches are less-well developed for microbes, but a noteworthy example may be nitrifying bacteria that oxidize nitrite to nitrate are slow growing specialists (Nealson 1997), which might therefore be good indicators of a vulnerable key group for benthic microbes. Second, the mode of action of the chemical might determine which main group of species is more sensitive. For instance, herbicides are designed to kill plants and would therefore be expected to mainly impact non-target benthic algae and macrophytes. However, even after identifying the most sensitive group to one herbicide, no single species is most sensitive to all herbicides (Giddings et al. 2013). An important research need is therefore to find a good method to identify vulnerable key benthic species.

**Table 2** Proposed protection goals for benthic organisms with their ecological entity and attribute based on the ecosystem services concept

| Organism group | Ecological entity | Attribute |
|---|---|---|
| Microorganisms | Functional group | Processes |
| Benthic algae | Population | Abundance, Biomass |
| Sediment rooted macrophytes | Population | Abundance, Biomass, Cover |
| Benthic invertebrates | Population | Abundance, Biomass |
| Benthic vertebrates | Individual to population | Survival, Growth, Abundance, Biomass |

## 4 Specific Protection Goals for Sediment Risk Assessment

Specific protection goals for SPUs are presented in Table 2. These goals are defined in terms of the ecological entities and attributes to be protected. Ecological entities concern the relevant level of biological organization to consider and attributes determine which endpoint to assess (Nienstedt et al. 2012). Each specific protection goal must be addressed by a different ERA scheme. This is particularly the case when addressing spatial differentiation in specific protection goals with various options, such as a threshold option (accepting negligible impacts on sensitive endpoints only) or a recovery option (accepting temporal impacts followed by a return to the base line).

Microorganisms are of major importance for many functions such as nutrient cycling, decomposition and water purification (Palmer et al. 2000). The functional redundancy and recovery potential of microorganisms is high (Van Beelen and Doelman 1997). We therefore followed the proposal of Nienstedt et al. (2012) to protect microorganisms on the level of functional group and focused on functional measurement endpoints in ERA. However, generating quantitative data on microbial diversity in polluted sediments is still important, since this type of information likely provides insight into causal relationships between microbial composition and shifts in processes mediated by microbes (Diepens et al. 2014b). For benthic algae, macrophytes and invertebrates, we propose the population as the ecological entity to be protected, since the functional redundancy concept is more difficult to apply to several provisioning and cultural ecosystem services provided by these organisms. In particular, rooted aquatic macrophytes and benthic invertebrates might include vulnerable key species that require protection at the population level to guarantee the protection of structural and functional biodiversity of benthic communities. Again following the line of reasoning of Nienstedt et al. (2012) for benthic vertebrates, we selected the individual-to-population level as an ecological entity to avoid mortality due to acute toxicity and prevent suffering of individual animals due to sediment exposure. The SPUs that we have proposed for benthic organisms, as well as their ecological entities and attributes to be considered in the ERA of organic contaminants in sediments (Tables 1 and 2), are similar to those identified by EFSA (2013) in their derivation of specific protection goals for water organisms

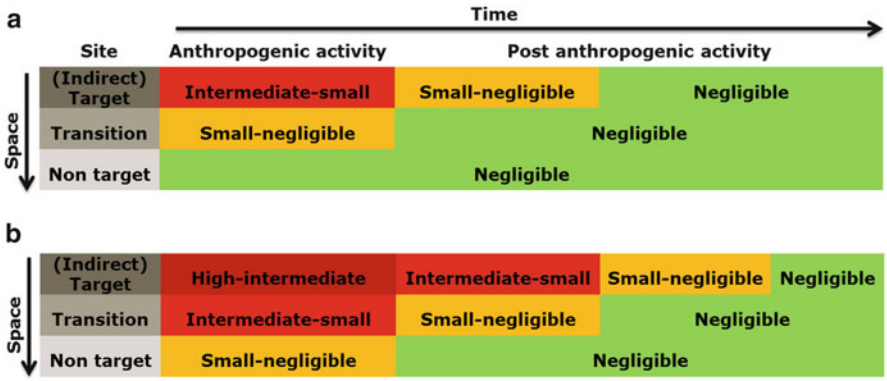


**Fig. 1** Example for a strict (**a**) and a less strict (**b**) option to define the magnitude of acceptable effects on a temporal and spatial scale. Note that sediments not often are target sites for application of regulated organic chemicals, but often hot spot sites of sediment exposure can be identified

for prospective ERA of pesticides. Furthermore, for benthic organisms and prospective ERA of pesticides, EFSA (2015) adopted specific protection goals that are very similar to our proposal. Although the specific protection goals derived for pelagic and benthic organisms are very similar this does not mean that the environmental risks of benthic organisms are covered by the ERA schemes developed for pelagic aquatic organisms. Note that, dependent on the chemicals and use pattern, the temporal profile of exposure may be very different between the water column and the sediment. For instance, hydrophobic chemicals like many insecticides more often are subject to shorter term pulse exposures in the water column, whereas sediment-bound chemicals are subject to much slower temporal dynamics.

The acceptability of an effect can be specified for each SPU by quantifying the acceptable magnitude of an effect and the associated temporal and spatial scale. Figure 1 shows possible options for a spatial-temporal differentiation of acceptable effects. Defining the spatial scale for an appropriate sediment ERA, particularly the spatial scale of possible acceptable effects, can be challenging. In most cases, sediments and sediment organisms are not the target of chemical applications, but sediments can act as a sink for chemicals from elsewhere. For example, with the exception of rice paddy fields, agrochemicals such as pesticides are not directly applied in aquatic ecosystems, but edge-of-field surface waters (e.g. ditches) might be considered a transition zone between agricultural fields (target site) and larger surface waters such as lakes and rivers (non-target site). Moreover, exposure might be very heterogeneous, both horizontally (sediment surface) and vertically (depth of the sediment profile). For example, antibiotics and biocides are used in aquaculture cages, and these chemicals eventually reach the sediment (Rico et al. 2014; Telfer et al. 2006). In this case, it would be useful to consider the situation in a 3D profile and define the area under and around the cages as an indirect target area. A more complicated example concerns antifouling paints on ships, as they travel large distances. Consequently, contamination from antifouling substances has been found worldwide in sediments (Konstantinou and Albanis 2004). Harbours often

are sedimentation areas for contaminated particles (Koelmans et al. 2010; van Noort and Koelmans 2012) and might therefore be considered as a main accumulation site—or 'hot spot'—for exposure to antifouling agents. Suspended solids also should be considered, which might carry contaminants away from the target or hot spot area. An important question is whether exposure via suspended solids should be addressed in aquatic or in sediment risk assessment schemes. A pragmatic approach could be to consider only settled particles in sediment ERA.

Thus, to sustain ecosystem structure and functioning, the effects of sediment-bound contaminants should be either preventable or reversible, even at target and/or hot spot sites. However, recovery of the selected attributes of the relevant ecological entities might be variable depending on the persistence of the chemical, its bioavailability and the ability of the affected benthic organisms to recover. Note that it is the responsibility of risk managers and policy makers to define the acceptable spatial and temporal effects.

## 5 Triggers for Prospective Sediment Risk Assessment in European Regulatory Frameworks

Ideally, triggers for conducting a sediment ERA should be based on the physico-chemical properties of the test compound that affect its adsorption and persistence in the sediment and on its toxicity potential for benthic organisms (Fig. 2). Maund et al. (1997) proposed the following triggers for sediment testing of pesticides: (1) an *adsorption trigger* consisting of an organic carbon-water partitioning coefficient ($K_{oc}$) greater than or equal to 1000 (or $\log K_{oc} > 3$), (2) a *persistence trigger* consisting of a laboratory aerobic soil half-life time greater than or equal to 30 days, and (3) a *toxicity trigger* consisting of a 48 h median effect concentration ($EC_{50}$) to *Daphnia* of less than 1 mg/L or a 21 days no observed effect concentration (NOEC) of less than 0.1 mg/L in water-only toxicity tests.

Criteria that are currently required to trigger sediment toxicity testing differ between existing European regulations and directives dealing with prospective ERAs (Table 3). The persistence trigger (more than 10 % of the applied radioactivity of the parent in sediment after day 14) is used for pesticides and medicinal products for humans, while the adsorption trigger ($\log K_{oc}$ or $\log K_{ow} > 3$) is used for chemicals under REACH, biocides and veterinary medicinal products.

In most regulatory documents, except those for pesticides, the toxicity trigger for sediment ERA is initially based on equilibrium partitioning (EP) and toxicity data for pelagic organisms (Table 3). EP theory states that partitioning of a chemical between two phases is governed by the chemical affinity of each phase. For a more detailed description of the EP approach in sediment ERA, see Sect. 9.2 below. In a decision scheme for conducting sediment-spiked toxicity tests for pesticides recently proposed by EFSA (2015), the initial trigger to conduct sediment toxicity tests is based on measured/predicted exposure concentrations in the sediment

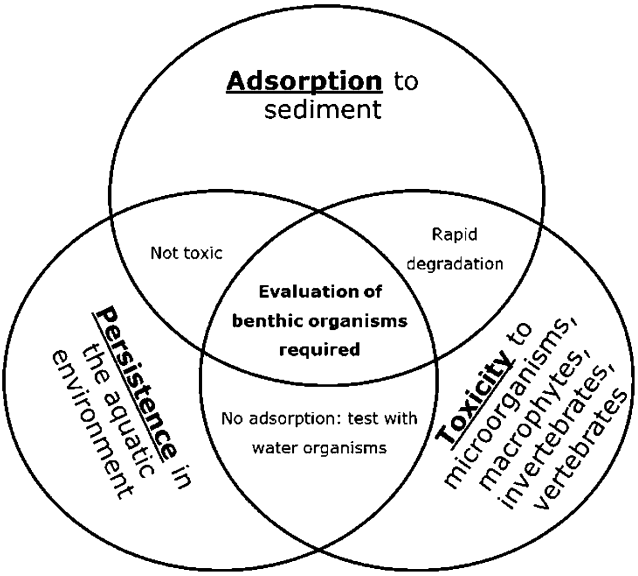


**Fig. 2** Theoretical basis for defining triggers for sediment toxicity studies based on Maund et al. (1997). The *circles* describe the three chemical characteristics that should be evaluated, and the overlap between the circles indicates the decision-making process for combinations of those characteristics

compartment and toxicity data of pelagic organisms. For pesticides, currently the toxicity trigger of a 21 days NOEC or $EC_{10}$ for *Daphnia* <0.1 mg/L is used, although another representative crustacean or insect may also be appropriate. Note, however, that EFSA (2015) proposed to use chronic toxicity data for algae and/or vascular plants as toxicity trigger in case of compounds with herbicidal properties that accumulate in sediments.

For veterinary medical products, a sediment ERA is not required if risks for pelagic aquatic invertebrates have not been demonstrated (Table 3). This disregards the fact that the environmental risks of hydrophobic veterinary chemicals for pelagic organisms may be predominantly acute, while those for benthic organisms will more often be chronic, at least if the chemical is persistent in the sediment compartment and remains bioavailable for a period that exceeds the generation time of benthic species.

Implementing a uniform set of triggers would improve harmonization between the guidance documents underlying the regulation/directives for various types of chemicals. A recent ECHA workshop recommended using a combination of triggers based on the physicochemical properties of the toxicant and the potential toxicity to benthic organisms (ECHA 2014c). In regulatory documents (see Table 3), hydrophobicity (log $K_{ow}$) and the organic carbon-water partitioning coefficient (log $K_{oc}$) are interchangeably used as triggers for the potential to adsorb to sediments from the water column. However, these are not equivalent; the values

**Table 3** Criteria that are currently required to trigger sediment toxicity testing as described in existing EU regulations and directives, and the guidelines accompanying these regulations

| Regulation | Trigger | Reference |
|---|---|---|
| Regulation EC/1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) | Sediment effect assessment is required if the chemical has a tonnage band $\geq$1000 tonnes per manufacturer or importer per year and a log $K_{oc}$ or log $K_{ow}$ of $\geq$3. | ECHA (2008) |
| | • log $K_{ow} > 3$: at least a screening assessment using the equilibrium partitioning (EP) method has to be performed. | |
| | • log $K_{ow}$ 3–5: the screening assessment using EP is considered appropriate, and no further testing is required if the risk quotient ($RQ = PEC_{sed}/PNEC_{sed;EP}$) <1. | |
| | • log $K_{ow} > 5$ or a correspondingly high adsorption or binding behaviour: a more comprehensive sediment assessment is needed. If using the EP approach, the risk quotient (RQ) is increased by an extra factor of 10 to take account of possible uptake via ingestion of sediment. If the RQ based on EP is >1, then a study, preferably long term, with benthic organisms using spiked sediment is recommended. | |
| | For substances that are highly insoluble and for which no effects are observed in aquatic studies, the application of the equilibrium partitioning method is not possible. In this case, at least one sediment test has to be performed. | |
| Regulation EC/1107/2009 concerning the placing of Plant Protection Products on the market | Sediment toxicity tests with benthic organisms are required: | Sanco (2002), EFSA (2013) |
| | • if in the water-sediment fate study >10 % of the applied radioactivity of the parent compound is present in the sediment at or after day 14 (OECD 308 (OECD 2002)), and the chronic toxicity value ($EC_{10}$ or NOEC) derived from the 21 days *Daphnia* test (or another comparable chronic toxicity tests with a relevant crustacean or insect) is <0.1 mg/L. | |
| | • compounds applied more than once, with a potential for accumulation of residues in the sediment, should also be considered for sediment testing (Sanco 2002). | |
| Directive 98/8/EC concerning the placing of biocidal products on the market[a] | A log $K_{oc}$ or log $K_{ow}$ of $\geq$3 can be used as a trigger value for sediment effects assessment. | European Commission (2003b) |
| | If the RQ (*based on EP*) is $\geq$1, then testing of sediment organisms is recommended. For substances with a log $K_{ow} > 5$, the RQ (*based on EP*) is increased by an extra factor of 10 to take account of possible uptake via ingestion of sediment. | |
| | If the RQ based on EP is >1, then a study, preferably long-term, with benthic organisms using spiked sediment, is recommended. | |

(continued)

**Table 3** (continued)

| Regulation | Trigger | Reference |
|---|---|---|
| Veterinary medicinal products | If the RQ for aquatic invertebrate is $\geq 1$ it is recommended to estimate the RQ for benthic organisms based on EP. If this RQ (*based on EP*) is $\geq 1$, then testing of sediment organisms is recommended. For substances with a log $K_{ow} > 5$, the RQ (*based on EP*) is increased by an extra factor of 10 to take account of possible uptake via ingestion of sediment. | VICH (2004) |
| | If the RQ based on EP is $>1$, then a study, preferably long term, with benthic organisms using spiked sediment is recommended. | |
| Guideline on the environmental risk assessment of medicinal products for human use | If a substance is not readily biodegradable and if the results from the water sediment study (OECD 308 (OECD 2002)) demonstrate significant shifting of the drug substance to the sediment, effects on sediment organisms should be investigated in Tier B. The criterion for sediment studies is met if more that 10 % of the substance at any time point after or at 14 days is present in sediment. A detailed strategy for further testing in order to refine the PNEC for the aquatic compartment can be found in the Technical Guidance document (European Commission 2003a). | EMEA (2006) |
| | If the RQ (*based on EP*) is $\geq 1$, then testing of sediment organisms is recommended. For substances with a log $K_{ow} > 5$, the RQ (*based on EP*) is increased by an extra factor of 10 to take account of possible uptake via ingestion of sediment. | |
| | If the RQ based on EP is $>1$, then a study, preferably long term, with benthic organisms using spiked sediment is recommended. | |

[a]Guidance documents underlying the new Biocidal Products Regulation (ECHA 2014b) are still in preparation

for log $K_{oc}$ can deviate substantially from log $K_{ow}$ (Koelmans et al. 2006, 2009; Mulligan et al. 2009; Poot et al. 2014; Seth et al. 1999). Because log $K_{oc}$ is a more direct measure for chemical binding to the sediment than log $K_{ow}$, using log $K_{oc}$ is preferred. Considering the information presented in Table 3, a log $K_{oc}$ (preferred) or log $K_{ow}$ of $\geq 3$ is generally used as a trigger value for sediment effect assessment. However, hydrophobic chemicals with a log $K_{oc}$ of $\geq 3$ do not necessarily need to be persistent in the sediment compartment. Therefore, we also recommend using the results of Organisation for Economic Co-operation and Development (OECD) guideline 308 (OECD 2002) to assess the persistence of the chemical in the sediment. For this purpose, the persistence trigger, as used for pesticides and medical products ($>10$ % of the substance is present in sediment at or after day 14), may be adopted for other chemicals as well.

A promising trigger to request sediment-spiked toxicity testing with benthic organisms is the EP approach that uses available chronic toxicity data for pelagic

organisms, at least if the taxonomic groups assessed for water ERA overlap with those required for sediment ERA. From Table 3 it appears that in regulatory documents for chemicals under REACH, biocides, and medical products (for veterinary and human use), the EP approach can be used as a screening method for chemicals with a log $K_{ow}$ 3–5, and that when the EP approach is used for chemicals with a log $K_{ow} > 5$, an extrapolation factor (EF) of 10 should be used to account for dietary uptake of the toxicant in the predicted no effect concentration for sediment based on the EP approach ($PNEC_{sed;EP}$) derivation. If the risk quotient ($RQ = PEC_{sed}/PNEC_{sed;EP}$) <1, then the environmental risks to benthic organisms are considered acceptable. The report of the ECHA workshop (ECHA 2014c), however, states that the EP approach is not valid for chemicals classified as ionizable, perfluorinated alkylated or insoluble. For these chemicals the $PNEC_{sed}$ should be derived on the basis of spiked sediment toxicity tests with benthic organisms. In addition, this ECHA report recommended exploring the validity of the EP approach for other organic chemicals. This can be done by comparing the screening level $PNEC_{sed;EP}$ with the $PNEC_{sed}$ derived from spiked sediment toxicity tests for a number of representative chemicals. The ECHA workshop report (ECHA 2014c) also suggested additional sediment tests for chemicals with a log $K_{ow} > 5$. As an initial screening approach in sediment ERA for pesticides, EFSA (2015) proposes the EP approach and an additional EF of 10 for benthic fauna to cover possible exposure due to ingestion of sediment particles. For benthic primary producers (e.g. rooted macrophytes) this additional EF of 10 is not considered necessary (EFSA 2015).

In order to explore the predictive value of the EP approach and the additional EF of 10, EFSA (2015) compared toxicity data of *Chironomus riparius* from water-spiked and sediment-spiked water-sediment toxicity tests for seven fungicides and insecticides. The calculated NOECs (in mg/kg sediment) based on the EP approach and the additional EF of 10 were for the tested insecticides a factor of 1.1–14 higher than the NOECs derived from sediment-spiked toxicity tests, while that was a factor of 1.8–135 for the tested fungicides. This suggests that, at least for pesticides, the EP approach and the additional EF of 10 results in a protective, but often conservative, estimate of sediment toxicity. EFSA (2015) also recommended evaluating the general applicability of the EP approach and the additional EF of 10 for a larger array of compounds and benthic species.

We recommend to further verify whether the EP approach and the EF of 10 can be considered a realistic worst case approach to derive a PNEC for benthic organisms and for different types of organic chemicals. Since the validation status of the EP approach has not yet been appropriately evaluated for a sufficient number of compounds, for the time being we propose using an EF of 10 to derive a $PNEC_{sed;EP}$ for organisms that ingest sediment particles. The reasoning for this proposal is further elaborated in Sect. 9.2 below.

# 6 Data Requirements for Effect Assessment

## 6.1 Toxicity Data Requirements in European Regulatory Frameworks

If the triggers, described in Section 5, are met, toxicity data for benthic organisms are required (Table 4). Hommen et al. (2010) provided an overview of data requirements for aquatic ERA. Current regulations do not always specify the requirements for sediment toxicity testing. Data requirements for freshwater benthic organisms especially concern tests with *Chironomus* sp. and *Lumbriculus variegatus*. Macrophyte tests (e.g. using the rooted macrophyte *Myriophyllum spicatum* (OECD 2014)) are only required by the Plant Protection Products regulation when specific triggers are met for substances with an herbicidal mode-of-action. For marine systems, no specific test species are mentioned in regulatory documents as data requirements, although examples are given in some regulations.

From Table 4 it appears that the data requirements may concern a water-sediment test with *Chironomus* using either spiked water or spiked sediment. We suggest that the spiked sediment test should have priority in sediment ERA. Exposure via sediment in spiked water OECD toxicity tests, however, may also be considered appropriate if the concentration in the top sediment layer is measured (or adequately predicted) and the biotic activity of the test species is highest in this layer. If a chemical is not stable, then a mean or time-weighted average (TWA) concentration for the duration of the sediment toxicity test may be required. This is particularly the case if it cannot be demonstrated with high certainty that the decrease in the bioavailable fraction of the compound is faster in the sediment of the laboratory toxicity test than that predicted for sediments in the field. To obtain a more realistic worst case effect estimate, the chronic $EC_{10}$/NOEC value can be calculated based upon the mean or TWA concentration of the chemical during the test. In case the bioavailable fraction of the compound in the sediment of the laboratory toxicity test decreases faster than that predicted (or measured) for field sediments, it may be appropriate to use the peak concentration in the sediment at the start of the sediment-spiked toxicity test as exposure metric in the effect estimate. The organic carbon (OC) content (%) of the sediment needs to be known to enable standardization of chemical concentration to OC or to express the toxicity value in terms of a fixed OC content per unit DW sediment.

Data requirements for prospective sediment risk assessment rely on official test protocols for standard test species. Diepens et al. (2014b) and Fojut et al. (2013) provided overviews of internationally accepted sediment tests for freshwater, estuarine, and marine invertebrates, as well as macrophytes. In the available protocol tests for marine/estuarine benthic organisms, amphipods seem to be overrepresented. For vertebrates, the whole-sediment toxicity test for larvae of the freshwater frog *R. pipiens* became available only in 2013 (ASTM 2013), so little experience has been acquired in conducting and interpreting this test. No official test guidelines exist for estuarine/marine rooted macrophytes and estuarine/marine vertebrates. Furthermore, no protocol tests for sediment-dwelling microbes are currently available. Most of the experience in tiered effect assessments therefore concerns benthic invertebrates.

**Table 4** Data that are currently required for sediment toxicity testing as described in existing EU regulations and directives, and the guidelines accompanying these regulations

| Regulation | What needs to be tested? | Reference |
|---|---|---|
| Regulation EC/1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) | Long-term test with *Lumbriculus variegatus* using spiked sediment | ECHA (2014a) |
| | Long-term test with *Chironomus* sp. using spiked sediment | |
| | Long-term tests with a further benthic species using spiked sediment. Selection of third species should supplement the first two species in terms of habitat, feeding strategy, taxa or life-stage. For example, the amphipod *Hyalella azteca* or the nematode *Caenorhabditis elegans* could be used | |
| | For the marine compartment, the same testing strategy is followed. However, for this compartment more tests may be necessary to reduce the higher assessment factor applied if only limited data are available. For possible test species, refer to available protocol tests developed for estuarine/marine species. | |
| Regulation EC/1107/2009 concerning the placing of plant protection products on the market | OECD (2004a). OECD Guideline 218: Sediment—water chironomid toxicity test using spiked sediment; adopted 13 April 2004. OECD Publishing. | EFSA (2013) |
| | OECD (2007). OECD Guideline 225: Sediment—water *Lumbriculus* toxicity test using spiked sediment; adopted 16 October 2007. OECD Publishing. | |
| | ISO (2010) ISO/DIS 16191 Water quality - Determination of the toxic effect of sediment and soil on the growth behaviour of Myriophyllum aquaticum. International Organization for Standardization, Geneva. | |
| | ISO (2010). ISO/DIS 16191 Water quality—Determination of the toxic effect of sediment and soil on the growth of *Myriophyllum aquaticum*. International Organization for Standardization, Geneva. | |
| | OECD (2014). OECD guideline 239 spiked sediment test with *Myriophyllum spicatum Glyceria*—in preparation | |

(continued)

**Table 4** (continued)

| Regulation | What needs to be tested? | Reference |
|---|---|---|
| Directive 98/8/EC concerning the placing of biocidal products on the market[a] | For freshwater ERAs, long-term sediment tests with *Chironomus* sp., *Lumbriculus variegatus* and a third benthic test species differing in taxonomy and/or feeding habit are required. | European Commission (2003b) |
| | For estuarine/marine ERAs sub-chronic and chronic sediment toxicity tests for the following species are mentioned as example: *Corophium* sp., *Leptocheirus plumulosus*, *Neanthes* (=*Nereis*) sp., *Arenicola marina*, *Echinocardium cordatum*. | |
| Veterinary medicinal products | Freshwater sediment invertebrate species: OECD 219 (spiked water water-sediment *Chironomus* test) is normally used. If exposure is through sediment or adsorbed to soil in run-off, OECD 218 (spiked sediment test with *Chironomus riparius*) should be used. | VICH (2004) |
| | Marine sediment invertebrate species: seek regulatory guidance (probably the standard protocol tests are referred to). | |
| Guideline on the environmental risk assessment of medicinal products for human use | Effects on a sediment dwelling organism (*Hyalella* sp.; *Lumbriculus* sp. or *Chironomus* sp.) should be investigated. | EMEA (2006) |

[a]Guidance documents underlying the new Biocidal Products Regulation (ECHA 2014b) are in preparation

## 6.2 *Main Differences Between Existing OECD, ASTM and US-EPA Guidelines*

As discussed by Faber and Bruns (2015) and EFSA (2015) one of the main differences between OECD technical guidelines for sediment-spiked toxicity tests and the corresponding guidelines from North America is the type of test sediment used. In the OECD test protocols pre-equilibrated artificial sediment is recommended whereas the US-EPA and ASTM technical guidelines recommend the use of field-collected sediment. In addition, the OECD and the US-EPA/ASTM

guidelines differ with respect to the recommended spiking procedure. The OECD recommends a pre-equilibrium period of 2–7 days (OECD 2004a, 2007) and US-EPA for freshwater sediment tests at least 1 month for persistent chemicals. However, sediment tests with industrial chemicals and tests with marine sediment should be started as soon as possible after spiking (EPA 1996a, b). During ageing, hydrophobic chemicals may become less bioavailable due to surface sorption to sediment particles and entrapment of the chemical within micropores and binding to organic complexes (e.g. Semple et al. 2003), which may affect exposure conditions in the tests. Differences in exposure conditions due to differences in sediment type (e.g. OC content) and aging may be partly accounted for by expressing the exposure concentrations in sediment as chemical mass per mass of OC, overlying water and preferable also in pore water (see above). Moreover, the use of (semi) static (OECD) versus semi static or flow through (US-EPA/ASTM) test systems is another main difference between the guidelines and can result in different exposure conditions. These differences hamper the comparability of results between sediment toxicity tests conducted according to different guidelines. Therefore, we recommend using pre-equilibrated artificial sediment for prospective toxicity testing, as described in Diepens et al. (2014b), or when field-collected sediment is used, to follow as much as possible the test design as currently proposed in OECD test guidelines with artificial sediment. However, we also support the recommendation of EFSA (2015) to initiate comparative studies to evaluate and understand the consequences of differences in OECD and US-EPA/ASTM guidelines (e.g. artificial vs. field-collected sediment; ageing period before starting sediment toxicity test; static vs flow through testing).

## *6.3 Recommendation for a Suite of Benthic Test Species*

Sediment risk assessment should ideally include a set of sediment toxicity tests to cover a relevant number of representatives of benthic communities and focus on long-term exposure and chronic endpoints (Diepens et al. 2014b). Test exposure durations should depend on the generation time of the tested species (e.g. shorter for microorganisms than for invertebrates). Preferably, a chronic toxicity test should cover the full life-cycle of the test organism, or should at least cover its most sensitive life-stage.

An important question at stake is whether the current data requirements underlying European regulations are adequate and whether currently available standard test protocols are sufficient. Sediment toxicity tests should consider the SPUs and associated ecological entities as discussed in Sect. 4, depending on the mode-of-action of the organic chemical under evaluation. The current suite of standard test species used in the European prospective sediment ERA is limited and does not cover all SPUs; benthic microbes, rooted macrophytes and vertebrates receive hardly any attention (Table 4). For instance, for pesticides in Europe the prescribed Tier-1 benthic test species are *Chironomus riparius* (insect), *Lumbriculus*

*variegatus* (oligochaete worm), and for herbicidal compounds that accumulate in sediment *Myriophyllum* (macrophyte) species (EFSA 2013). It remains to be investigated whether the current Tier-1 approach based on chronic toxicity tests with these benthic standard test species, together with the proposed assessment factor, sufficiently covers the protection of all SPUs. Furthermore, a harmonized testing strategy between freshwater and estuarine/marine environment is not yet in place. For a suite of freshwater, estuarine and marine benthic test species and methods, including microorganisms, macrophytes and invertebrates, is referred to Diepens et al. (2014b). Since sediment toxicity testing with benthic vertebrates was not discussed in that review, this topic is addressed briefly in Sect. 9.8.

## 7 Factors Affecting the Exposure of Sediment-Dwelling Organisms

Exposure plays an important role in both sediment toxicity testing (the focus of this paper) and in predicting the field exposure concentrations in sediments. In this paper, exposure is defined as the external concentration of the chemical in environmental media potentially affecting sediment-dwelling organisms, together with the processes that affect its bioaccessibility and its bioavailability, including bioaccumulation.

For any organism, exposure is the net result of chemical uptake and depuration fluxes between the organism and its direct environment (see Diepens et al. 2014b and references therein). For benthic invertebrates, uptake may take place through fluxes from pore water, overlying water, and particle contact and ingestion (Diepens et al. 2014b; Selck et al. 2012). Transport to pore water takes place through desorption from the bulk sediment. If uptake through particle or food (prey) ingestion occurs, particle or diet composition is important. Depuration may include passive elimination, defecation, transformation and exudation. Chemical concentrations in organisms may also be reduced by growth dilution. For rooted macrophytes, partitioning to roots and shoots, translocation between roots and shoots and growth dilution are important (Diepens et al. 2014a). This means that uptake is a complex, time-dependent process, because the relative importance of the individual processes varies with environmental and life-stage changes over time. In addition, the relative importance of these uptake processes may differ between chemicals and benthic organisms.

In assessing exposure of benthic organisms, four types of influential factors are particularly important: chemical, biological, spatial and temporal (ECHA 2014c). These factors are addressed in the subsections below.

## 7.1 Chemical Factors

Traditional exposure assessment concepts use total sediment concentrations and the EP model for a first-tier screening approach to estimate exposure in field sediments (Diepens et al. 2014b; ECHA 2014c). Single sorption domain EP models, however, are known to work well only for partitioning of conventional organic substances to sediment amorphous organic matter phases. The EP model will not work for ionisable chemicals, perfluorinated alkylated substances, Non-Aqueous Phase Liquids (NAPLs), long aged sediments, or in the presence of sedimentary condensed organic matter pools like soot or black carbon (BC). Therefore, specific $K_d$ models should be used to estimate exposure concentrations in field sediments (Diepens et al. 2014b; ECHA 2014c; Koelmans et al. 2006, 2009; Poot et al. 2014; Redman et al. 2014). If the traditional single domain EP approach is used, condensed organic matter phases may increase actual $K_d$ values by two to three orders of magnitude, leading to a substantial overestimation of exposure (Koelmans et al. 2006). A realistic worst case approach would be to use a correction of one order of magnitude on the previous EP-based $K_d$ values. For other chemicals, Quantitative Structure Property Relationship (QSPR) models can be used. These models are based on molecular descriptors, such as the Abraham parameters (Nguyen et al. 2005), and are available for many compound classes. For degradable compounds, however, exposure is dynamic in time, and it may be necessary to account for degradation products in the exposure assessment if they are also toxic. Sufficiently accurate predictive models to describe degradation in time or to translate laboratory degradation data into field-relevant rates have not been developed as yet.

## 7.2 Biological Factors

Species traits such as body size, lipid content, surface area-to-volume, respiratory strategies, diet, digestive processes and dietary assimilation affect bioaccumulation (Gaskell et al. 2007; Rubach et al. 2011) and thus internal exposure. Particle or food ingestion depends on diet and plays a dominant role for some benthic invertebrates such as *C. volutator* (Diepens et al. Under revision), *Lumbriculus variegatus* (Gaskell et al. 2007; Leppänen and Kukkonen 1998; Sidney et al. in prep), *Arenicola marina* (Diepens et al. Under revision; Kaag et al. 1997) and *Macoma balthica* (Diepens et al. Under revision; Kaag et al. 1997; McLeod et al. 2008; McLeod et al. 2007) whereas for other species such as *Ilyodrilus templetoni* (Lu et al. 2004) water uptake is dominant. For conventional organic substances, EP-based approaches predict biota sediment accumulation factors (BSAFs) values of approximately 1 or 2. For benthic invertebrates, however, much higher values are often observed (Besseling et al. 2013; Diepens et al. Under revision; Hecht et al. 2004), which can be explained from food ingestion. A recent model analysis showed how actual parameter distributions contribute to this variation (Selck

et al. 2012). On the other hand, values much lower than 1 or 2 are sometimes observed (Koelmans et al. 2006; Moermond et al. 2005). This can be explained by binding to black carbon as mentioned above. In that case, the EP approach would be over-protective, unless a black carbon-inclusive EP approach is used. For organisms like benthic algae and sediment-rooted macrophytes, black carbon effects are similar, but food ingestion does not occur and thus will not add to variance in accumulation. Established models for invertebrates (Diepens et al. Under revision; Hendriks 1995; Janssen et al. 2009; McLeod et al. 2008; Thomann et al. 1995) are available to quantify biological factors on BSAFs.

Experiments with the rooted macrophytes *Elodea canadensis* and *Myriophyllum spicatum* showed that an equilibrium state is not reached within 28 days, a timeframe that is even longer than the duration (7–14 days) of a standard macrophyte test (Diepens et al. 2014a). This means that maximum internal exposure might not be reached and that when conducting spiked sediment toxicity tests with rooted macrophytes, test durations should be increased. Alternatively, mechanistic models might be used as extrapolation tools to calculate maximum levels of internal exposure (Diepens et al. 2014a; Gobas et al. 1991; Heine et al. 2015; Vanier et al. 2001).

For any food web that includes the sediment compartment, exposure of sediment-associated chemicals along the food chain may occur. Whether or not a chemical will bioaccumulate and/or biomagnify depends on the hydrophobicity and persistence of the chemical, the feeding relationships and length of the chain, and the capacity to metabolise and eliminate the chemical by the respective species (Weisbrod et al. 2009). A novel approach to detect secondary poisoning is to directly assess the relative chemical fugacity in an organism at a certain trophic level by equilibrating its tissues with passive samplers in a closed system.

## 7.3 Spatial Factors

Both contaminant concentrations and presence of benthic organisms in field sediment are patchy (horizontally heterogeneous), and ‘exposure hot spots’ are present, which may be identified by appropriate spatial sampling strategies and geostatistics (ECHA 2014c). Similarly, colonization potentials of benthic organisms are influenced by spatial factors. This information is important for the development of realistic exposure assessment goals and exposure scenarios. An exposure scenario can be defined as the set of variables determining chemical exposure (De Laender et al. 2015). These exposure scenarios will yield spatially explicit exposure assessments on which spatially explicit ERA’s can be based. An alternative approach is to deal with spatial heterogeneity through probabilistic modelling (ECHA 2014c). This results in a point estimate of exposure for a heterogeneous region, where the heterogeneity is accounted for by the uncertainty interval in the point estimate.

Besides the abovementioned horizontal heterogeneity, vertical gradients may also affect the exposure of benthic organisms. Sediment exposure usually varies with sediment depth and, consequently, also relates to the biologically active layer, which may be different for various types of sediment-dwelling organisms. This means that vertical heterogeneity also has to be considered to in ERA.

### *7.4 Temporal Factors*

Sediments can act as a buffer against fluctuations of chemical concentrations in the overlying water. Flushing or run-off events may cause sudden peaks in exposure in the water column and sequentially at the sediment-water interface and in the biologically relevant sediment top layer where exposure may last longer than in the water column (ECHA 2014c). This indicates that chronic exposure generally is more relevant for sediment assessment than acute exposures. The buffering is stronger for pore water concentrations than for near-sediment overlying water concentrations. Chemical exposure would thus be more variable in time for benthic species that are partly or fully exposed to overlying waters and suspended solids. Furthermore, the temporal dynamics of sediment re-suspension and deposition downstream may be relevant if re-deposited sediments are heavily contaminated.

As discussed before in Sect. 6.2, another important factor affecting exposure of benthic organisms to sediment-bound toxicants is the decrease in bioavailability due to ageing.

## 8 Exposure Concentration in Sediment ERA

### *8.1 The Ecotoxicologically Relevant Concentration for Sediment-Dwelling Organisms*

In a prospective risk assessment, predicted no effect concentrations (PNEC) are evaluated against predicted environmental exposure concentrations (PECs), where the PEC/PNEC ratio often is used as an indicator of risk (Karman 2000). Lack of a clear conceptual basis for the interface between the exposure and effect assessment may lead to a low overall scientific quality of the risk assessment (Boesten et al. 2007). This interface is defined by EFSA (2005) and Boesten et al. (2007) as the concentration that correlates appropriately with ecotoxicological effects; it is called the ecotoxicologically relevant concentration (ERC). In prospective ERA, the ERC must be consistently applied so that sediment exposure estimates ($PEC_{sed}$) and effect estimates for sediment-dwelling organisms (such as $PNEC_{sed}$) can be compared. More specifically, the 'C' in the $PEC_{sed}$ estimate should be consistent with the 'C' in the $PNEC_{sed}$ estimate. From a theoretical point of view, the internal

concentration (body burden) at the target site in the benthic organism under evaluation would be the most appropriate ERC. Concentrations are hard to measure directly at the target site, especially for small animals. Therefore, whole body internal concentrations can be used (Di Guardo and Hermens 2013). In the vast majority of toxicity studies with benthic organisms, however, internal concentrations are not measured (Brock 2013) and in none of the regulatory guidelines is it given as a recommended measurement endpoint in ecotoxicological studies. Consequently, the 'C' in the $PEC_{sed}$ and $PNEC_{sed}$ estimates usually refers to external exposure concentrations.

An important question is whether the $PEC_{sed}$ and $PNEC_{sed}$ estimates should be expressed in freely dissolved chemical concentration in pore water, ingested particles or total sediment concentration. Since the bioavailability of organic toxicants may be affected by the OC content of the sediment, an additional question is whether the total sediment concentration should be normalized to standard sediment or expressed in terms of OC content of the dry sediment.

The current OECD sediment test protocols (OECD 218 (OECD 2004a), 219 (OECD 2004b), 225 (OECD 2007), 233 (OECD 2010)) advocate the use of artificial sediments containing 4–5 % peat, while EPA OPPTS 850.173.5 (EPA 1996b) advocates the use of clean, field-collected sediments. All protocols require the determination of OC content of the sediment, enabling the recalculation of effect concentrations based on OC content. In toxicity tests retrieved from the literature, different types of sediments varying in OC are used, hampering a direct comparison of test results. To allow comparison of sediment toxicity data from different sources, sediment toxicity data may be standardized to concentrations normalized on sediment OC content. An alternative approach might be to standardize all toxicity data to sediment with an organic matter content of 5 % (which equals approximately 2.5 % of OC), an approach often followed in Europe. The basic principle, however, is the same. To appropriately link exposure and effects, the $PEC_{sed}$ and $PNEC_{sed}$ estimates should be expressed either in terms of mg/kg DW standard sediment with a fixed OC content (=$PEC_{sed\text{-}tot}$ or $PNEC_{sed\text{-}tot}$) or in terms of mg/kg OC in dry sediment (=$PEC_{sed\text{-}oc}$ or $PNEC_{sed\text{-}oc}$). In our paper we have normalized the total concentration of the organic chemical in the sediment to organic carbon ($PEC_{sed\text{-}oc}$ and $PNEC_{sed\text{-}oc}$).

The sediment-water chironomid tests using spiked sediment (OECD Guidelines 218 (OECD 2004a) and 233 (OECD 2010)) specify that—as a minimum—the concentrations in overlying water, pore water, and sediment should be measured. According to OECD guideline 218, effect concentrations should be expressed as concentrations in sediment, based on dry weight, at the beginning of the test. OECD Guideline 233, however, does not explicitly specify on what basis the concentration in the $L(E)C_X$ or NOEC values should be expressed, although in daily practice the concentration in the sediment at start of the test is generally used. The *L. variegatus* toxicity test using spiked sediment (OECD Guideline 225) specifies that the concentration in sediment and overlying water should be verified by measurement. The guideline also outlines a method for isolation and subsequent measurement of

chemicals in pore water. The effect concentration should be expressed in mg/kg sediment on dry weight basis (OECD 2007).

The United States Environmental Protection Agency (EPA) OPPTS 850.1735 Guideline (whole sediment acute toxicity invertebrates, freshwater) states that 'Concentrations of spiked chemicals may be measured in sediment, interstitial water, and overlying water . . .', but does not specify on what basis effect concentrations should be expressed, other than 'In some cases it may be desirable to normalize sediment concentrations to factors other than dry weight, such as OC for non-ionic organic compounds or acid volatile sulfides for certain metals' (EPA 1996b). The various guidelines lack clarity and are mutually inconsistent on these aspects.

The EFSA has recently published a Scientific Opinion on the assessment of exposure of organisms to pesticides in soils (EFSA 2010a). They recommend that the ERC should be reported both in concentration units of mass of pesticide per mass of dry soil and as a concentration in pore water (EFSA 2009, 2010a). If the rationale behind the recommended use of both measures of exposure would also apply to sediment, which seems likely, then this would suggest that toxicity data generated for sediment organisms should also be reported along with concentrations in pore water and in sediment mass or in sediment OC mass. This is not in line with OECD and EPA guidelines, where the most common recommendation is to report effect concentrations on the basis of sediment mass only. If the pore water concentration is not measured, or is difficult to measure, then an appropriate modelling approach to estimate pore water concentrations might be used. In a toxicity test the final response of the test organism in most cases will be influenced by the dynamics in exposure concentration during the test. We therefore propose as a minimum requirement to always measure exposure at the start and the end of the experiment. For organic chemicals that are expected to rapidly dissipate from sediment, we recommend measuring exposure concentrations, including ecotoxicologically relevant metabolites, at different time intervals during the test. Measurement of dynamics in exposure concentrations in pore water, total sediment, overlying water, and test organisms is advisable if chemical equilibrium is not reached between the different environmental compartments during the test period.

In conclusion, the $PEC_{sed}$ and $PNEC_{sed}$ used in the RQ should be expressed in the same type of concentration. Ideally, internal concentrations should be measured during the experiment. We recognise that in sediment-spiked toxicity tests, different exposure routes play a role, and that the relative importance of these routes depends on the properties of the chemical, the test organism and the test system. For the time being, and taking into account the current technical guidelines for sediment-spiked toxicity tests, we consider it a pragmatic and realistic worst-case approach to measure chemical concentrations in sediment (OC normalized), overlying water and pore water. This allows for flexibility when referencing toxicity estimates to OC mass concentration, pore water concentrations or a combination, dependent on the organism. Models may be used to calculate chemical concentrations in environmental compartments in which data is lacking.

## 8.2 Overview of Fate and Exposure Models

Fate models are essential for understanding and evaluating the required time for chemical equilibrium between sediment and pore water and to optimize other aspects of the tests, such as the water-sediment ratio, water renewal and pre-equilibration after spiking. There is a need for approaches to translate biodegradation process parameters obtained from lab tests to parameters that are relevant in the field. The development of passive samplers for more classes of chemical can provide more accurate input for such models.

Exposure models have been reviewed (Guillén et al. 2012; Koelmans et al. 2001; Pistocchi et al. 2010) and four basic approaches have been identified: multiple box models, single point multi-media models, numerical solutions to advection-dispersion transport models and meta-models. Geographic information system (GIS)-based modelling was proposed as a convenient fifth approach (Pistocchi et al. 2010). Single point multi-media models typically provide average concentrations in environmental compartments for a region or country using emission data and mass balance equations or material flow analysis (e.g. EUSES (Vermeire et al. 1997), SIMPLEBOX (Brandes et al. 1996)). However, spatially and temporally explicit models use more detailed and realistic process descriptions to simulate concentrations in aquatic systems as a function of place and time (e.g. DUFLOW (Clemmens et al. 1993), TOXSWA (Adriaanse 1996), GREAT-ER (Feijtel et al. 1997)). In exposure modelling of aquatic systems, single point multi-media models can be considered as a lower tier approach and spatially and temporally explicit models as a higher tier approach. For prospective ERAs, however, the development of exposure scenarios is a prerequisite to successfully apply exposure models. Consequently, more realistic exposure models are needed for emerging chemical classes like ionizable organics and polar substances; such models should also take degradation processes into account.

## 8.3 Linking Exposure to Effects in Sediment ERA

For exposure in chronic risk assessment, either the peak concentration (max) in total sediment normalized to organic carbon content ($PEC_{sed\text{-}oc;max}$) or pore water ($PEC_{sed\text{-}pw;max}$), or the TWA concentration in total sediment ($PEC_{sed\text{-}oc;TWA}$) or pore water ($PEC_{sed\text{-}pw;TWA}$) can be used to compare with the predicted no effect concentration for sediment based on chronic toxicity data (either $PNEC_{sed\text{-}oc;ch}$ or $PNEC_{sed\text{-}pw;ch}$). In the text below, when referring to $PEC_{sed}$ and $PNEC_{sed}$ estimates, this may be either the concentration in total sediment normalized to OC or in pore water.

In principle, the $PEC_{sed;max}$ or $PEC_{sed;TWA}$ should be lower than the $PNEC_{sed;ch}$. However, if using the $PEC_{sed;TWA}$ in the risk assessment, the time window for the $PEC_{sed;TWA}$ estimate should be equal to or shorter than the time window for the

chronic effect estimate that drives the risk (i.e. the duration of tests delivering the critical chronic $EC_{10}$ values that drive the $PNEC_{sed;ch}$). In addition, proof of reciprocity in toxicity tests should be provided in order to use the $PEC_{sed;TWA}$ in the risk assessment. Reciprocity refers to Haber's law, which assumes that toxicity depends on the product of concentration and time (Giesy and Graney 1989; Karman 2000).

We recommend that the effect estimate derived from sediment toxicity tests be expressed in terms of TWA or mean exposure concentration during the test. However, in current sediment toxicity tests the effect estimate (such as $EC_x$ and NOEC) is usually expressed in terms of initial exposure concentration. If the effect estimate is expressed in terms of initial exposure concentration, it should be shown that the exposure profile and bioavailable fraction in the toxicity test is worst-case relative to that in the field. Therefore, to assure a more realistic worst-case risk assessment when using the initial exposure concentration, the $PEC_{sed;max}$ concentration should always be used.

# 9 Tiered Effect Assessment for Benthic Test Species and Spiked Sediments

## *9.1 Tiered Approach*

In the tiered approach, test complexity and ecological realism increase when moving up tiers (Boesten et al. 2007; Posthuma et al. 2008; Solomon et al. 2008). This provides a cost-effective procedure, both for industry and regulatory agencies. The tiered system as a whole should be (i) appropriately protective, (ii) internally consistent, (iii) cost-effective and it should (iv) address the problem with a higher degree of realism and complexity when going from lower to higher tiers (see Fig. 3) (Boesten et al. 2007; Posthuma et al. 2008; Solomon et al. 2008). Furthermore, a tiered ERA scheme must be developed for each specific protection goal. An additional advantage of the tiered approach is that higher tiers can be used to calibrate the lower tiers (van Wijngaarden et al. 2015). Appropriate field observations may be used to verify the tiered effect assessment approach based on experimentation.

Below, a tiered ERA scheme for benthic invertebrates and rooted macrophytes is presented and discussed. Most data and experience with spiked sediment tests is available for these taxa. Despite the scarcity of spiked sediment toxicity tests with microorganisms and vertebrates, in this paper we also discuss sediment ERA approaches for these organisms. In principle, however, all tiers can be used for different groups of sediment organisms.

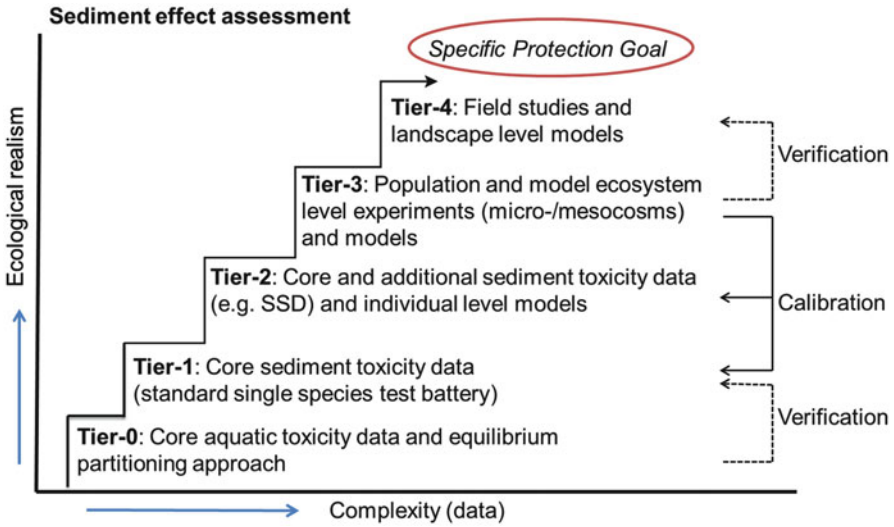


**Fig. 3** Schematic overview of a tiered approach in prospective risk assessment. In each tier an assessment factor (AF) may be necessary to derive a predicted no effect concentration (PNEC). The higher tiers can be used to calibrate the lower tiers (adapted from Diepens et al. (2014b))

## *9.2 Tier-0 Effect Assessment Based on Equilibrium Partitioning*

Di Toro et al. (1991) showed that the bioavailability of non-ionic organic chemicals is a function of their distribution between environmental phases (e.g. organic matter and interstitial water). This understanding was the foundation for using EP to derive mechanistic sediment quality guidelines. Assuming that the toxicity of a non-ionic organic chemical is proportional to its concentration in water, then the sediment concentration of this chemical that will cause toxicity can be estimated if the relationship between the chemical concentration in the pore water and that in sediment is understood. The partitioning of a chemical between OC phase in the sediment and pore water can be represented by a simple equilibrium equation (European Commission 2011a):

$$C_{sed\text{-}oc} = C_{pw} * K_{oc} \quad (1)$$

In which $C_{sed\text{-}oc}$ is the concentration of the chemical in the sediment per unit mass of OC (μg/kg OC), $C_{pw}$ is the concentration of the chemical in pore water (μg/L) and $K_{oc}$ is the partition coefficient of the chemical to sediment OC (L/kg OC). When replacing $C_{pw}$ by the predicted no effect concentration for surface water based on chronic toxicity data ($PNEC_{sw;ch}$) derived for pelagic water organisms on basis of water toxicity tests, the $C_{sed\text{-}oc}$ becomes the $PNEC_{sed;ch\text{-}EP}$.

An essential step in the application of the EP approach is the derivation of an appropriate $K_{oc}$, such as with OECD 106 (OECD 2000a). Because reported $K_{oc}$ values may have a high variability, we recommend using the geometric mean value, since $K_{oc}$ values usually show a log-normal distribution (EFSA 2014a). If no $K_{oc}$ is available, then this value can be estimated from $K_{ow}$ using quantitative structure-activity relationship (QSAR) models (European Commission 2003a).

Research in the past decade has shown that the EP theory does not accurately predict in situ partitioning (Morrison et al. 1996). This is because field $K_{oc}$ values typically are two to three orders of magnitude higher than those in the laboratory due to the ubiquitous presence of condensed carbon phases, such as black carbon (Cornelissen et al. 2005; Koelmans et al. 2006; Moermond et al. 2005). Consequently, the chemical concentration in sediment that causes toxicity also will be two to three orders of magnitude higher. When the used $K_{oc}$ value is based on sediment lacking a condensed carbon phase we recommend a worst case approach in Tier-0. This approach accounts for the effect of black carbon by using a $K_{oc}$ value in Eq. (1), which is only ten times higher than the $K_{oc}$ values traditionally used in the EP approach. This means that Eq. (1) will return toxic thresholds for sediments that are a factor of ten higher. Another shortcoming of the EP approach is that it neglects sediment ingestion as a relevant uptake pathway. EP also neglects specific species traits and is adequate only as long as the chemical transfer occurs through passive organic matter-water-lipid partitioning. EP-based approaches predict BSAF values of approximately 1 or 2. However, this has been shown to be inadequate for organisms such as the mayfly *Hexagenia* sp. with a BSAF up to 20 for PCB153 (Selck et al. 2012), the annelid *L. variegatus* with a BSAF up to 99 for chlorpyrifos (Jantunen et al. 2008), the marine amphipod *C. volutator* with a BSAF ranging from 16 to 218 for PCBs (Diepens et al. Under revision), the marine polychaete worm *A. marina* with a BSAF ranging from 10 to 40 for PCBs (Besseling et al. 2013; Diepens et al. Under revision) and the marine decapod *Chasmagnathus granulata* with a BSAF ranging from 0.1 to 44 for a range of organochlorine pesticides (Menone et al. 2004). These organisms thus accumulate up to two orders of magnitude higher concentrations than EP theory predicts. Therefore, to be protective, a Tier-0 approach should take this into account, and produce a toxic threshold in sediment that is a factor of 100 lower than calculated by the original Eq. (1). The two effects—the black carbon effect and the sediment ingestion effect—act in the opposite direction, and thus partly compensate for each other, but still yield a net effect of $100/10 = 10$ as an extra safety factor to be applied to the effect threshold calculated for a Tier-0 for invertebrates and vertebrates that ingest sediment. For microorganisms, benthic algae and sediment-rooted macrophytes, ingestion does not play a role—but these organisms may have the capacity to extract a fast-desorbed fraction of the organic contaminant. For these organisms, we propose that the extra safety factor is not needed when using the EP approach. In Sect. 5 we already mentioned the research recommendation to verify whether the EP approach and the EF of 10 can be considered a realistic worst case approach to derive a PNEC for benthic fauna and for different types of organic chemicals.

## 9.3 Tier-1 Effect Assessment Based on Protocol Tests for Benthic Invertebrates and Macrophytes

The following approach can be used to derive a chronic Tier-1 PNEC value based on sediment toxicity tests with the freshwater, estuarine and marine standard test species that were described in Sect. 6:

1: For the chemical of concern, collect the Tier-1 and additional toxicity data for (pelagic) water organisms in the compartment overlying water.
2: Identify the taxonomic group(s) of water organisms that is/are likely to be most sensitive.
3: Collect the available spiked sediment toxicity data for benthic freshwater and estuarine/marine standard test species (see sections above).
4: Determine whether the most sensitive taxonomic group for Tier-1 water column organisms is likely to be represented in the core data set of benthic test species according to standard protocols.
5: If so, use Table 5 to conduct the Tier-1 effect assessment for benthic organisms in freshwater and estuarine/marine ecosystems. If not, determine whether the most sensitive taxonomic group is also represented in the additional toxicity data, which can then be added to the core data set of benthic test species, or try other approaches (such as the EP approach).

## 9.4 Tier-2 Approach on Basis of Laboratory Toxicity Data for Standard and Additional Benthic Invertebrates and/or Rooted Macrophytes

### 9.4.1 Geometric Mean Approach

If valid toxicity data from several species are available, but this number is too low to apply the species sensitivity distribution (SSD) approach, EFSA (2005, 2013) proposed the option of the geometric mean-AF approach. In this approach, the geometric mean toxicity value is calculated for species from the same taxonomic group (e.g. crustaceans, insects, annelids, nematodes, bivalves) and the same measurement endpoint (e.g. $LC_{50}$ values). The lowest geometric mean value for the various taxonomic groups is selected, and the same AF normally used in the Tier-1 effect assessment is applied. For the acute aquatic effect assessment of pelagic species exposed to insecticides, the geometric mean approach was recently calibrated by van Wijngaarden et al. (2015) with threshold concentrations for effects derived from aquatic micro/mesocosm tests. This study demonstrated that the geometric mean approach proposed by EFSA for acute effect assessment of insecticides provides sufficient protection to water organisms.

Given the requirements described above, the geometric mean approach could also be applied to sediment ERA that uses acute and/or semi-chronic $LC_x$ values for benthic species of the same taxonomic group and that have the same feeding

**Table 5** Proposal for assessment factors (AF) to be applied to the lowest sediment toxicity value for standard tests with spiked sediment and benthic organisms (adapted from EFSA 2013; ECHA 2008; European Commission 2011a)

| Available data | AF |
|---|---|
| Three chronic $EC_{10}$/NOEC values for different taxonomic/feeding groups, of which at least two test species, including the most sensitive, are representative for the ecosystem under evaluation (freshwater or marine/estuarine) | 10[a] |
| Three chronic $EC_{10}$/NOEC values for different taxonomic/feeding groups, of which only the most sensitive is representative for the ecosystem under evaluation (e.g. freshwater test species for an marine/estuarine ERA) | 30[a] |
| Three chronic $EC_{10}$/NOEC values for different taxonomic/feeding groups, of which one is representative for the ecosystem under evaluation (e.g. freshwater test species for an marine/estuarine ERA), but this species is not the most sensitive | 50[a] |
| Two chronic $EC_{10}$/NOEC values for different taxonomic/feeding groups and representative for the ecosystem under evaluation (freshwater or marine/estuarine) | 50 |
| Two chronic $EC_{10}$/NOEC values for different taxonomic/feeding groups of which one value each is representative for respectively freshwater and marine/estuarine ecosystems | 100 |
| Three chronic $EC_{10}$/NOEC values for different taxonomic/feeding groups and not representative for the ecosystem under evaluation | 100[a] |
| Three semi-chronic (10 days) L(E)$C_{10}$/NOEC values for different taxonomic/feeding groups and for standard benthic test species typical for the ecosystem (freshwater or marine/estuarine) under evaluation | 30–100[a;b] |
| Two chronic $EC_{10}$/NOEC values for different taxonomic/feeding groups that are not representative for the ecosystem under evaluation (e.g. freshwater test species for an marine/estuarine ERA) | 200 |
| Three semi-chronic (10 days) L(E)$C_{50}$ values for different taxonomic/feeding groups and for standard benthic test species typical for the ecosystem (freshwater or marine/estuarine) under evaluation | 30–100[a;b] |
| Three semi-chronic (10 days) L(E)$C_{50}$ values for different taxonomic/feeding groups and not all test species are typical for the ecosystem (freshwater or marine/estuarine) under evaluation, but the most sensitive test species is typical. | 30–100[a;b] |
| Two semi-chronic (10 days) L(E)$C_{50}$ values for different taxonomic/feeding groups and for standard benthic test species typical for the ecosystem (freshwater or marine/estuarine) under evaluation | 30–100[a;b] |

[a]For substances with a specific toxic mode of action (e.g. insecticides and herbicides) it may suffice to test two representative species of the potentially sensitive taxonomic group(s). This is demonstrated when the representative test species of the sensitive taxonomic group(s) that drive the risk are an order of magnitude more sensitive than the other test species in the chronic aquatic effect assessment for pelagic species

[b]For extrapolate semi-chronic toxicity data a range in AF is proposed to acknowledge differences in toxic mode-of-action and associated differences in time to onset-of-effects. An AF in the lower range may be selected for compounds with a short time to onset-of-effects and an AF in the higher range if latent effects likely will occur (informed by toxicity data of pelagic organisms and read across using data for compounds with a similar mode of action)

strategy. However, in the chronic effect assessment based on spiked sediment toxicity data, the geometric mean approach might be more difficult to use. This is because the chronic toxicity data for different species within the same taxonomic and/or feeding group in the majority of cases concern different measurement

endpoints—such as mortality, growth, biomass and emergence—in tests with different durations. Furthermore, the evaluation of the predictive value of the geometric mean approach by EFSA (2005) was predominantly based on acute toxicity data. Consequently, for the time being, we propose restricting the geometric mean approach for deriving a $PNEC_{sed;ch}$ on the basis of (10 days) semi-chronic $L(E)C_{50}$ values for benthic species of the same taxonomic group and with the same feeding strategy. For this purpose, an AF of 100–300 (if at least three taxa representative for the system under evaluation are available) or 200–500 (if less than three taxa representative for the system under evaluation are available) as proposed in Table 5 should be applied to the geometric mean $L(E)C_{50}$ value for comparable semi-chronic toxicity of all species belonging to the most sensitive taxonomic group. An AF in the lower range may be selected for compounds with a short time to onset-of-effects and an AF in the higher range if latent effects likely will occur (informed by toxicity data of pelagic organisms and read across using data for compounds with a similar mode of action). In the future, when more chronic spiked sediment laboratory toxicity data become available for organic chemicals and benthic organisms of the same taxonomic group, as well as appropriate semi-field experiments to evaluate the ecological relevance of these laboratory data, the geometric mean approach to derive chronic sediment PNECs based on chronic toxicity data and sub-lethal endpoints can be reconsidered.

### 9.4.2 Species Sensitivity Distribution (SSD) Approach

The SSD concept is an important probabilistic tool for ERA and accounts for differences in species sensitivity to different chemicals. SSDs are cumulative probability distributions of toxicity values for different species and assume a randomly distributed sensitivity for species. The model calculates hazardous concentration for x% of the species ($HC_x$). The use of the SSD approach in ERA is described in Posthuma et al. (2002). In current prospective ERA for pelagic water organisms, toxicity data for at least eight species (for pesticides EFSA 2013) and ten species (for other toxicants European Commission 2011b)—but preferably more—are needed to apply the SSD approach.

The predictive value of the SSD approach to avoid population and community-level effects predominantly has been evaluated for pelagic organisms and acute toxicity data whereas comparable toxicity data for benthic species are scarce. Whether the SSD approach based on chronic toxicity data and using measurement endpoints that often differ between species of different taxonomic groups, is over or under protective, remains to be investigated. Nevertheless, the SSD approach is widely accepted to set PNECs for pelagic organisms in technical guidance documents underlying European regulations and directives (e.g. EC 2011a; EFSA 2013). We, therefore, consider the SSD approach also feasible for sediment ERA.

Given the limited number of test protocols currently available for benthic species, as well as the limited published sediment toxicity data for organic

chemicals, it will be difficult to collect chronic toxicity data for more than ten benthic species. For sediment ERA, we propose—as a minimum—toxicity data for eight benthic species representing at least five different taxonomic/feeding groups, except when the ERA based on water organisms shows that a specific taxonomic group is at least an order magnitude more sensitive that other taxonomic groups. For example, this may be the case for toxicants with a specific toxic mode-of-action such as insecticides, for which arthropods (insects and crustaceans) are particularly sensitive, and herbicides, for which algae and macrophytes usually are the most sensitive groups. In case of organic toxicants with a specific toxic mode-of-action, the eight species with toxicity data to construct the SSD should preferably be selected from the sensitive taxonomic group(s) (EFSA 2013; Maltby et al. 2005; Maltby et al. 2009). We consider this minimum number of eight toxicity values as a reasonable and pragmatic solution to derive a chronic $PNEC_{sed;ch}$ when using the SSD approach, but we also recommend applying an AF to the hazardous concentration to 5 % of the species tested as calculated from the SSD ($HC_5$) to address the remaining uncertainty.

Since benthic species of freshwater and marine/estuarine ecosystems have many traits in common, we assume that sediment toxicity data for both freshwater and marine/estuarine benthic species can be combined to construct the SSD curve. Again, an AF may be applied to address the remaining uncertainty in deriving a $PNEC_{sed;ch}$ for marine/estuarine benthic species based on an $HC_5$ calculated from an SSD curve largely constructed with toxicity data from freshwater species and the other way around when deriving a $PNEC_{sed;ch}$ for freshwater species mainly based on marine/estuarine data. Guidance for criteria that can be used to select the size of the AF is shown in Table 6. The use of the SSD approach is valid only if it has been verified that the selected toxicity data show an appropriate fit with the model used to calculate the SSD curve (e.g. the Anderson-Darling test for goodness-of-fit is accepted) (Aldenberg and Jaworska 2000; Aldenberg et al. 2002; Van Vlaardingen et al. 2004).

Preferably, to derive a $PNEC_{sed;ch}$ based on the SSD approach, the SSD should be constructed with chronic $EC_{10}$/NOEC data addressing sub-lethal endpoints. However, if for an essential taxon, such as the species number eight in the SSD, a valid chronic toxicity value is missing but a valid semi-chronic toxicity value is available, then the approach described in Table 7 may be an option to derive the corresponding chronic $EC_{10}$/NOEC. The size of the EF to be applied should be based on read-across information on toxicity data for pelagic and benthic species and compounds with a similar toxic mode-of-action. EFs in the lower range may be appropriate for compounds with a short time to onset-of-effects (e.g. pyrethroid insecticides) while EFs in the higher range may be more appropriate for compounds with more latent effects e.g. if they have hormone disruptive properties (e.g. tributyltin). We recommend using this extrapolation approach for no more than two species in the chronic SSD curve, which means that minimal six species with chronic data is available. Another approach is to use semi-chronic data (e.g. 10 days $L(E)C_{50}$ values) separately to construct an SSD and to calculate a corresponding semi-chronic $HC_5$. A $PNEC_{sed;ch}$ can be estimated with the approach

**Table 6** Criteria, based on European guidance documents (EFSA 2013; European Commission 2011b), that can be used to select the size of the assessment factor (AF) to be multiplied with the median $HC_5$ (SSD approach) to derive a $PNEC_{sed;ch}$ for benthic organisms

| AF | Criteria |
|---|---|
| 1 | • ≥10 chronic toxicity data (spiked sediment) |
| | • ≥8 different taxonomic/feeding groups[a] |
| | • ≥5 taxa from the type of ecosystem under evaluation (freshwater or marine/estuarine) |
| | • Lower limit $HC_5$ is less than a factor of 5 lower than the median $HC_5$ |
| 2 | • ≥10 chronic toxicity data (spiked sediment) |
| | • ≥8 different taxonomic/feeding groups[a] |
| | • ≥5 taxa from the type of ecosystem under evaluation (freshwater or marine/estuarine) |
| | • Lower limit $HC_5$ is more than a factor of 5 lower than the median $HC_5$ but less than a factor of 10 |
| 3 | • ≥8 chronic toxicity data (spiked sediment) |
| | • ≥5 different taxonomic/feeding groups[a] |
| | • ≥4 taxa from the type of ecosystem under evaluation (freshwater or marine/estuarine) |
| | • Lower limit $HC_5$ is less than a factor of 10 lower than the median $HC_5$ |
| 4 | • ≥8 chronic toxicity data (spiked sediment) |
| | • ≥5 different taxonomic/feeding groups[a] |
| | • ≥4 taxa from the type of ecosystem under evaluation (freshwater or marine/estuarine) |
| | • Lower limit $HC_5$ is more than a factor of 10 lower than the median $HC_5$ |
| 5 | • ≥8 chronic toxicity data (spiked sediment) |
| | • ≥5 different taxonomic/feeding groups[a] |
| | • <4 taxa from the type of ecosystem under evaluation (freshwater or marine/estuarine) |

[a]The default option is to select taxa belonging to different phylogenetic phyla or orders, unless (a) evidence is provided that a second benthic species selected for the same Phylum/Order has another feeding strategy, or (b) a specific taxonomic group is most sensitive (e.g. Arthropoda for insecticides). If (b), it suffices to select the required number of taxa from different Genera within the specific sensitive taxonomic group unless the second benthic species selected within a Genus has another feeding strategy (e.g. deposit feeder, suspension feeder, predator)

**Table 7** Proposed extrapolation factor to be applied to an individual semi-chronic or chronic toxicity value to estimate the corresponding chronic NOEC/$EC_{10}$ to be used in the SSD curve

| Available toxicity value | Extrapolation factor |
|---|---|
| 10 days $LC_{50}$ | 10–30 |
| 10 days $EC_{50}$ | 5–15 |
| 10 days NOEC | 3–10 |
| ≥21–28 days L(E)$C_{50}$ | 2–5 |

described in Table 6 (but using semi-chronic instead of chronic toxicity data in the SSD) as well as an extra AF of 5–10. An AF in the lower range may be selected for compounds with a short time to onset-of-effects and an AF in the higher range for compounds with latent effects (read across).

## 9.5 Tier-3 Approach Based on Semi-Field Experiments

An important requirement for the use of micro/mesocosm test systems to derive a chronic PNEC value for sediment-dwelling organisms is that the concentration-response relationships for benthic organisms are expressed in terms of exposure concentrations measured in the sediment compartment. Lipophilic organic chemicals that enter aquatic ecosystems via the water compartment will easily sorb to sediment particles in the upper sediment layer. In addition, many benthic invertebrates can be found in this layer, because of more favourable food and oxygen conditions. Consequently, the measurement and/or calculation of exposure concentrations in micro/mesocosm test systems to derive concentration-response relationships for benthic organisms should focus not only on the overlying water column but also on the upper sediment layer of these test systems. However, it may be useful to measure the dynamics in exposure concentrations in different sediment layers because of variations in the habitat occupied by different benthic taxa. We propose measuring the dynamics in exposure concentration (freely dissolved pore water concentration; total concentration in sediment normalised on the basis of OC content) in different sediment layers, for example 0–1, 1–2.5, 2.5–5 and 5–10 cm. Depending on the habitat preference of the benthic organism at risk, the exposure concentration in the appropriate sediment layer can be selected (e.g. the 0–1 cm layer for epibenthos or 0–10 cm layer for rooted macrophytes).

We propose microcosm experiments with spiked sediment, in which the colonisation success by benthic organisms is studied, as an option for the third tier. A design with larger test systems (mesocosms) is possible but might be relatively labour-intensive due to the spiking procedure of sediment and the large volume of spiked sediment that is required. The advantage of using spiked sediments when constructing microcosm test systems is that the contaminant under investigation is homogeneously distributed in the sediment compartment, at least initially. A possible disadvantage of such a design is that the benthic community is not yet established when exposure starts. However, spiked sediment microcosm tests can be used to study the impact of different sediment concentrations on the colonization of the sediment compartment by benthic organisms (seeded or spontaneous) and on their dynamics in population densities. Since the exposure regime of organic chemicals that accumulate in sediments, and for which an ERA has to be performed, is long term, the duration of spiked sediment microcosm tests should be relatively long as well (at least several months), allowing a sufficiently long colonization period for most benthic invertebrates and rooted plants.

Alternatively micro/mesocosm test systems with a well-established aquatic community can be used by spiking the water compartment with the contaminant. The advantage of this approach is that benthic populations already present in the test systems become exposed. A disadvantage, however, is that initially the benthic organisms are primarily exposed via the overlying water, while in a later phase sediment exposure becomes more important. In addition, this experimental design requires a more detailed assessment of the dynamics in exposure concentrations in

different sediment layers and the overlying water. Expressing the treatment-related responses of benthic organisms in terms of sediment exposure concentrations most likely will result in a relatively worst case assessment for epi-benthic taxa in particular, since the initial high exposure via overlying water will also affect these organisms. Note that in spiked water micro/mesocosm tests, the peak concentration of the organic contaminant in the sediment compartment is usually measured days to weeks after the application (Crum and Brock 1994).

## 9.6 Tier-4 Approach Based on Field Studies

Currently, too little data and experience are available to give specific recommendations for a Tier-4 approach based on field studies. However, chemical and biological monitoring studies in the sediment compartment of aquatic ecosystems may be used as a quality check of prospective ERA procedures for sediment organisms. Due to the lack of data and experience we do not discuss Tier-4 any further.

## 9.7 Effect Models to Supplement the Experimental Tiers

Current ERA schemes focus largely on toxicity and bioaccumulation at the individual level, while specific protection goals, as proposed in Sect. 4, focus mainly on the population level. Effect models can be used to extrapolate results of experimental tiers, amongst others, in linking spatial-temporal variability from exposure to effect, in predicting concentration-response relationships at different levels of biological organisation and different spatial and temporal scales, and in addressing ecological recovery times, bioaccumulation in food-webs and food-web interactions in ecosystems (Forbes et al. 2011; Galic et al. 2010; Hommen et al. 2010; Koelmans et al. 2001; van Beusekom et al. 2006). Despite their ability to include and extrapolate effects that cannot be captured by the experimental tiers, effect models are rarely recommended in technical documents of ERA (Galic et al. 2010; Hommen et al. 2010).

Although a wide variety of effect models have been developed (Bartell et al. 2003; Galic et al. 2010; Koelmans et al. 2001; Pastorok et al. 2003; Schmolke et al. 2010), most of these models address specific scientific research questions and are not directly suitable in ERA. Limitations of the use of ecological models have been described by Rykiel (1996) and Scheffer and Beets (1994). The use of effect models in ERA and their potential to address the requirements of protection goals in EU directives have been assessed previously (Galic et al. 2010; Hommen et al. 2010). Recently, EFSA (2014b) published a scientific opinion on good modelling practice in the context of mechanistic effect models for risk assessment of plant protection products, in which critical steps to implement the use of effect models in ERA were identified. *First*, a clear problem formulation is needed that

defines one or more specific questions according to the available data and specific protection goals and consider how the output matches with the specific protection goal. *Second*, the application domain of the model, and thus its predictive power, must to be considered to validate the broader conclusions based on model output. This means that either sufficient data should be available for model validation, or there is the potential to generate this data. *Third*, focal species must be selected, as not all species present in the ecosystem under evaluation can be modelled. Logically, these focal species should be vulnerable representatives of the main taxonomic groups of benthic organisms at risk. *Fourth*, realistic worst case environmental scenarios must be defined in relation to the specific protection goal and problem definition. An environmental scenario is a conceptual and quantitative description of the environmental system relevant to ERA, and has been defined by EFSA (2014b) as a combination of abiotic, biotic and agronomic parameters, thus including both exposure and effect. Scenarios from exposure models should be in line with those of the effect models, as they may share common variables (De Laender et al. 2015; Rico et al. 2015). EFSA (2014b) recommends that several scenarios should be considered, including a control/baseline and a toxic standard. A future research activity would be to develop and link scenarios in exposure and effect models that include the sediment compartment. For ERA, a set of freely available scientific sound robust models with a user friendly interface and a well-defined set of scenarios are needed (EFSA 2014b).

Currently, most effect models used in ERA focus on pelagic organisms and freshwater ecosystems, while marine systems (Galic et al. 2010), benthic organisms and the sediment compartment in general are usually disregarded. Below, we discuss effect models at the individual, population, ecosystem and spatial explicit level, which include benthic invertebrates and/or the sediment compartment or have the potential to do so.

### 9.7.1 Individual Level Models

Individual level models can be used as an addition to Tier 2. Given the characteristics of spatial and temporal variable exposure in the heterogeneous sediment compartment and the role of different exposure routes (e.g. exposure via pore water and food), the simplest models to use for linking exposure to effect at the individual level are TKTD models (e.g. GUTS) (Ashauer et al. 2006; Jager et al. 2011). TKTD models mechanistically account for time-varying exposure and effects of chemicals on individuals. More complex models that can be used are dynamic energy budget (DEB) models (Jager et al. 2013), which embed individual growth and development to account for growth dilution. For some freshwater benthic invertebrates (*Asellus aquaticus*, *Gammarus pulex*, and *C. riparius*), models that link exposure and effect have been developed and parametrized, while for other benthic species such as *M. balthica* (McLeod et al. 2008), uptake models exist but have not yet been linked to effect. Uptake, elimination and effects of contaminants are complicated for aquatic macrophytes

because roots in the sediment as well as leaf and stem surfaces in the water layer contribute to these processes (Diepens et al. 2014a; Heine et al. 2015). A model describing these processes has been developed for *E. canadensis* and *M. spicatum* (Diepens et al. 2014a) and for *M. spicatum* exposure has been coupled to effects (Heine et al. 2015).

### 9.7.2 Population-Level Models

Population models can be divided into three types: Lotka-Volterra type models, matrix models and individual-based models (IBM) (Galic et al. 2010), and can be used as an addition to the experimental Tier-3. IBMs are a convenient approach to deal with the complexity arising from complex life cycles of the organisms, seasonality and small- and large-scale spatial heterogeneity (Schmolke et al. 2010). Relevant population endpoints are recovery times after a peak exposure and population growth rate in case of chronic exposure and sub-lethal effects (Van der Ploeg et al. 2011). In the latter case, a more analytical approach to model structured populations is possible. Individual models can be connected to population models to link individual responses to chemical exposure (Baveco et al. 2014). For the freshwater (epi)benthic species (*Asellus aquaticus* and *Gammarus pulex*) and sediment dwelling species (*C. riparius*), models have been developed previously (Galic et al. 2013; Van den Brink et al. 2007). However, these models disregard sediment exposure via direct contact and ingestion of food and sediment particles. Because this may lead to an underestimation of actual exposure (Diepens et al. Under revision; Thomann et al. 1992), these models should be extended with exposure via this additional pathway. Recently, sediment uptake was explicitly added to a TKTD model integrated in an IBM to assess effect of sediment ingestion on the population level for *C. riparius* (Diepens et al. Submitted-a). This study showed that simultaneous exposure via water and ingestion of contaminated organic matter leads to a larger impact and a delayed recovery compared to exposure via water only. This highlights the importance of sediment and food ingestion as an exposure pathway for benthic invertebrates and underpins the need for sediment toxicity tests in ERA. For marine and estuarine organisms, *C. volutator* is the only benthic species for which a simple Leslie-matrix population model has been presented (Smit et al. 2006). This model has not yet been linked to exposure, which may constitute a direction for future research. Another possibility is to integrate the existing TKTD models for *M. spicatum* with an existing population model, such as that from Best and Boyd (1999).

### 9.7.3 Ecosystem Level Models

Ecosystem level models can be used as an addition to the experimental Tier 3. Only a few models have included higher levels of biological organisation, and mainly freshwater ecosystem models, such as AQUATOX (Park et al. 2008), have been applied in ERA (Galic et al. 2010). Food web accumulation modelling is a good

approach to assess secondary poisoning. Such models are flexible, usually well calibrated and have been evaluated. Several of these models, some including benthic organisms, have been confirmed and recommended for use in the regulatory context (Koelmans et al. 2001).

### 9.7.4 Spatially Explicit Models

Spatially explicit models can be used as an addition to field studies in Tier 4. Depending on the combination of exposure pattern and species at hand, it may be important to explicitly consider spatiotemporal dynamics of both exposure and populations by modelling spatially-structured populations. This approach is relevant when there is a spatial differentiation in the exposure patterns, with some parts of the system being exposed to higher concentrations than others. Clearly, dealing with this heterogeneity becomes more urgent when larger systems, such as watersheds, are being considered. Also, the species at hand should have limited mobility relative to the scale of the system (Baveco et al. 2014). At the lowest level of spatial complexity, we may deal with relatively simple uniform systems representing streams, ditches and ponds, as in the FOCUS surface water scenarios (FOCUS 2007) used for edge-of-field evaluation of plant protection products, or patches of estuarine and marine ecosystems. Ultimately, the larger spatial scale can be considered, for instance addressing both exposure and population dynamics in a complex ditch system (Focks et al. 2014), a larger watershed or interconnected patches of an estuarine/marine ecosystem. For *Chironomus*, landscape-level approaches can be developed, possibly based on Galic et al. (2013) and Focks et al. (2014). In those studies, however, the focus was on the overlying water compartment. A future activity could be to integrate exposure via the sediment into the landscape/watershed level, for example by using the recently developed sediment-including IBM model for *C. riparius* (Diepens et al. Submitted-a).

## *9.8 Effect Assessment for Vertebrates*

A comprehensive review on the use of fish for sediment toxicity assessment was given by Hallare et al. (2011). This review discusses the use of cell line assays, fish embryos, fish microarrays and whole fish tests. European Directive 2010/63/EU states that in the Member States of the European Union, testing with vertebrates should be minimized because of ethical considerations such as animal welfare. Therefore, as an animal friendly first-tier approach, cell line assays of vertebrate species can be used, such as the activated luciferase gene expression (CALUX) assay (Murk et al. 1996). These tests are designed to assess the sensitivity of a chemical for a specific mode of action such as dioxin-like activity or estrogenic activity (Houtman et al. 2006; Legler et al. 1999). However, we

consider the cell line assays not yet appropriate to be used in prospective ERA, since there is a lack of established cell lines. In addition, knowledge about the relationship between toxicant-induced cell line responses and effects on individuals and populations of vertebrates is insufficient (Bal-Price et al. 2014; Castano et al. 2003; Groothuis et al. 2015; Jha 2004; Lee and Steinert 2003). Therefore, an important topic for future research is the development of in vitro cell line assays and the evaluation of their ecotoxicological relevance. An alternative for cell line assays could be the sediment contact assay using zebrafish embryos (Hollert et al. 2003). Also newer approaches seem promising, including receptors and gene arrays in fish cells to identify the mode of action of sediment-bound chemicals (Hallare et al. 2011). As a more conventional Tier-1 assessment, the 10-day single species test (ASTM E2591 – 07 (ASTM 2013)) for amphibians may be used. Considering the very limited experience with benthic vertebrates, we will not provide a tiered ERA scheme for this group in this paper. However, the Tier-0 EP approach might provide a sufficiently conservative $PNEC_{sed;ch}$ estimate for benthic vertebrates.

## *9.9 Effect Assessment for Microorganisms*

Although advanced molecular techniques to determine functional and community responses exist, none of them are subjected to ring tests and described as standard tests (Diepens et al. 2014b). Moreover, experience with microorganisms in prospective sediment tests is limited. Several issues must be considered in a tiered ERA for microorganisms. Microorganisms might be negatively affected or stimulated by contaminants. Furthermore, functional redundancy is high among microorganisms. Consequently, even if there is a clear effect on the community composition, this may not result in an effect on their function (Van Beelen and Doelman 1997). This challenges the interpretation of the test outcomes, depending on which specific protection goal was adopted. Another challenge is to link exposure and effect, as microorganisms affect exposure by degradation and transformation of the contaminant. However, such feedback loops between toxicity and exposure play a role in all sediment tests, as it is very difficult to exclude microorganisms from a test system (Diepens et al. Submitted-b).

Although single species microbial tests do exist their ecological relevance requires support. A single species tests with *V. fischeri* test has been proposed within the first tier in retrospective risk assessment (Nendza 2002) and several International Organization for Standardization (ISO) tests with microorganisms are available. According to EFSA (2015), however, these tests are of limited use in prospective ERA and more research and method development is needed. The single-species test approach is hampered by the quite low representativeness of one species to the vast microbial geno- and phenotypic diversity of sediment systems. In addition, the overwhelming majority of microorganisms currently

cannot be cultured as pure culture isolates, but rather can be studied only in the context of more or less complex natural communities (EFSA 2015). Also ECHA (2014c) concluded that effects assessment for microbes should, when possible, evaluate the impact on the ecosystem or community level, rather than on single species level.

As a higher tier option, simple laboratory microcosm tests with spiked sediment in which functional endpoints of microbes, such as nitrification and denitrification, are determined can be used. These microcosm tests also allow the consideration of the community composition of microorganisms. For the terrestrial ERA, the nitrogen transformation test (OECD 216 (OECD 2000b)) is currently recommended. Ideally, a set of standard functional endpoints should be tested, guided by knowledge about the mode of action of the chemical. Another higher-tier option could be a microcosm or mesocosm study in which benthic invertebrates, macrophytes and microorganisms are tested simultaneously. For microorganisms, the same endpoints as in the laboratory microcosm can be used.

## 10 Sediment Effect Assessment: Case Studies

In this section we present three case studies with ivermectin, chlorpyrifos and tributyltin to investigate the tiered approach in sediment risk assessment as described above, with a focus on benthic invertebrates. These chemicals were selected based on data availability and type of chemical group. In the subsections below, a distinction is made between semi-chronic toxicity tests (test duration usually 10 days), and chronic toxicity tests (test duration usually $\geq$21–28 days). However, not all tests reported in the literature as chronic considered sub-lethal endpoints and/or covered the whole life cycle (or the most sensitive life-stage) of the test organisms. All sediment toxicity data provided in the cases are expressed in μg/g OC, based on the OC of the sediment as reported in the original papers and/or assuming an OC content of 2.5 % in standard OECD sediment with a peat content of 4–5 %.

### *10.1 The Pharmaceutical Ivermectin*

#### 10.1.1 Evaluation of Standard and Additional Toxicity Data for Pelagic Organisms and Ivermectin

The laboratory toxicity data for typical pelagic organisms and the pharmaceutical ivermectin are shown in Table 8.

It can be concluded from the information in Table 8 that invertebrate populations most likely are the most sensitive taxonomic group on which a chronic effects assessment for sediment-dwelling organisms should focus. Note that the reported

**Table 8** Toxicity data for typical water column organisms and the pharmaceutical ivermectin

| Test species | Acute toxicity | Chronic toxicity | Reference |
|---|---|---|---|
| *Pseudokirchneriella subcapitata* (green alga) | | 72 h $EC_{50} \geq 4$ mg/L<br>72 h NOEC = 391 µg/L | Garric et al. (2007) |
| *Daphnia magna* (*Crustacea*) | 48 h<br>$EC_{50} = 5.7$ ng/L | 21 days<br>NOEC = 0.0003 ng/L | Garric et al. (2007) |
| *Oncorhynchus mykiss* (fish) | 96 h<br>$LC_{50} = 3.0$ µg/L | | Halley et al. (1989) |
| *Salmo salar* (fish) | 96 h<br>$LC_{50} = 17$ µg/L | | Kilmartin et al. (1996) |
| Tier-1 $PNEC_{sw;ch}$ | | 0.0003/10 = 0.00003 ng/L | |
| Invertebrate community in mesocosms | | 10–97 days<br>NOEC ≤ 30 ng/L | Sanderson et al. (2007) |

toxicity values for the crustacean *Daphnia magna* are at least two orders of magnitude more sensitive than for the green alga and the fish. Another striking phenomenon is the high acute-to-chronic ratio that is reported for *Daphnia magna*. The Tier-1 $PNEC_{sw;ch}$ ($3 \times 10^{-5}$ ng/L) is based on the application of an AF of 10 to the lowest chronic toxicity value (for *D. magna*).

### 10.1.2 Tier-0 Effect Assessment for Ivermectin on Basis of Equilibrium Partitioning

The following equation is used to calculate the $PNEC_{sed;ch;EP}$:

$$PNEC_{sed;ch;EP} = PNEC_{sw;ch} * K_{oc} * 0.1 \quad (2)$$

In which $PNEC_{sed;ch;EP}$ is the concentration of the chemical in the sediment per unit mass of OC (µg/kg OC), $PNEC_{sw;ch}$ is the concentration of the chemical in pore water (µg/L) and $K_{oc}$ is the partition coefficient of the chemical to sediment OC (L/kg OC). We selected the tier-1 $PNEC_{sw;ch}$ of $3 \times 10^{-5}$ ng/L (Table 8) and a $K_{oc}$ geometric mean of 12,497 L/kg (n = 5) from a values range of 4000–25,800 L/kg (Krogh et al. 2008). The geometric mean $K_{oc}$ value, resulting in $PNEC_{sed;ch;EP}$ value of $3.75 \times 10^{-5}$ ng/g OC.

### 10.1.3 Tier-1 Effect Assessment for Benthic Organisms and Ivermectin

Chronic sediment toxicity data for three standard benthic freshwater organisms are available (insect, oligochaete, and nematode) (Table 9). In addition, the tests were conducted largely in accordance with internationally accepted guidelines: *C. riparius* (OECD 218), *L. variegatus* (OECD 225), and *C. elegans* (ISO

**Table 9** Sediment toxicity data for benthic organisms and the pharmaceutical ivermectin

| Species and test protocol | Effect endpoint | Toxicity endpoint | Toxicity value (µg/g OC) | Reference |
|---|---|---|---|---|
| *Chironomus riparius* Insecta (freshwater; OECD 218) | Mortality | 10 days $LC_{50}$ | 2.75 | Egeler et al. (2010) |
| | Mortality | 10 days $LC_{10}$ | 1.46 | |
| | Mortality | 10 days NOEC | 1.07 | |
| | Individual dry weight | 10 days NOEC | 0.13 | |
| | Female emergence | 28 days $EC_{50}$ | 0.39 | |
| | **Female emergence** | **28 days $EC_{10}$** | **0.14** | |
| | Female emergence | 28 days NOEC | 0.27 | |
| *Lumbriculus variegatus* Oligochaeta (freshwater: OECD 225) | Total dry weight | 28 days $EC_{50}$ | 131.86 | Egeler et al. (2010) |
| | **Total dry weight** | **28 days $EC_{10}$** | **28.76** | |
| | Total dry weight | 28 days NOEC | 7.08 | |
| *Caenorhabditis elegans* Nematoda (freshwater; ISO/CD 10872) | **Reproduction** | **4 days NOEC** | **4.31** | Liebig et al. (2010) |
| *Arenicola marina* Polychaeta (marine; non-standard test with field collected sediment) | Mortality | 10 days $LC_{50}$ | 16.48[a] | Allen et al. (2007), Thain et al. (1997) |
| | Mortality | 10 days NOEC | 12.50 | Thain et al. (1997) |
| | Mortality | 100 days $LC_{50}$ | 15.56 | Allen et al. (2007) |
| | Casting | 10 days $EC_{50}$ | 5.19 | |
| | Casting | 10 days NOEC | 2.16 | |
| | Casting | 100 days $EC_{50}$ | 6.41 | |
| | Casting | 100 days NOEC | <0.43 | |
| *Corophium volutator* Crustacea (marine; test with field collected sediment) | **Mortality** | **10 days $LC_{50}$** | **10.68[a]** | Davies et al. (1998), Thain et al. (1997) |
| | Mortality | 10 days NOEC | 1.67 | Davies et al. (1998) |
| | Mortality | 28 days $LC_{50}$ | 14.56 | Allen et al. (2007) |
| *Asterias rubens* Echinodermata (marine; non-standard test with field collected sediment) | Mortality | 10 days $LC_{50}$ | 11,800 | Davies et al. (1998) |
| | Mortality | 10 days NOEC | 2500 | |

The values in bold concern the standard toxicity data used in the Tier-1 effect assessment and were acquired in accordance with internationally accepted guidelines (see Table 2 in Diepens et al. 2014b)

[a]Geometric mean

10872). In the chronic effect assessment, 28 days $EC_{10}$ values are preferred over 28 days NOEC values.

In Table 9, *C. riparius* shows lower toxicity values than *L. variegatus* and *C. elegans*. Selecting the 28 days $EC_{10}$ of 0.14 µg/g OC of *C. riparius* and the application of an assessment factor of 10 (Table 5) results in a Tier-1 $PNEC_{sed;ch}$ of 0.014 µg/g OC for sediment-dwelling organisms in freshwater ecosystems. This Tier-1 PNEC value is lower than all toxicity values reported for freshwater and marine benthic organisms presented in Table 9, but is considerably higher than the Tier-0 $PNEC_{sed;ch;EpP}$ calculated above (Fig. 4).

For marine benthic organisms, toxicity data are available but the tests were not conducted according to standard test protocols, with the possible exception of the test with the crustacean *C. volutator*. The Tier-1 $PNEC_{sed;ch}$ for marine/estuarine benthic organisms can be derived on the basis of Table 5 in different ways. To demonstrate the concept of the table, we will show all possibilities. One option is to use the three chronic toxicity data for standard freshwater test species by applying an AF of 100 to the lowest chronic NOEC/$EC_{10}$ (Table 5). Applying an AF of 100 to the 28 days $EC_{10}$ of 0.14 µg/g OC of *C. riparius* results in a Tier-1 $PNEC_{sed;ch}$ of 0.0014 µg/g OC for sediment-dwelling organisms in marine/estuarine ecosystems. A second option is to use three semi-chronic toxicity data for marine organisms by applying and AF of 30–100 to the lowest semi-chronic 10 days L(E)$C_{10}$/NOEC (Table 5). In this case we selected an AF of 100 since the acute to chronic ratio for *Daphnia magna* was very large (Table 8). Applying an AF of 100 to the 10 days NOEC of 1.67 µg/g OC of *C. volutator* results in a Tier-1 $PNEC_{sed;ch}$ of 0.0167 µg/g OC for sediment-dwelling organisms in marine/estuarine ecosystems. A third option is to use three semi-chronic toxicity data for marine organisms by applying an AF of 100–300 to the lowest semi-chronic 10 days L(E)$C_{50}$ (Table 5). Again we selected an AF in the higher range since the acute to chronic ratio for *Daphnia magna* was very large (Table 8). Applying an AF of 300 to the 10 days $EC_{50}$ of 5.19 µg/g OC of *C. volutator* results in a Tier-1 $PNEC_{sed;ch}$ of 0.0173 µg/g OC for sediment-dwelling organisms in marine/estuarine ecosystems. Each of the Tier-1 PNEC values is lower than all toxicity values reported for freshwater and marine benthic organisms presented in Table 9 and again is considerably higher than the Tier-0 $PNEC_{sed;ch;EpP}$ calculated above. Options 2 and 3 based on marine species are very similar, but these options are an order of magnitude higher than the Tier-1 $PNEC_{sed;ch}$ derived for marine/estuarine ecosystems from the freshwater chronic toxicity data (due to the extra factor of 10 for the freshwater—marine extrapolation) (Fig. 4). To assess the $PNEC_{sed;ch}$ for estuarine/marine benthic species, it is logical to prefer options 2 and 3, since these options use toxicity data for marine/estuarine benthic organisms.

### 10.1.4 Tier-2 Effect Assessment Based on Standard and Additional Test Species for Ivermectin

Geometric Mean Approach

When analysing the toxicity data presented in Table 9, the geometric mean approach cannot be used since all toxicity data concern test species from different taxonomic groups.

Species Sensitivity Distribution Approach

When analysing the toxicity data presented in Table 9, the SSD approach cannot be used since semi-chronic or chronic toxicity values for fewer than eight benthic species are available.

### 10.1.5 Tier-3 Effect Assessment Based on Micro/Mesocosm Experiments for Ivermectin

The effects of ivermectin exposure were investigated in indoor freshwater microcosms using ivermectin-spiked sediments, with a focus on the response of the nematode community (Brinke et al. 2010). An overall microcosm NOEC for Nematoda was observed at 0.4 μg/g OC. This value is approximately a factor of 10 lower than the 4 days NOEC observed for the nematode *C. elegans* in a laboratory test. To date, it remains a research question whether this NOEC for the populations of Nematoda is representative for populations of other potentially sensitive taxonomic groups (e.g. arthropods, Oligochaeta and Polychaeta)

### 10.1.6 Conclusions from the Ivermectin Toxicity Data for Benthic Organisms

- Applying the concept of EP to the $PNEC_{sw;ch}$ (based on water toxicity data for pelagic organisms) results in a very conservative estimate of the $PNEC_{sed;ch;EP}$ (Tier 0) (Fig. 4)
- The semi-chronic sediment toxicity data for freshwater and marine benthic organisms overlap
- The derived $PNEC_{sed;ch}$ based on the Tier-1 approach (Table 5) was remarkably similar for freshwater and marine/estuarine species, at least when using the corresponding toxicity data
- In microcosms, the overall NOEC of the Nematode community was approximately a factor of 10 lower than the NOEC of the standard test nematode *C. elegans*

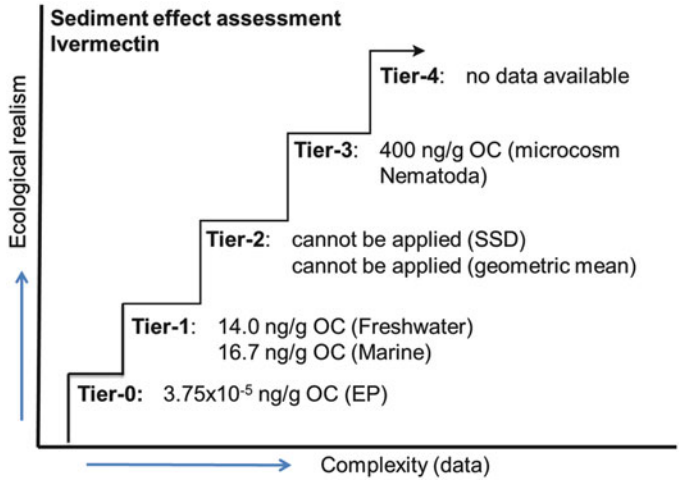


**Fig. 4** Predicted no effect concentration (ng/g OC) for ivermectin derived for different tiers

## *10.2 The Insecticide Chlorpyrifos*

### 10.2.1 Evaluation of Standard and Additional Toxicity Data for Pelagic Organisms and Chlorpyrifos

The laboratory toxicity data for typical pelagic organisms and the insecticide chlorpyrifos are shown in Table 10.

It can be concluded from the information in Table 10 that invertebrate populations, and arthropods in particular, are probably the most sensitive taxonomic group on which a chronic effects assessment for sediment-dwelling organisms should focus. Note that the reported toxicity values for aquatic arthropods are at least one to two orders of magnitude lower than for algae and fish. The acute-to-chronic ratio for aquatic arthropods is approximately a factor of 10.

### 10.2.2 Tier-0 Effect Assessment for Chlorpyrifos Based on Equilibrium Partitioning

$K_{oc}$ values reported for chlorpyrifos have a geometric mean of 10,617 L/kg (n = 7) in the range of 3000–25,565 L/kg (Gebremariam et al. 2012). Initially we selected the lower tier $PNEC_{sw;ch}$ of 0.00046 µg/L (see Table 10) and the abovementioned geometric mean $K_{oc}$ value, resulting in a $PNEC_{sed;ch;EP}$ value of 0.00049 µg/g OC using Eq. (2). We then selected the higher-tier $PNEC_{sw;ch}$ of 0.0033 µg/L (see Table 10) and the abovementioned geometric mean $K_{oc}$ value, resulting in a $PNEC_{sed;ch;EP}$ value of 0.0035 µg/g OC using Eq. (2). We consider this latter value to be more realistic, since it is based on higher-tier information.

**Table 10** Toxicity data for typical water column organisms and the insecticide chlorpyrifos

| Test species | Acute toxicity | Chronic toxicity | Reference |
|---|---|---|---|
| *Skeletonema costatum* (marine diatom) | | EC50 = 403 µg/L | Alterra database |
| *Daphnia magna* (Crustacea) | 48 h $EC_{50}$ = 0.4 µg/L | 21 days NOEC = 0.057 µg/L | Alterra database |
| *Chironomus riparius* (Insecta) | 96 h $EC_{50}$ = 0.09 µg/L | | Alterra database |
| *Americamysis bahia* (Crustacea) | 96 h $EC_{50}$ = 0.04 µg/L | 35 days NOEC = 0.0046 µg/L | Alterra database |
| *Oncorhynchus mykiss* (fish) | 96 h $LC_{50}$ = 3.0 µg/L | 21 days NOEC = 0.51 µg/L | Alterra database |
| *Tier-1 $PNEC_{sw;ch}$* | | 0.00046 µg/L | Application of AF of 10 to the chronic NOEC of *A. bahia* |
| *SSD aquatic arthropods* | Acute $HC_5$ = 0.042 µg/L (n = 42) | | Alterra database |
| *Lowest NOEC micro/mesocosm* | 0.033–0.10 µg/L for arthropods (pulsed exposure) | 0.01 µg/L for arthropods (more or less constant exposure) | Alterra database |
| *Higher tier $PNEC_{sw;ch}$* | | 0.005 µg/L | Application of AF of 2 to threshold level of 0.01 µg/L in chronic micro/mesocosm study |

### 10.2.3 Tier-1 Effect Assessment for Benthic Organisms and Chlorpyrifos

For one freshwater benthic insect species (*C. riparius*) a chronic sediment toxicity value is available (21 days NOEC of 0.32 µg/g OC), although this value was not derived according to standard guidelines (Table 11). Furthermore, 10 days $LC_{50}$ values are available for the freshwater insect *C. dilutus*, for the freshwater/marine amphipod *H. azteca*, for the estuarine amphipod *E. estuarius* and for the marine amphipod *A. abdita*. These tests were conducted essentially in accordance with USA guidelines.

The freshwater invertebrate species listed in Table 11 comprise only two taxonomic groups (insects and crustaceans) and the species *C. riparius*, *C. dilutus*, and *H. azteca*. The insect *C. riparius* showed the lowest toxicity values (21 days NOEC of 0.32 µg/g OC; 21 days $LC_{50}$ of 0.43 µg/g OC) but this test was not conducted according to standard test guidelines. However, the semi-chronic tests conducted with *C. dilutus* and *H. azteca* can be considered standard ASTM tests. Because of the specific mode of action of chlorpyrifos, the inhibition of acetylcholinesterase, two species are sufficient. Following the Tier-1 effect

**Table 11** Sediment toxicity data for benthic organisms and the insecticide chlorpyrifos

| Species and test protocol | Effect endpoint | Toxicity endpoint | Toxicity (µg/g OC) | Reference |
|---|---|---|---|---|
| *Chironomus riparius* Insecta (Freshwater; field collected sediment) | Mortality | 4 days $LC_{50}$ | 1.58[a] | Hooftman et al. (1993) |
| | Mortality | 21 days $LC_{50}$ | 0.43[a] | |
| | Mortality | 21 days NOEC | 0.32[a] | |
| *Chironomus dilutus* Insecta (freshwater; ASTM E1706) | **Mortality** | **10 days $LC_{50}$** | **7.19[a]** | Ankley et al. (1994), Harwood et al. (2009) |
| *Hyalella azteca* Crustacea; Amphipoda (fresh/estuarine: ASTM E1706) | **Mortality** | **10 days $LC_{50}$** | **2.8[a]** | Amweg and Weston (2007), Hintzen et al. (2009), Weston et al. (2009) |
| *Ampelisca abdita* Crustacea; Amphipoda (marine: ASTM E1367) | **Mortality** | **10 days $LC_{50}$** | **15.9** | Anderson et al. (2008) |
| *Eohaustorius estuarius* Crustacea; Amphipoda (estuarine: ASTM E1367) | **Mortality** | **10 days $LC_{50}$** | **13.2** | Anderson et al. (2008) |
| *Amphiascus tenuiremus* Crustacea; Copepoda; field collected sediment | Mortality | 4 days $LC_{50}$ | 1.74 | Green et al. (1996) |

The values in bold concern the toxicity data acquired essentially in accordance with internationally accepted guidelines (see Table 2 in Diepens et al. 2014b)
[a]Geometric mean

assessment according to Table 5, an AF of 100–300 has to be applied to the lowest 10 days $LC_{50}$ value of *C. dilutus* and *H. azteca*. In this case we selected an AF of 100 since the toxicity data for pelagic organisms showed a relatively low acute to chronic ration, suggesting a fast time to onset-of-effects. The amphipod *H. azteca* (geomean 10 days $LC_{50}$ of 2.8 µg/g OC) is the most sensitive, resulting in a Tier-1 $PNEC_{sed;ch}$ of 0.028 µg/g OC for sediment-dwelling organisms in freshwater ecosystems. This Tier-1 $PNEC_{sed;ch}$ value is substantially lower than all toxicity values reported for freshwater and marine benthic organisms presented in Table 11. Furthermore, this Tier-1 $PNEC_{sed;ch}$ value is higher than the Tier-0 $PNEC_{sed;ch;EP}$ calculated from the lower tier $PNEC_{sw;ch}$ and higher tier $PNEC_{sw;ch}$ (Fig. 5).

In Table 11, semi-acute toxicity data for three marine/estuarine benthic organisms are shown. These data were acquired according to ASTM guidelines using the amphipods *H. azteca*, *A. abdita* and *E. estuarius*. These taxa comprise only one taxonomic/feeding group. However, when the 4 days $LC_{50}$ value for the marine copepod *A. tenuiremus* is included in the Tier-1 core data set, the marine toxicity data then comprise two feeding strategies and two taxonomic groups. The Tier-1 $PNEC_{sed;ch}$ for marine/estuarine benthic organisms can be derived by applying an AF of 100–300 to the lowest $LC_{50}$ for the combination *H. azteca*, *A. abdita*, *E. estuarius*, and *A. tenuiremus*. Again we selected and AF in the lower range because of the relatively low acute to chronic ration for pelagic organisms. Although not a standard test species, the marine benthic copepod has the lowest $LC_{50}$ value (1.74 μg/g OC), resulting in a Tier-1 $PNEC_{sed;ch}$ of 0.0174 μg/g OC for sediment-dwelling organisms in marine/estuarine ecosystems. This Tier-1 $PNEC_{sed}$ value is substantially lower than all toxicity values reported for freshwater and marine benthic organisms presented in Table 11. Again, this Tier-1 $PNEC_{sed;ch}$ value is higher than the Tier-0 $PNEC_{sed;ch;EP}$ calculated from the lower tier $PNEC_{sw;ch}$, but equals Tier-0 $PNEC_{sed;ch;EP}$ values calculated from the higher tier $PNEC_{sw;ch}$ (Fig. 5).

### 10.2.4 Tier-2 Effect Assessment Based on Standard and Additional Test Species for Chlorpyrifos

Geometric Mean Approach

When analysing the data presented in Table 11, the geometric mean approach is only possible for the 10 days $LC_{50}$ values for the amphipods *H. azteca*, *A. abdita* and *E. estuarius*. The geometric mean $LC_{50}$ for these taxa is 8.4 μg/g OC. This value is higher than the 10 days $LC_{50}$ of 2.8 μg/g OC for *H. azteca* (the most sensitive species in the freshwater data set) and the 4 days $LC_{50}$ of 1.74 μg/g OC for *A. tenuiremus* (the most sensitive species in the marine/estuarine data set). Applying the geometric mean approach (AF of 100 as used in Tier-1 and the geometric mean $LC_{50}$ of 8.4 μg/g OC), results in a Tier-2 $PNEC_{sed;ch}$ values of 0.084 μg/g OC. This value can be used for both freshwater and marine taxa since for both types of organisms sufficient semi-chronic toxicity data are available.

Species Sensitivity Distribution Approach

When analysing the toxicity data presented in Table 11, the SSD approach cannot be used since sediment toxicity data are available for fewer than eight benthic species.

### 10.2.5 Tier-3 Effect Assessment Based on Micro/Mesocosm Experiments

An appropriate micro/mesocosm test that allowed concentration-response relationships for benthic organisms and sediment exposure concentrations to be derived could not be found in the open literature.

### 10.2.6 Conclusions from the Chlorpyrifos Toxicity Data for Benthic Organisms for Chlorpyrifos

- Applying the concept of EP to the higher-tier $PNEC_{sw;ch}$ (based on a microcosm test with a chronic exposure regime) results in a lower $PNEC_{sed;ch;EP}$ (Tier-0) estimate when compared with the Tier-1 $PNEC_{sed;ch}$ estimates for both freshwater and marine/estuarine ecosystems (Fig. 5)
- The available sediment toxicity data are limited to arthropods and are predominantly semi-chronic in nature
- The sediment toxicity data for freshwater and marine benthic arthropods overlap

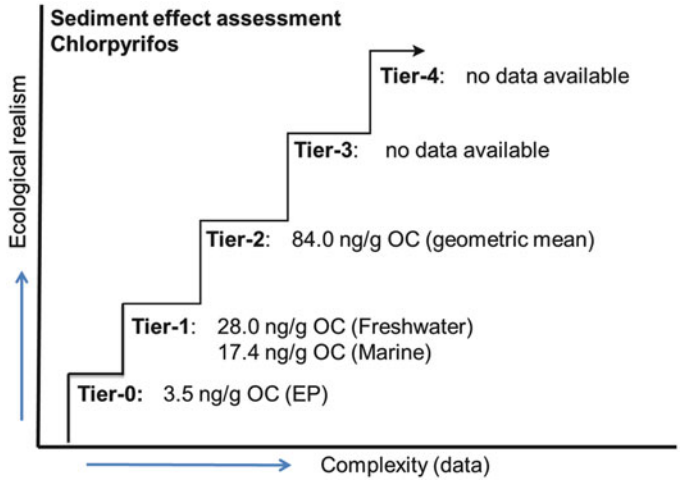


**Fig. 5** Predicted no effect concentration (ng/g OC) for chlorpyrifos derived for different tiers

## *10.3 The Biocide Tributyltin*

### 10.3.1 Evaluation of Standard and Additional Toxicity Data for Pelagic Organisms and Tributyltin

The laboratory toxicity data for water organisms and long-term water exposure to the biocide tributyltin are shown in Table 12.

It can be concluded from the information in Table 12 that Mollusca are probably the most sensitive taxonomic group. However, the chronic toxicity values for aquatic arthropods are reported to be relatively low as well. The $PNEC_{sw;ch}$ for pelagic organisms can be derived by applying an AF of 10 to the chronic NOEC of *Nucella lapillus*, resulting in a value of 0.0002 µg/L. This value is similar to the annual average quality standard (AA-QS) (0.0002 µg/L) derived for tributyltin compounds as part of the Water Framework Directive (European Commission 2005).

**Table 12** Chronic toxicity data for water organisms and the biocide tributyltin (data from IPCS 1999; EPA 1997; Hall et al. 2000)

| Test species | Criterion | Chronic toxicity |
|---|---|---|
| Algae | $IC_{50}$ (primary production) | 0.92–320 µg/L |
| *Daphnia magna* (Crustacea; Cladocera) | 21 days NOEC (life cycle test) | 0.14–0.25 µg/L |
| *Acartia tonsa* (Crustacea; Copepoda) | 6 days geometric mean of NOEC/LOEC | 0.014 µg/L |
| *Euryptemora affinis* (Crustacea; Copepoda) | 13 days geometric mean of NOEC/LOEC (Life Cycle test) | <0.088 and 0.15 µg/L |
| *Acanthomysis scuppta* (Crustacea; Mysidae) | 63 days geometric mean of NOEC/LOEC (Life Cycle test) | 0.13 µg/L |
| *Mytilus edulus* (Mollusca; Bivalvia) | 33 days geometric mean of NOEC/LOEC | 0.017 µg/L |
| *Crassostrea gigas* (Mollusca; Bivalvia) | geometric mean of NOEC/LOEC Shell thickening | 0.02 µg/L |
| *Nucella lapillus* (Mollusca; Gastropoda) | 2 year geometric mean of NOEC/LOEC (imposex) | 0.002 µg/L |
| *Oncorhynchus mykiss* (fish) | 110 days; 20 % growth reduction | 0.2 µg/L |
| *Pimephales promelas* (fish) | 33 days geometric mean of NOEC/LOEC (Early life stage test) | 0.26 µg/L |
| $PNEC_{sw;ch}$ | Application of AF of 10 to the chronic NOEC of *Nucella lapillus* | 0.0002 µg/L |

### 10.3.2 Tier-0 Effect Assessment for Tributyltin Based on Equilibrium Partitioning

$K_{oc}$ values reported for tributyltin compounds have a geometric mean of 1317 L/kg (n = 16) with a range of 188–2814 (Langston and Pope 1995). We selected the $PNEC_{sw;ch}$ of 0.0002 μg/L (see Table 12) and the geometric mean $K_{oc}$ value of 1317 L/kg, resulting in a $PNEC_{sed;ch;EP}$ value of $2.63 \times 10^{-5}$ μg/g OC using Eq. (2).

### 10.3.3 Tier-1 Effect Assessment for Benthic Organisms and Tributyltin

An overview of the toxicity data for benthic invertebrates and spiked sediment tests with tributyltin is presented in Table 13. Note that in several of the studies reported in this table, toxicity values were expressed in terms of ng Sn/g DW sediment. These values were converted to μg TBT/g OC with a factor of 2.6 (=118.7/307.06), derived by the division of the molecular mass of tin by the molecular mass of tributyltin.

**Table 13** Sediment toxicity data for benthic organisms and the biocide tributyltin

| Species and test protocol | Effect endpoint | Toxicity endpoint | Toxicity (μg TBT/g OC) | Reference |
|---|---|---|---|---|
| *Chironomus riparius* Insecta (Fresh; artificial sediment; semi-artificial sediment) | Mortality | 28 days $LC_{50}$ | 227.9 | Marinković et al. (2011) |
| | Mortality | 28 days NOEC | 76.0 | |
| | **Male emergence time** | **28 days $EC_{10}$[a]** | **14.7** | |
| | Growth | 10 days $EC_{50}$ | 750.3 | Day et al. (1998) |
| | Growth | 10 days NOEC | 296.6 | |
| *Hexagenia* Insecta (fresh: semi-artificial sediment) | Mortality | 21 days $LC_{50}$ | 296.6 | Day et al. (1998) |
| | Growth | 21 days $EC_{50}$ | 104.7 | |
| | **Growth** | **21 days NOEC** | **52.3** | |
| *Tubifex tubifex* Oligocheate (fresh: semi-artificial sediment) | Mortality | 28 days $LC_{50}$ | 2320.8 | Day et al. (1998) |
| | Growth | 28 days $EC_{50}$ | 279.2 | |
| | **Growth** | **28 days NOEC** | **122.1** | |
| *Hyalella azteca* Crustacea; Amphipoda (fresh/estuarine: field collected sediment; semi-artificial sediment) | Mortality | 28 days $LC_{50}$ | 189.8 | Bartlett et al. (2004) |
| | Mortality | 70 days $LC_{50}$ | 121.3 | |
| | **Mortality** | **70 days $LC_{10}$[a]** | **26.0** | |
| | Reproduction | 70 days $EC_{50}$ | 30.9 | |
| | Growth | 14 days $EC_{50}$ | 244.3 | Day et al. (1998) |
| | Growth | 14 days NOEC | 139.6 | |

(continued)

**Table 13** (continued)

| Species and test protocol | Effect endpoint | Toxicity endpoint | Toxicity (µg TBT/g OC) | Reference |
|---|---|---|---|---|
| *Potamopyrgus antipodarum* Mollusca; Gastropoda (freshwater; artificial sediment) | Mortality | 28 days $LC_{50}$ | 58.5 | Duft et al. (2003) |
| | Mortality | 56 days $LC_{50}$ | 44.8 | |
| | Total embryos development | 28 days $EC_{50}$ | 18.0 | |
| | Total embryos development | 56 days $EC_{50}$ | 9.8 | |
| | Total embryos development | 28 days $EC_{10}$ | 1.103 | |
| | Total embryos development | 56 days $EC_{10}$ | 0.365 | |
| *Corophium volutator* Crustacea; Amphipoda (marine; field collected sediment) | **Mortality** | **10 days $LC_{50}$** | **5.7** | Stronkhorst et al. (1999) |
| *Eohaustorius washingtonianus* Crustacea; Amphipoda (marine: field collected sediment) | Mortality | 9 days $LC_{50}$ | 170 | Meador et al. (1997) |
| | Mortality | 41 days $LC_{50}$ | 78 | |
| *Rhepoxynius abronius* Crustacea; Amphipoda (marine; field collected sediment) | Mortality | 10 days $LC_{50}$ | 3500 | Meador et al. (1997) |
| *Armandia brevis* P olychaeta (marine: field collected sediment) | Mortality | 10 days $LC_{50}$ | 930 | Meador et al. (1997) |
| | Mortality | 42 days $LC_{50}$ | 158.2 | Meador and Rice (2001) |
| | Growth | 42 days $EC_{50}$ | 38.7 | |
| | Growth | 42 days $EC_{10}$ | 5.9 | |
| *Echinocardium cordatum* Echinodermata (marine; field collected sediment) | Mortality | 14 days $LC_{50}$ | 10.5 | Stronkhorst et al. (1999) |
| | Mortality | 28 days $LC_{50}$ | 4.1 | |
| | Mortality | 28 days NOEC | 2.94 | |
| *Ruppia maritima* Aquatic macrophyte (marine: field collected sediment) | Relative growth rate | 21 days $EC_{10}$[a] | 0.692 | Jensen et al. (2004) |

The values in bold concern toxicity data acquired essentially in accordance with internationally accepted guidelines (see Table 2 in Diepens et al. 2014b). Note that in several of the studies reported in this table, toxicity values were expressed in terms of ng Sn/g DW sediment

[a]Estimated value from graphs

The chronic NOEC/L(E)$C_{10}$ toxicity values for standard freshwater benthic invertebrates concern the insect *C. riparius* (28 days $EC_{10}$ of 14.7 µg TBT/g OC), the insect *Hexagenia* (21 days NOEC of 52.3 µg TBT/g OC), the crustacean *H. azteca* (28 days $LC_{10}$ of 26.0 µg TBT/g OC) and the oligocheate *T. tubifex* (28 days NOEC of 122.1 µg TBT/g OC) (Table 13). Another chronic toxicity value for a freshwater benthic organism concerns the freshwater snail *Potamopyrgus antipodarum* (56 days $EC_{10}$ of 0.365 µg TBT/g OC) (Table 13). Although the latter species is not a standard test species, it is considered a relevant Tier-1 test species, since the information presented in Table 12 shows that molluscs in particular are the most sensitive taxonomic group.

Following the Tier-1 effect assessment according to Table 5, an AF of 10 has to be applied to the lowest chronic NOEC/$EC_{10}$ value for the combination *C. riparius*, *Hexagenia*, *H. azteca*, *P. antipodarum* and *T. tubifex*. The snail *P. antipodarum* (56 days $EC_{50}$ of 0.365 µg TBT/g OC) is the most sensitive, resulting in a Tier-1 $PNEC_{sed;ch}$ of 0.0365 µg TBT/g OC for sediment-dwelling organisms in freshwater ecosystems. This value is considerably higher than the Tier-0 $PNEC_{sed;ch;EP}$ value mentioned above based on the EP concept (Fig. 6).

In Table 13, chronic NOEC/$EC_{10}$ values are available for four marine/estuarine benthic organisms: the amphipod *H. azteca*, the polychaete *Armandia brevi*, the echinoderm *E. cordatum* and the aquatic macrophyte *Ruppia maritime*. Only *H. azteca* is a standard test species. Furthermore, for one standard test species (the amphipod *C. volutator*) a 10 days $LC_{50}$ is available. However these taxa do not comprise Mollusca, the most sensitive taxonomic group mentioned in Table 13 (water exposure tests). Consequently, the freshwater snail *P. antipodarum* (56 days $EC_{10}$ of 0.365 µg TBT/g OC) was also considered when deriving a Tier-1 $PNEC_{sed;ch}$ for marine/estuarine ecosystems. Following the Tier-1 effect assessment according to Table 5, an AF of 10 has to be applied to the lowest chronic NOEC/$EC_{10}$ for the combination *H. azteca*, *A. breva*, *E. cordatum*, *Ruppia maritime*, and *P. antipodarum*. The snail *P. antipodarum* (56 days $EC_{10}$ of 0.365 µg TBT/g OC) is the most sensitive, resulting in a Tier-1 $PNEC_{sed;ch}$ of 0.0365 µg TBT/g OC for sediment-dwelling organisms in estuarine/marine ecosystems. Again, this value is considerably higher than the Tier-0 $PNEC_{sed;ch;EP}$ value mentioned above based on the EP concept (Fig. 6). Alternatively, a Tier-1 $PNEC_{sed;ch}$ for marine/estuarine ecosystems can be derived by using the semi-chronic toxicity data for the amphipods *H. azteca* (14 days $EC_{50}$ of 244.3 µg TBT/g OC), *C. volutator* (10 days $LC_{50}$ of 5.7 µg TBT/g OC), *E. washingtonianus* (9 days $LC_{50}$ of 170 µg TBT/g OC), and *R. abronius* (10 days $LC_{50}$ is 3500 µg TBT/g OC), the polychaete *A. brevis* (10 days LC50 is 930 µg TBT/g OC) and the echinoderm *E. cordatum* (14 days $LC_{50}$ is 10.5 µg TBT/g OC). These marine taxa comprise three taxonomic groups, so that an AF of 100–300 (see Table 5) can be applied to the lowest semi-chronic L(E)$C_{50}$ to derive a $PNEC_{sed;ch.}$ We selected an AF of 300 since the available toxicity data reveal latent effects and hormone-disrupting properties of TBT. Applying and AF of 300 to the lowest 10 days $LC_{50}$ (5.7 µg TBT/g OC for *C. volutator*) results in a $PNEC_{sed;ch}$ of 0.019 µg TBT/g OC for marine/estuarine benthic organisms. Note that this $PNEC_{sed;ch}$ value is lower than the Tier-1 $PNEC_{sed;ch}$ of 0.0365 µg TBT/g

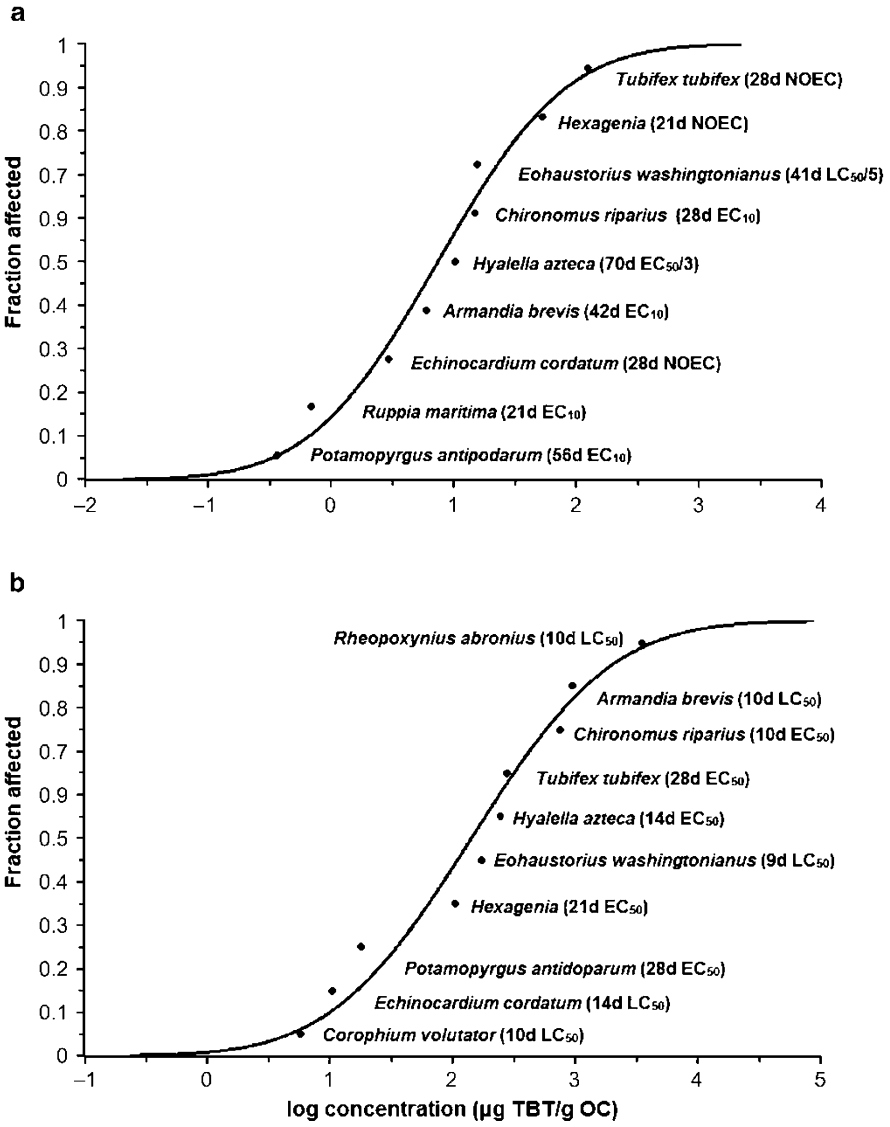


**Fig. 6** Species Sensitivity Distribution (SSD) for tributyltin constructed with (**a**) (estimated) chronic $EC_{10}$/NOEC values for freshwater and marine benthic invertebrates (n = 9) and (**b**) semi-chronic $L(E)C_{50}$ values for freshwater and marine benthic invertebrates (n = 10) (data from Table 14)

OC for sediment-dwelling organisms in estuarine/marine ecosystems derived on the basis of chronic toxicity data. However, the chronic Tier-1 $PNEC_{sed;ch}$ was selected in the effect assessment, since an assessment based on chronic toxicity data overrules that based on semi-chronic toxicity data.

### 10.3.4 Tier-2 Effect Assessment Based on Standard and Additional Test Species for Tributyltin

Geometric Mean Approach

Considering the data presented in Table 13, and the criteria for the geometric mean approach mentioned in Sect. 9.4, this approach seems possible only for the 9–10 days $LC_{50}$ values for the marine amphipods *C. volutator*, *E. washingtonianus*, and *R. abronius*, resulting in a geometric mean $LC_{50}$ of 150.2 μg TBT/g OC for these marine amphipod taxa. For two other marine taxonomic groups, a single semi-chronic $LC_{50}$ value is available: for the polychaete *A. brevis* (10 days $LC_{50}$ of 930 μg TBT/g OC) and the echinoderm *E. cordatum* (14 days $LC_{50}$ of 10.5 μg TBT/g OC). The value for *E. cordatum* is lower than the geometric mean $LC_{50}$ for marine amphipods, so this value has to be selected for the Tier-2 $PNEC_{sed;ch}$ derivation according to the geometric mean approach, although only a single value is available for Echinodermata. To derive a $PNEC_{sed;ch}$, an AF of 100–300 (see Table 5) can be applied to the geometric mean semi-chronic $L(E)C_{50}$ value of the most sensitive taxonomic group. We selected an AF of 300 since the available toxicity data reveal latent effects and hormone-disrupting properties of TBT. Applying an AF of 300 (see Table 5) to the $LC_{50}$ of 10.5 μg TBT/g OC for *E. cordatum* results in a $PNEC_{sed;ch}$ estimate of 0.035 μg TBT/g OC for marine/estuarine benthic organisms. Note that for estuarine/marine benthic organisms this Tier-2 $PNEC_{sed;ch}$ (based on semi-chronic toxicity data) is somewhat higher that the Tier-1 $PNEC_{sed;ch}$ value of 0.019 μg TBT/g OC based on semi-chronic toxicity data. Since the Tier-2 $PNEC_{sed;ch}$ value based on the geometric mean approach is somewhat lower than the Tier-1 $PNEC_{sed;ch}$ of 0.0365 μg TBT/g OC for sediment-dwelling organisms in estuarine/marine ecosystems derived on basis of chronic toxicity data, the geometric mean approach in this case does not help to refine the effect assessment (Fig. 7).

Species Sensitivity Distribution Approach

Table 14 gives an overview of the $PNEC_{sed;ch}$ derivation based on the SSD approach and by using the chronic or semi-chronic toxicity values presented in Table 14. Since chronic $EC_{10}$/NOEC are available for only seven species, the procedure described in Table 7 was used to estimate the chronic NOEC/$EC_{10}$ based on chronic $L(E)C_{50}$ values. To illustrate the SSD approach as recommended in Sect. 9.4, several SSDs were constructed. Two SSDs were constructed with chronic toxicity data, one with nine species (A in Table 14) and the other with eight species (B in Table 14). In addition, three SSDs were constructed with semi-chronic toxicity data for ten species (C in Table 14), nine species (D in Table 14) and eight species (E in Table 14). For all the SSDs constructed and summarized in Table 14, the Anderson-Darling test for normality was accepted at all levels, indicating that

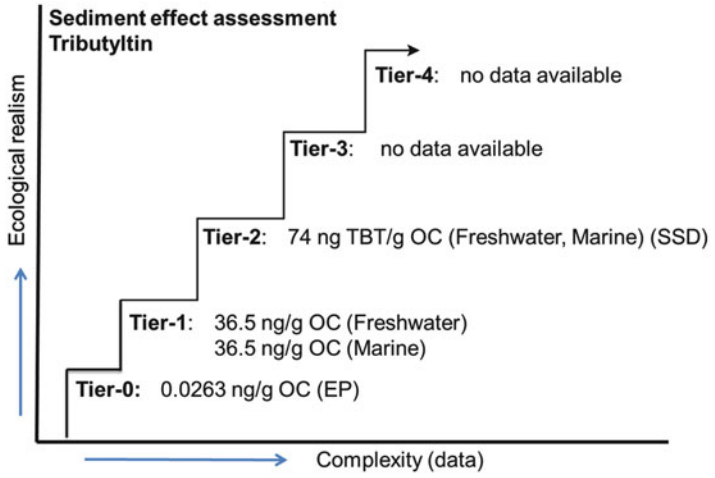


**Fig. 7** Predicted no effect concentration (ng/g OC) for tributyltin for different tiers

the curves fitted the toxicity data well. Figure 6 presents the SSD curve constructed with chronic toxicity data for nine species of benthic freshwater and marine/estuarine organisms (A; upper panel) as well as the SSD curve constructed with semi-chronic toxicity data for ten species (B; lower panel).

The median $HC_5$ values for tributyltin based on semi-chronic data are in most cases more than a factor 10 higher than the $HC_5$ values based on chronic data. We proposed that a $PNEC_{sed;ch}$ can be estimated using the semi-chronic $HC_5$ by applying an AF according to the criteria mentioned in Table 6, as well as an extra AF of 5–10. Because of the hormone-disruptive properties of TBT we propose to select the extra AF in the high range (10).

The $PNEC_{sed;ch}$ estimates based on the SSD approach as presented in Table 14 are remarkably similar between procedures that use the same number of species with chronic and semi-chronic toxicity data. For example the procedure using eight species with chronic toxicity data resulted in a $PNEC_{sed;ch}$ of 0.055 µg TBT/g OC, while the procedure using eight species with semi-chronic toxicity data resulted in a $PNEC_{sd;ch}$ of 0.048 µg TBT/g OC for freshwater taxa and 0.064 µg TBT/g OC for marine taxa (Table 14). This suggests that the SSD approach as proposed in Sect. 9.4 works well. However, a $PNEC_{sed;ch}$ preferably should be derived based on chronic toxicity data and a $PNEC_{sed;ch}$ thus obtained overrules a $PNEC_{sed;ch}$ derived based on semi-chronic toxicity data. The preferred chronic $PNEC_{sd;ch}$ of 0.074 µg TBT/g OC is higher the PNEC derived in Tier-0, Tier-1 and in the geometric mean approach in Tier-2 (Table 6).

The data presented in Table 14 also show that the median $HC_5$ value increases and its confidence interval decreases if a larger number toxicity data is used to construct the SSD. This indicates that it may be rewarding in the Tier-2 effect assessment to generate spiked sediment toxicity data for a higher number of benthic taxa.

**Table 14** Overview of $PNEC_{sed;ch}$ values (µg TBT/g OC) for tributyltin derived by means of SSDs constructed with chronic or semi-chronic toxicity data for benthic organisms (see Table 13)

| | Endpoints | No of species | No of taxonomic groups | Lower limit $HC_5$ (µg TBT/g OC) | Median $HC_5$ (µg TBT/g OC) | Upper limit $HC_5$ (µg TBT/g OC) | $HC_5$/ lower $HC_5$ | AF[a] fresh | AF[a] marine | SSD-$PNEC_{sed;ch}$ Fresh (µg TBT/g OC) | SSD-$PNEC_{sed;ch}$ Marine (µg TBT/g OC) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| A | Chronic | 9 | 7 | 0.024 | 0.296 | 1.145 | 12 | 4 | 4 | 0.074 | 0.074 |
| B | Chronic | 8 | 7 | 0.012 | 0.220 | 0.999 | 19 | 4 | 4 | 0.055 | 0.055 |
| C | Semi-chronic | 10 | 6 | 0.334 | 4.124 | 17.087 | 12 | 4*10[b] | 4*10[b] | 0.103 | 0.103 |
| D | Semi-chronic | 9 | 6 | 0.185 | 3.401 | 16.556 | 18 | 4*10[b] | 4*10[b] | 0.085 | 0.085 |
| E | Semi-chronic | 8 | 5 | 0.078 | 2.424 | 14.355 | 31 | 5*10[b] | 4*10[b] | 0.048 | 0.061 |

*A*: SSD constructed with chronic toxicity data for 9 species as presented in Fig. 6. *B*: SSD constructed with chronic toxicity data for 8 species similar to those presented in Fig. 6, except *Eohautorius washingtonianus*. *C*: SSD constructed with semi-chronic toxicity data for 10 species similar to those presented in Fig. 7. *D*: SSD constructed with semi-chronic toxicity data for 9 species similar to those presented in Fig. 7 except Hexagenia. *E*: SSD constructed with semi-chronic toxicity data for 8 species similar to those presented in Fig. 7 except Hexagenia and *Tubifex tubifex*

[a]For criteria see Table 6

[b]An additional AF of 10 is applied to account for the extrapolation of semi-chronic toxicity data to chronic toxicity data

### 10.3.5 Tier-3 Effect Assessment Based on Micro/Mesocosm Experiments for Tributyltin

Appropriate spiked sediment micro/mesocosm tests could not be found.

### 10.3.6 Conclusions from the Tributyltin Toxicity Data for Benthic Organisms

- Applying the concept of EP to the $PNEC_{sw;ch}$ (based on water toxicity data for pelagic organisms) results in a conservative estimate of the $PNEC_{sed;ch;EP}$ (Tier-0) (Fig. 7)
- The chronic NOEC/$EC_{10}$ value (spiked sediment test) was lowest for a mollusc, which is in accordance with available toxicity data for water organisms and water exposure tests
- The sediment toxicity data for freshwater and marine arthropods overlap
- The toxicity data for both freshwater and marine benthic organisms can be used to construct an SSD with an appropriate fit
- The $PNEC_{sed;ch}$ value for tributyltin derived on the basis of the SDD approach is approximately a factor of 2 higher than the Tier-1 $PNEC_{sed;ch}$

## *10.4 Main Outcomes from the Case Studies*

In general, it can be concluded that the available sediment toxicity data are limited and the reported measurement endpoints are variable. Sediment toxicity data for freshwater and marine/estuarine benthic organisms often overlapped. Available data were mainly limited to arthropods and were predominantly sub-chronic in nature. For the insecticide chlorpyrifos, however, the focus on benthic arthropods is logical considering its specific toxic mode-of-action and the extensive dataset for water column organism, which indicates that aquatic arthropods are the sensitive taxonomic group

Applying the concept of EP to the $PNEC_{sw;ch}$ (based on water toxicity data for pelagic organisms) results in a very conservative estimate of the $PNEC_{sed;ch;EP}$ (Tier-0) for ivermectin and a conservative estimate for chlorpyrifos and tributyltin. For chlorpyrifos, however, by using the higher tier $PNEC_{sw;ch}$ (on basis of a chronic micro/mesocosm study) in the equation then the Tier-0 $PNEC_{sed;ch;EP}$ resembles the Tier-1$PNEC_{sed;ch}$ estimate for estuarine and marine species, but is a factor of 2–3 lower than the Tier-1 $PNEC_{sed;ch}$ for freshwater species. Aquatic data can provide good indicators for the most sensitive species group, as was shown for tributyltin, where the chronic NOEC/$EC_{10}$ value (spiked sediment test) was lowest for a mollusc, which is in accordance with available toxicity data for water organisms and water exposure tests.

The case studies illustrate that the geometric mean approach is of limited value in the chronic effect assessment for benthic organisms. However, these studies also show that toxicity data for both freshwater and marine benthic organisms can be used to construct an SSD with an appropriate fit. For tributyltin, the $PNEC_{sed;ch}$ values derived on the basis of the SDD approach are approximately a factor of 2 higher than the Tier-1 $PNEC_{sed;ch}$.

In microcosms in which the sediment was spiked with ivermectin, the overall NOEC of the nematode community was approximately a factor of 10 lower than the NOEC of the standard test nematode *C. elegans*.

# 11 Main Recommendations for Prospective ERA for Sediment-Bound Organic Chemicals and Outlook

## *11.1 Specific Protection Goals*

For benthic organisms we recommend adopting similar specific protection goals as developed for pelagic organisms. For benthic algae, macrophytes and invertebrates we propose to select the population as ecological entity to be protected and the functional group for microorganisms. For benthic vertebrates the ecological entity to be protected may be the individual—to population level.

## *11.2 Triggers for Prospective Sediment ERA*

We recommend using a combination of triggers for sediment testing based on toxicity, persistence and adsorption. A trigger to request sediment-spiked toxicity testing with benthic organisms is based on the EP approach that uses available toxicity data for pelagic organisms and an extra extrapolation factor of 10 for benthic fauna that consume sediment particles. As a trigger for persistence, log $K_{oc}$ is preferred over log $K_{ow}$ since log $K_{oc}$ is a more direct measure for chemical binding to sediment. Because reported $K_{oc}$ values may have a high variability, we recommend using the geometric mean value, as $K_{oc}$ values usually show a log-normal distribution. For a persistence trigger we recommend using e.g. $>10$ % of the substance present in sediment at or after day 14 in an OECD guideline 308 test or $>10$ % of the annual dose applied occurring in sediment at the time of maximum $PEC_{sed}$.

## 11.3 Linking Exposure to Effects

For prospective toxicity testing, we recommend using pre-equilibrated artificial sediment, or when field-collected sediment is used to follow as much as possible the test design as currently proposed in OECD test guidelines with artificial sediment. During testing, we advise to measure chemical concentrations in total sediment (in units of mass of organic chemical per mass of dry sediment) and preferably also in pore water as well as in the overlying water and to measure the organic matter content (%) of the dry sediment. The $PEC_{sed}$ and the $PNEC_{sed}$ used in the risk quotient should be expressed in the same unit.

We recommend using a mean or TWA for the duration of the toxicity test if the chemical is not stable. However, if the bioavailable fraction of the compound in the sediment of the laboratory toxicity test decreases faster than that predicted (or measured) for field sediments, it may be appropriate to use the peak concentration in the sediment at the start of the sediment-spiked toxicity test as exposure metric in the effect estimate.

## 11.4 The Tiered Approach in Effect Assessment

Using the EP concept and chronic toxicity data for pelagic organisms is a worst case and cost-effective screening-level approach to evaluate the potential risks of sediment exposure to benthic organisms if the taxonomic groups assessed for water ERA overlap with those required for sediment ERA and the organic compounds are not ionizable, perfluorinated alkylated or insoluble. We propose using an extrapolation factor of 10 to derive a $PNEC_{sed;EP}$ for organisms that ingest sediment particles to account for ingestion and binding to black carbon. It is recommended to verify whether the EP approach and the proposed extrapolation factor can be considered a realistic worst case approach to derive a PNEC for benthic fauna and for different types of organic chemicals.

Since benthic species of freshwater and marine/estuarine ecosystems have many traits in common, we assume that sediment toxicity data for both freshwater and marine/estuarine species can be used in the effect assessment, at least of the taxonomic group occurring in the ecosystem under evaluation.

Ideally, the Tier-1 effect assessment should be based on chronic $EC_{10}$/NOEC values for different taxonomic/feeding groups, of which at least two test species—including the most sensitive—are representative for the ecosystem under evaluation (freshwater or marine/estuarine). The Tier-1 PNEC is calculated by selecting the lowest $EC_{10}$/NOEC value and the application of an assessment factor of 10. For substances with a specific toxic mode-of-action (e.g. insecticides and herbicides) testing two representative species of the potentially sensitive taxonomic group (s) may suffice.

In the Tier-1 effect assessment based on internationally accepted protocol tests for benthic organisms it should be checked whether the most sensitive taxonomic group for Tier-1 water column organisms is likely represented in the core data set for benthic species. If not, it should be determined whether this taxonomic group is represented in the available additional toxicity data for benthic organisms and whether the quality of this information is high enough for use in the effect assessment.

If sediment-spiked toxicity data for both standard and additional benthic test species are available, a Tier-2 effect assessment might be based on the geometric mean and species sensitivity distribution (SSD) approaches. For the time being, we propose restricting the geometric mean approach for deriving $PNEC_{sed}$ values on the basis of semi-chronic toxicity data (e.g. 10 days $L(E)C_{50}$ values), while SSDs can be constructed either with semi-chronic or chronic toxicity data.

For the effect assessment based on the SSD approach we propose—as a minimum—to construct the SSD with toxicity data for eight benthic species representing at least five different taxonomic/feeding groups. However, when the ERA based on water organisms shows that a specific taxonomic group is at least an order of magnitude more sensitive than other taxonomic groups, the eight species should preferably be selected from the sensitive taxonomic group.

Preferably, the SSD should be constructed with chronic $EC_{10}$/NOEC data addressing sub-lethal endpoints. However, considering the scarcity of sediment-spiked toxicity data we propose the following. If for an essential taxon, such as the eighth species in the chronic SSD, a valid chronic toxicity value is missing but a valid semi-chronic (e.g. 10 days $EC_{50}$ value) is available, an appropriate extrapolation factor might be used to derive a "surrogate" $EC_{10}$/NOEC value for this species that can be used in the chronic SSD. Furthermore, a $PNEC_{sed;ch}$ on basis of an SSD fully constructed with (10 days) semi-chronic $L(E)C_{50}$ values may be used by applying an appropriate extrapolation technique.

We propose microcosm experiments with spiked sediment, in which the colonisation success by benthic organisms is studied, as a possible Tier-3 option. Alternatively, micro-/mesocosm test systems with a well-established aquatic community can be used by spiking the water compartment with the contaminant. The latter experimental design requires a detailed assessment of the dynamics in exposure concentrations in different sediment layers and in the overlying water. Higher tiers should be used to calibrate the lower tiers. Moreover, effect model approaches should be integrated into the effect assessment. We recommend that these models link scenarios from exposure and effect models.

Sediments are often contaminated with a mixture of chemicals. Therefore, future efforts should be made to move from the current ERA, which is based on single substance exposure, to an approach that deals with multiple chemicals. The TKTD approach may be a good tool to deal with multiple exposures. Exposure to multiple stressors requires clear scenarios that combine exposure and ecology related elements (Beyer et al. 2014).

Moreover, the development of novel endpoints/techniques such as genomics, epigenetics, biomarkers, adverse outcome pathways, their ecological relevance and

impact on sediment risk assessment is an important future research activity (e.g. Ankley et al. 2010).

Overall, a holistic approach that combines experimental work and fate and effect modelling is needed to develop better and more cost-effective prognostic tools for sediment risk assessment.

## 12 Summary

Benthic organisms provide important ecosystem services and functions, and should therefore be protected. However, a broadly accepted framework for prospective ERA of sediment-bound organic chemicals is currently lacking. Such a framework requires clear protection goals, evidence-based concepts that link exposure to effects and a transparent tiered effect assessment. SPUs identified based on the ecosystem service concept are microorganisms, benthic algae, sediment-rooted macrophytes, benthic invertebrates and benthic vertebrates for both freshwater and marine sediments, which are similar to SPUs derived for the aquatic system. The proposed SPUs and their specific protection goals should be generally accepted and implemented to operationalize sediment risk assessment schemes.

There is an urgent need for harmonization of data requirements, test protocols and risk assessment frameworks between regulations/directives. The first step is to determine and agree on a set of harmonized triggers for sediment testing. These triggers should consist of a combination of chemical properties and toxicity triggers. When testing is required, sediment-spiked laboratory toxicity tests with pre-equilibrated artificial sediment as described in Diepens et al. (2014b) or field-collected sediment and standard and/or additional benthic test species should focus on long-term tests with chronic endpoints. The range of standard test species for sediment testing currently in use in Europe should be extended with species that differ in taxonomy, feeding traits and ecosystem, such as estuarine and marine species.

When defining guidance for both prospective exposure and effect assessment, chemical, biological, spatial and temporal factors should be taken into account in experimental and model approaches. For fate models there is a need for approaches to translate biodegradation process parameters obtained from lab tests to parameters that are relevant in the field. The development of passive samplers for more classes of chemical can provide more accurate input for such models. For prospective exposure modelling, more realistic exposure models are needed for emerging chemical classes like ionizable organics and polar substances; these models should also take degradation processes into account. Development of realistic exposure scenarios is a prerequisite to successfully apply exposure models.

To correctly link exposure and effect, the ERC for the $PEC_{sed}$ and $PNEC_{sed}$ used in the RQ should be expressed in the same type of concentration. Ideally, internal concentrations should be measured during the experiment. As advised in current technical guidelines, chemical concentrations in total sediment (in units of mass of

organic chemical per mass of dry sediment) and preferably also in pore water as well as the concentration in the overlying water and the organic matter content (%) of the dry sediment should be measured. Model approaches may be used to calculate chemical concentrations in environmental compartments in which data is lacking. For exposure in chronic risk assessment, either the $PEC_{sed;max}$ or $PEC_{sed;TWA}$ can be used to compare with the $PNEC_{sed;ch}$. Guidelines should give a clear and uniform description of the concentration that should be used both in exposure and effect assessment. They should also specify where (organism, water and sediment compartments, sediment layer) and when the exposure concentration should be measured.

For the first step in effect assessment, prior to actual testing, a cost-effective Tier-0 screening based on aquatic toxicity data and EP with an extrapolation factor of 10 that accounts for BC and ingestion is recommended (for benthic fauna only). This approach gives important information on the most sensitive groups and in some cases provides conservative protection levels. The case studies showed that this approach is moderately to very conservative for these chemicals. It is recommended to verify whether the EP approach and the extrapolation factor of 10 can be considered a realistic worst case approach to derive a PNEC for benthic fauna and for different types of organic chemicals.

In the Tier-1 approach to derive a $PNEC_{sed}$, spiked sediment laboratory toxicity testing with standard benthic test species and the application of an appropriate assessment factor (AF) is common practice. The size of the proposed AF to be applied depends on the number of available species with chronic and semi-chronic toxicity data and the taxonomy, feeding traits and ecosystem preference of the test species used.

Possible Tier-2 options are the geometric mean and SSD approach. Freshwater, estuarine and marine species can be combined in the Tier-2 approaches. For the time being, we recommend using the geometric mean approach only to conduct effect assessments based on acute/semi-chronic toxicity data (e.g. 10 days $L(E)C_{50}$'s) for test species in the same taxonomic group (e.g. benthic insects, crustaceans, oligochaetes or polychaetes). Whether the geometric mean approach can also be applied to chronic toxicity data of the same taxonomic group addressing different measurement endpoints still needs to be investigated. We propose that the SSD approach be used if toxicity data are available for eight or more benthic species. The SSD curve should be constructed with either chronic or acute/semi-chronic toxicity data. The derivation of a $PNEC_{sed}$ based on the SSD approach is done by applying an appropriate AF to the $HC_5$. We propose basing the size of this AF on the number of species and quality of the available toxicity data used in the SSD. Ideally, the proposed assessment factors to derive PNECs for the Tier-1 and Tier-2 should be calibrated/validated with results of semi-field and field tests.

We propose microcosm experiments with spiked sediment, in which the colonisation success by benthic organisms is studied, as a Tier-3 option, although only limited experience is available with these types of tests. Alternatively, micro/mesocosm test systems with a well-established aquatic community can be used by spiking the water compartment with the contaminant. Effect models can be used

to complement experimental data to link exposure to effect at different levels of biological organization and at different spatial and temporal scales. In a regulatory context, scenarios relevant for aquatic ecosystems in different EU Member States using patterns of organic chemicals that integrate exposure and effects are a prerequisite. An important future research activity, therefore, would be to develop and link scenarios in exposure and effect models that include the sediment compartment and selected standard and appropriate vulnerable benthic species.

To evaluate the consistency of the tiered approach as described in this paper for the effect assessment of sediment exposure, the higher tiers (e.g. spiked sediment microcosm tests) should be used to calibrate the lower tiers. However, hardly any data for calibration of the tiered approach is currently available. Moreover, there is an urgent need to derive tiered ERA schemes for vertebrates and microorganisms, as insufficient data, methods and experience are currently available to do so. Also the development of novel endpoints/techniques such as genomics, epigenetics, biomarkers, adverse outcome pathways, their ecological relevance and impact on sediment risk assessment is an important future research activity.

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## Appendix 1: List of Workshop Participants

The workshop "Prospective Sediment Risk Assessment" was held on 24-02-14 in Wageningen, the Netherlands

| Name | Surname | Affiliation | Country |
|---|---|---|---|
| Gertie | Arts | Alterra Wageningen UR | The Netherlands |
| Hans | Baveco | Alterra Wageningen UR | The Netherlands |
| Theo | Brock | Alterra Wageningen UR | The Netherlands |
| Eric | Bruns | Bayer | Germany |
| Noël | Diepens | Wageningen University | The Netherlands |
| Andreas | Focks | Alterra Wageningen UR | The Netherlands |
| Malyka | Galay-Burgos | Ecetoc | Belgium |
| Mick | Hamer | Syngenta | United Kingdom |
| Bruno | Hubesch | CEFIC | Belgium |
| Bart | Koelmans | Wageningen University | The Netherlands |
| Stuart | Marshall | Unilever | United Kingdom |
| Andreu | Rico | Wageningen University | The Netherlands |
| Mauricio | Rocha Dimitrov | Wageningen University | The Netherlands |

(continued)

| Name | Surname | Affiliation | Country |
|---|---|---|---|
| Cor | Schipper | Deltares | The Netherlands |
| Livia | Sidney | Wageningen University | The Netherlands |
| Hauke | Smidt | Wageningen University | The Netherlands |
| Ariadna | Szczybelski | Wageningen University | The Netherlands |
| Paul | Van den Brink | Alterra Wageningen UR/Wageningen University | The Netherlands |
| Martine | Van den Heuvel-Greve | IMARES Wageningen UR | The Netherlands |
| Bert | Van Hattum | VU University Amsterdam | The Netherlands |
| Erik | Verbruggen | RIVM | The Netherlands |
| Arjan | Wijdeveld | TU Delft | The Netherlands |

## Appendix 2: List of Abbreviations

| | |
|---|---|
| AF | Assessment factor |
| ASTM | American Society for Testing and Materials |
| BSAF | Biota sediment accumulation factor |
| $C_{pw}$ | Concentration of the chemical in pore water |
| $C_{sed;oc}$ | Concentration of the chemical in the sediment per unit mass of organic carbon |
| ECHA | European Chemicals Agency |
| $EC_x$ | Effect concentration x percent |
| EF | Extrapolation factor |
| EFSA | European Food Safety Authority |
| EMEA | European Medicines Agency |
| EP | Equilibrium partitioning |
| EPA | United States Environmental Protection Agency |
| ERA | Environmental risk assessment |
| ERC | Ecotoxicologically relevant concentration |
| GIS | Geographic information system |
| $HC_5$ | Hazardous concentrations to 5 % of the test species |
| IBM | Individual-based modelling |
| ISO | International Organization for Standardization |
| $K_d$ | Sediment-water partitioning coefficient |
| $K_{oc}$ | Organic carbon-water partitioning coefficient |
| $K_{ow}$ | Octanol-water partition coefficient |
| $LC_X$ | Lethal concentration x percent |
| NOEC | No effect concentration |
| OC | Organic carbon |
| OECD | Organisation for Economic Co-operation and Development |
| PEC | Predicted environmental exposure concentrations |
| $PEC_{sed}$ | Sediment exposure estimates |

(continued)

| | |
|---|---|
| $PEC_{sed;max}$ | Sediment exposure estimates based on peak concentration |
| $PEC_{sed;TWA}$ | Sediment exposure estimates based on time-weighted average concentration |
| PNEC | Predicted no effect concentration |
| $PNEC_{sed}$ | Effect estimates for sediment-dwelling organisms |
| $PNEC_{sed;ch}$ | Predicted no effect concentration for sediment based on chronic toxicity data |
| $PNEC_{sed;ch;EP}$ | Predicted no effect concentration for sediment based on chronic toxicity data calculated by equilibrium partitioning |
| $PNEC_{sw;ch}$ | Predicted no effect concentration for surface water based on chronic toxicity data |
| PPP | Plant Protection Products |
| QSAR | Quantitative Structure Activity Relationship |
| QSPR | Quantitative Structure Property Relationship |
| REACH | Registration, Evaluation, Authorisation and Restriction of Chemicals |
| RQ | Risk Quotient (RQ = PEC/PNEC) |
| SPU | Service providing units |
| SSD | Species sensitivity distribution |
| TKTD | Toxicokinetic toxicodynamic |
| TWA | Time-weighted average |
| VICH | Veterinary International Conference on Harmonization |

## References

Adams WJ, Kimerle RA, Barnett JW (1992) Sediment quality and aquatic life assessment. Environ Sci Technol 26:1864–1875. doi:10.1021/es00034a001

Adriaanse PI (1996) Fate of pesticides in field ditches: the TOXSWA simulation model vol 90. SC-DLO, Wageningen

Aldenberg T, Jaworska JS (2000) Uncertainty of the hazardous concentration and fraction affected for normal species sensitivity distributions. Ecotoxicol Environ Saf 46:1–18. doi:10.1006/eesa.1999.1869

Aldenberg T, Jaworska JS, Traas TP, Posthuma L (2002) Normal species sensitivity distributions and probabilistic ecological risk assessment. In: Posthuma L, Traas T, Suter G (eds) Species sensitivity distributions in risk assessment. CRC Press, Boca Raton, FL, pp 49–102

Allen YT, Thain JE, Haworth S, Barry J (2007) Development and application of long-term sublethal whole sediment tests with Arenicola marina and Corophium volutator using Ivermectin as the test compound. Environ Pollut 146:92–99. doi:10.1016/j.envpol.2006.06.007

Amweg EL, Weston DP (2007) Whole-sediment toxicity identification evaluation tools for pyrethroid insecticides: I. Piperonyl butoxide addition. Environ Toxicol Chem 26:2389–2396. doi:10.1897/07-017r.1

Anderson BS, Lowe S, Phillips BM, Hunt JW, Vorhees J, Clark S, Clark S, Tjeerdema RS (2008) Relative sensitivities of toxicity test protocols with the amphipods Eohaustorius estuarius and Ampelisca abdita. Ecotoxicol Environ Saf 69:24–31. doi:10.1016/j.ecoenv.2007.05.005

Ankley GT, Call DJ, Cox JS, Kahl MD, Hoke RA, Kosian PA (1994) Organic carbon partitioning as a basis for predicting the toxicity of chlorpyrifos in sediments. Environ Toxicol Chem 13:621–626. doi:10.1002/etc.5620130411

Ankley GT et al (2010) Adverse outcome pathways: a conceptual framework to support ecotoxicology research and risk assessment. Environ Toxicol Chem 29:730–741. doi:10.1002/etc.34

Ashauer R, Boxall A, Brown C (2006) Predicting effects on aquatic organisms from fluctuating or pulsed exposure to pesticides. Environ Toxicol Chem 25:1899–1912. doi:10.1897/05-393r.1

ASTM (2013) ASTM E2591-07(2013), Standard guide for conducting whole sediment toxicity tests with amphibians. ASTM, West Conshohocken, PA. doi:10.1520/E2591-07R13

Bal-Price A et al (2014) Considerations in the development of in vitro toxicity testing methods intended for regulatory use. In: In vitro toxicology systems, Methods in pharmacology and toxicology. Springer, New York, NY, pp 551–569. doi:10.1007/978-1-4939-0521-8_25

Bartell SM, Pastorok RA, Akçakaya HR, Regan H, Ferson S, Mackay C (2003) Realism and relevance of ecological models used in chemical risk assessment. Hum Ecol Risk Assess 9:907–938. doi:10.1080/713610016

Bartlett AJ, Borgmann U, Dixon DG, Batchelor SP, Maguire RJ (2004) Accumulation of tributyltin in *Hyalella azteca* as an indicator of chronic toxicity: survival, growth, and reproduction. Environ Toxicol Chem 23:2878–2888. doi:10.1897/03-521.1

Baveco JM, Norman S, Roessink I, Galic N, Van den Brink PJ (2014) Comparing population recovery after insecticide exposure for four aquatic invertebrate species using models of different complexity. Environ Toxicol Chem 33:1517–1528. doi:10.1002/etc.2605

Beketov MA, Cedergreen N, Wick LY, Kattwinkel M, Duquesne S, Liess M (2012) Sediment toxicity testing for prospective risk assessment—a new framework and how to establish it. Hum Ecol Risk Assess 19:98–117. doi:10.1080/10807039.2012.683741

Besseling E, Wegner A, Foekema EM, van den Heuvel-Greve MJ, Koelmans AA (2013) Effects of microplastic on fitness and PCB bioaccumulation by the Lugworm Arenicola marina (L.). Environ Sci Technol 47:593–600. doi:10.1021/es302763x

Best EPH, Boyd WA (1999) A simulation model for growth of the submersed aquatic macrophyte Eurasian Watermilfoil (*Myriophyllum spicatum* L.). Technical Report A-99-3 US Army Corps of Engineers

Beyer J, Petersen K, Song Y, Ruus A, Grung M, Bakke T, Tollefsen KE (2014) Environmental risk assessment of combined effects in aquatic ecotoxicology: a discussion paper. Mar Environ Res 96:81–91. doi:10.1016/j.marenvres.2013.10.008

Boesten JJTI, Köpp H, Adriaanse PI, Brock TCM, Forbes VE (2007) Conceptual model for improving the link between exposure and effects in the aquatic risk assessment of pesticides. Ecotoxicol Environ Saf 66:291–308

Brandes L, den Hollander H, van de Meent D (1996) SimpleBox 2.0: a nested multimedia fate model for evaluating the environmental fate of chemicals. Rijksinstituut voor Volksgezondheid en Milieu RIVM, Bilthoven

Brinke M, Hoss S, Fink G, Ternes TA, Heininger P, Traunspurger W (2010) Assessing effects of the pharmaceutical ivermectin on meiobenthic communities using freshwater microcosms. Aquat Toxicol 99:126–137. doi:10.1016/j.aquatox.2010.04.008

Brock TCM (2013) Priorities to improve the ecological risk assessment and management for pesticides in surface water. Integr Environ Assess Manag 9:e64–e74. doi:10.1002/ieam.1429

Castano A et al (2003) The use of fish cells in ecotoxicology. The report and recommendations of ECVAM Workshop 47. Altern Lab Anim 31:317–351

Clemmens A, Holly F, Schuurmans W (1993) Description and evaluation of program: duflow. J Irrig Drain Eng 119:724–734. doi:10.1061/(ASCE)0733-9437(1993)119:4(724)

Cornelissen G, Gustafsson Ö, Bucheli TD, Jonker MTO, Koelmans AA, van Noort PCM (2005) Extensive sorption of organic compounds to black carbon, coal, and kerogen in sediments and soils: mechanisms and consequences for distribution, bioaccumulation, and biodegradation. Environ Sci Technol 39:6881–6895. doi:10.1021/es050191b

Covich AP, Palmer MA, Crowl TA (1999) The role of benthic invertebrate species in freshwater ecosystems: zoobenthic species influence energy flows and nutrient cycling. Bioscience 49:119–127

Covich AP et al (2004) The role of biodiversity in the functioning of freshwater and marine benthic ecosystems. Bioscience 54:767–775. doi:10.1641/0006-3568(2004)054[0767:trobit]2.0.co;2

Crum SJ, Brock TC (1994) Fate of chlorpyrifos in indoor microcosms and outdoor experimental ditches. In: Hill I, Heimbach F, Leeuwangh P, Matthiesen P (eds) Freshwater field tests for hazard assessment of chemicals. Lewis Publishers, Chelsea, MI, pp 315–322

Davies IM, Gillibrand PA, McHenery JG, Rae GH (1998) Environmental risk of ivermectin to sediment dwelling organisms. Aquaculture 163:29–46. doi:10.1016/S0044-8486(98)00211-7

Day KE, Maguire RJ, Milani D, Batchelor SP (1998) Toxicity of tributyltin to four species of freshwater benthic invertebrates using spiked sediment bioassays. Water Qual Res J Can 33:111–132

De Laender F, Morselli M, Baveco H, Van den Brink PJ, Di Guardo A (2015) Theoretically exploring direct and indirect chemical effects across ecological and exposure scenarios using mechanistic fate and effects modelling. Environ Int 74:181–190. doi:10.1016/j.envint.2014.10.012

Di Guardo A, Hermens JLM (2013) Challenges for exposure prediction in ecological risk assessment. Integr Environ Assess Manag 9:e4–e14. doi:10.1002/ieam.1442

Di Toro D et al (1991) Technical basis for the equilibrium partitioning method for establishing sediment quality criteria. Environ Toxicol Chem 11:1541–1583

Diepens NJ, Beltman W, Koelmans AA, Van den Brink PJ, Baveco H. Under revision. Dynamics and recovery of a sediment exposed *Chironomus riparius* population: A modelling approach *Environmental Pollution*

Diepens NJ, Dimitrov MR, Koelmans AA, Smidt H. Online. Molecular assessment of bacterial community dynamics and functional endpoints during sediment bioaccumulation tests. *Environmental Science & Technology*. doi:10.1021/acs.est.5b02992

Diepens NJ, Van den Heuvel-Greve M, Koelmans AA. Online. Modeling of bioaccumulation in marine benthic invertebrates using a multispecies experimental approach. *Environmental Science & Technology*. doi: 10.1021/acs.est.5b02500

Diepens N, Arts G, Focks A, Koelmans AA (2014a) Uptake, translocation and elimination in sediment-rooted macrophytes: a model-supported analysis of whole sediment test data. Environ Sci Technol 48:12344–12353. doi:10.1021/es503121x

Diepens NJ, Arts GHP, Brock TCM, Smidt H, Van den Brink PJ, Van den Heuvel-Greve MJ, Koelmans AA (2014b) Sediment toxicity testing of organic chemicals in the context of prospective risk assessment: a review. Crit Rev Environ Sci Technol 44:255–302. doi:10.1080/01496395.2012.718945

Duft M, Schulte-Oehlmann U, Tillmann M, Markert B, Oehlmann J (2003) Toxicity of triphenyltin and tributyltin to the freshwater mud snail Potamopyrgus antipodarum in a new sediment biotest. Environ Toxicol Chem 22:145–152. doi:10.1002/etc.5620220119

ECHA (2008) Guidance on information requirements and chemical safety assessment. Chapter R.10: Characterisation of dose [concentration]-response for environment. Guidance for the implementation of REACH. European Chemicals Agency, Helsinki

ECHA (2014a) Guidance on information requirements and chemical safety assessment. Chapter R.7b: Endpoint specific guidance. European chemicals agency, Helsinki

ECHA (2014b) Guidance on the biocidal products regulation. Volume IV: Environment: Part A: Information requirements. European chemicals agency, Helsinki

ECHA (2014c) ECHA Principles for environmental risk assessment of the sediment compartment. In: Jose V, Tarazona BV, Janssen C, De Laender F, Vangheluwe M, Knight D (eds) Proceedings of the topical scientific workshop, 7-8 May 2013. European Chemicals Agency, Helsinki

EFSA (2005) Opinion of the scientific panel on plant health, plant protection products and their residues on a request from the EFSA related to the assessment of the acute and chronic risk to aquatic organisms with regard to the possibility of lowering the assessment factor if additional species were tested. EFSA J 301:1–45

EFSA (2009) The usefulness of total concentrations and pore water concentrations of pesticides in soil as metrics for the assessment of ecotoxicological effects. EFSA J 922:1–90

EFSA (2010a) Scientific opinion on outline proposals for assessment of exposure of organisms to substances in soil. EFSA J 8:1442–1478
EFSA (2010b) Scientific Opinion on the development of specific protection goal options for environmental risk assessment of pesticides, in particular in relation to the revision of the Guidance Documents on Aquatic and Terrestrial Ecotoxicology (SANCO/3268/2001 and SANCO/10329/2002). EFSA J 8:55. doi:10.2903/j
EFSA (2013) Guidance on tiered risk assessment for plant protection products for aquatic organisms in edge of field surface waters. EFSA J 11:186
EFSA (2014a) EFSA Guidance Document for evaluating laboratory and field dissipation studies to obtain DegT50 values of active substances of plant protection products and transformation products of these active substances in soil. EFSA J 12:37. doi:10.2903/j.efsa.2014.3662
EFSA (2014b) Scientific Opinion on good modelling practice in the context of mechanistic effect models for risk assessment of plant protection products. EFSA J 12:92. doi:10.2903/j.efsa.2014.3589
EFSA (2015) Scientific opinion on the effect assessment for pesticides on sediment organisms in edge-of-field surface water. EFSA J 13:145. doi:10.2903/j.efsa.2015.4176
Egeler P, Gilberg D, Fink G, Duis K (2010) Chronic toxicity of ivermectin to the benthic invertebrates Chironomus riparius and Lumbriculus variegatus. J Soils Sediments 10:368–376. doi:10.1007/s11368-010-0197-3
EMEA (2006) Guideline on the environmental risk assessment of medicinal products for human use EMEA/CHMP/SWP/4447/00. European Medicines Agency, London
EPA (1996a) Ecological effects test guidelines OPPTS 850.1740. Whole sediment acute toxicity invertebrates, marine. U.S. Environmental Protection Agency, Washington, DC
EPA (1996b) Ecological effects test guidelines: OPPTS 850.1735: whole sediment acute toxicity invertebrates, freshwater. U.S. Environmental Protection Agency, Washington, DC
EPA U (1997) Ambient water quality criteria for tributyltin – draft. EPA, Washington, DC
European Commission (2003a) Technical Guidance Document (TGD) in support of commission directive 93/67/EEC on risk assessment for new notified substances, Commission Regulation (EC) No 1488/94 on risk assessment for existing substances and Directive 98/8/EC of the European parliament and the council concerning the placing of biocidal products on the market vol Edition 2. EUR 20418 EN/2. European Commission Joint Research Centre, Ispra
European Commission (2003b) Technical Guidance Document on risk assessment in support of Commission Directive 93/67/EEC, Commission Directive 98/8/EC, Commission Regulation (EC) No 1488/94, Commission Directive 93/67/EEC. European Commission, Ispra
European Commission (2005) Common Implementation Strategy for the Water Framework Directive. Environmental Quality Standards (EQS) Substance Data Sheet Tributyltin compounds. European Commission, Ispra
European Commission (2011a) Common implementation strategy for the Water Framework Directive (2000/60/EC). Guidance Document No. 27. Technical Guidance Document for deriving Environmental Quality Standards, Technical Report- 2011-055
European Commission (2011b) Technical guidance document for deriving environmental quality standards vol Draft version 5.0 (29 January 2010). European Commission Joint Research Centre, Ispra. doi:10.2779/43816
Faber D, Bruns E (2015) Future challenges in sediment toxicity testing for the risk assessment of plant protection products. Poster. Paper presented at the SETAC Europe 25th Annual Meeting, 3–7 May 2015, Barcelona Spain
Feijtel T et al (1997) Development of a geography-referenced regional exposure assessment tool for European rivers - great-er contribution to great-er #1. Chemosphere 34:2351–2373. doi:10.1016/S0045-6535(97)00048-9
Fenchel TM (1978) The ecology of micro-and meiobenthos. Annu Rev Ecol Syst 9:99–121. doi:10.2307/2096745

Focks A, Horst MT, Van de Berg E, Baveco H, Van den Brink PJ (2014) Integrating chemical fate and population-level effect models for pesticides on the landscape scale: new options for risk assessment. Ecol Model 280:102

FOCUS (2007) Landscape and mitigation factors in aquatic risk assessment. Volume 1. Extended summary and recommendations, volume 2 Detailed Technical Reviews. Report of the FOCUS working group on landscape and mitigation factors in ecological risk assessment. EC Document Reference SANCO/10422/2005

Fojut T, Vasquez M, Poulsen A, Tjeerdema R (2013) Methods for deriving pesticide aquatic life criteria for sediments. In: Whitacre DM (ed) Reviews of environmental contamination and toxicology, vol 224. Springer, New York, NY, pp 97–175. doi:10.1007/978-1-4614-5882-1_4

Forbes VE, Calow P (2013) Use of the ecosystem services concept in ecological risk assessment of chemicals. Integr Environ Assess Manag 9:269–275. doi:10.1002/ieam.1368

Forbes VE et al (2011) Adding value to ecological risk assessment with population modeling. Hum Ecol Risk Assess 17:287–299. doi:10.1080/10807039.2011.552391

Galic N, Hommen U, Baveco JM, Van den Brink PJ (2010) Potential application of population models in the European ecological risk assessment of chemicals II: Review of models and their potential to address environmental protection aims. Integr Environ Assess Manag 6:338–360. doi:10.1002/ieam.68

Galic N, Hengeveld GM, Van den Brink PJ, Schmolke A, Thorbek P, Bruns E, Baveco HM (2013) Persistence of aquatic insects across managed landscapes: effects of landscape permeability on re-colonization and population recovery. PLoS One 8:e54584

Garric J et al (2007) Effects of the parasiticide ivermectin on the cladoceran *Daphnia magna* and the green alga *Pseudokirchneriella subcapitata*. Chemosphere 69:903–910. doi:10.1016/j.chemosphere.2007.05.070

Gaskell PN, Brooks AC, Maltby L (2007) Variation in the bioaccumulation of a sediment-sorbed hydrophobic compound by benthic macroinvertebrates: patterns and mechanisms. Environ Sci Technol 41:1783–1789. doi:10.1021/es061934b

Gebremariam S, Beutel M, Yonge D, Flury M, Harsh J (2012) Adsorption and desorption of chlorpyrifos to soils and sediments, vol 215, Reviews of environmental contamination and toxicology. Springer, New York, NY, pp 123–175. doi:10.1007/978-1-4614-1463-6_3

Gérino M et al (2003) Macro-invertebrate functional groups in freshwater and marine sediments: a common mechanistic classification. Vie et milieu 53:221–231

Giddings JM, Arts G, Hommen U (2013) The relative sensitivity of macrophyte and algal species to herbicides and fungicides: an analysis using species sensitivity distributions. Integr Environ Assess Manag 9:308–318. doi:10.1002/ieam.1387

Giesy JP, Graney RL (1989) Recent developments in and intercomparisons of acute and chronic bioassays and bioindicators. Hydrobiologia 188–189:21–60. doi:10.1007/bf00027770

Gobas F, McNeil EJ, Lovettdoust L, Haffner GD (1991) Bioconcentration of chlorinated aromatic hydrocarbons in aquatic macrophytes. Environ Sci Technol 25:924–929. doi:10.1021/es00017a015

Gray JS (1981) The ecology of marine sediments: an introduction to the structure and function of benthic communities. Cambridge University Press, Cambridge

Green AS, Chandler TG, Piegorsch WW (1996) Life-stage-specific toxicity of sediment-associated chlorpyrifos to a marine, infaunal copepod. Environ Toxicol Chem 15:1182–1188. doi:10.1002/etc.5620150725

Groothuis FA, Heringa MB, Nicol B, Hermens JLM, Blaauboer BJ, Kramer NI (2015) Dose metric considerations in in vitro assays to improve quantitative in vitro–in vivo dose extrapolations. Toxicology 332:30–40. doi:10.1016/j.tox.2013.08.012

Guillén D, Ginebreda A, Farré M, Darbra RM, Petrovic M, Gros M, Barceló D (2012) Prioritization of chemicals in the aquatic environment based on risk assessment: analytical, modeling and regulatory perspective. Sci Total Environ 440:236–252. doi:10.1016/j.scitotenv.2012.06.064

Hall LW, Scott MC, Killen WD, Unger MA (2000) A probabilistic ecological risk assessment of tributyltin in surface waters of the Chesapeake Bay watershed. Hum Ecol Risk Assess 6:141–179. doi:10.1080/10807030091124482

Hallare A, Seiler T-B, Hollert H (2011) The versatile, changing, and advancing roles of fish in sediment toxicity assessment—a review. J Soils Sediments 11:141–173. doi:10.1007/s11368-010-0302-7

Halley BA, Jacob TA, Lu AYH (1989) The environmental impact of the use of ivermectin: environmental effects and fate. Chemosphere 18:1543–1563. doi:10.1016/0045-6535(89)90045-3

Harwood AD, You J, Lydy MJ (2009) Temperature as a toxicity identification evaluation tool for pyrethroid insecticides: toxicokinetic confirmation. Environ Toxicol Chem 28:1051–1058. doi:10.1897/08-291.1

Hecht SA, Gunnarsson JS, Boese BL, Lamberson JO, Schaffner C, Giger W, Jepson PC (2004) Influences of sedimentary organic matter quality on the bioaccumulation of 4-nonylphenol by estuarine amphipods. Environ Toxicol Chem 23:865–873. doi:10.1897/03-220

Heine S, Schmitt W, Schäffer A, Görlitz G, Buresová H, Arts G, Preuss TG (2015) Mechanistic modelling of toxicokinetic processes within *Myriophyllum spicatum*. Chemosphere 120:292–298. doi:10.1016/j.chemosphere.2014.07.065

Hendriks AJ (1995) Modelling equilibrium concentrations of microcontaminants in organisms of the Rhine delta: can average field residues in the aquatic food chain be predicted from laboratory accumulation? Aquat Toxicol 31:1–25. doi:10.1016/0166-445X(94)00052-R

Hintzen EP, Lydy MJ, Belden JB (2009) Occurrence and potential toxicity of pyrethroids and other insecticides in bed sediments of urban streams in central Texas. Environ Pollut 157:110–116. doi:10.1016/j.envpol.2008.07.023

Hollert H, Keiter S, König N, Rudolf M, Ulrich M, Braunbeck T (2003) A new sediment contact assay to assess particle-bound pollutants using zebrafish (*Danio rerio*) embryos. J Soils Sediments 3:197–207. doi:10.1065/jss2003.09.085

Hommen U, Baveco JM, Galic N, Van den Brink PJ (2010) Potential application of ecological models in the European environmental risk assessment of chemicals I: Review of protection goals in EU directives and regulations. Integr Environ Assess Manag 6:325–337. doi:10.1002/ieam.69

Hooftman RN, Van de Guchte K, Roghair CJ (1993) Development of ecotoxicological test systems to assess contaminated sediments. Joint report no. 1: Acute and (sub)chronic tests with the model compound chlorpyrifos. IMW-R 91/111; RIVM-719102022; RIZA-93.090X. RIVM, Bilthoven

Houtman CJ et al (2006) Estrogenic and dioxin-like compounds in sediment from Zierikzee harbour identified with CALUX assay-directed fractionation combined with one and two dimensional gas chromatography analyses. Chemosphere 65:2244–2252. doi:10.1016/j.chemosphere.2006.05.043

Hyde K, Jones EBG, Leaño E, Pointing S, Poonyth A, Vrijmoed LP (1998) Role of fungi in marine ecosystems. Biodivers Conserv 7:1147–1161. doi:10.1023/a:1008823515157

IPCS (1999) Concise international chemical assessment documents, No. 13, Triphenyltin compounds. World Health Organization, Geneva

ISO (2010) ISO/DIS 16191 Water quality—Determination of the toxic effect of sediment and soil on the growth behaviour of Myriophyllum aquaticum. International Organization for Standardization, Geneva

Jager T, Albert C, Preuss TG, Ashauer R (2011) General unified threshold model of survival - a toxicokinetic-toxicodynamic framework for ecotoxicology. Environ Sci Technol 45:2529–2540. doi:10.1021/es103092a

Jager T, Martin BT, Zimmer EI (2013) DEBkiss or the quest for the simplest generic model of animal life history. J Theor Biol 328:9–18. doi:10.1016/j.jtbi.2013.03.011

Janssen EML, Croteau M-N, Luoma SN, Luthy RG (2009) Measurement and modeling of polychlorinated biphenyl bioaccumulation from sediment for the marine polychaete Neanthes

arenaceodentata and response to sorbent amendment. Environ Sci Technol 44:2857–2863. doi:10.1021/es901632e
Jantunen APK, Tuikka A, Akkanen J, Kukkonen JVK (2008) Bioaccumulation of atrazine and chlorpyrifos to *Lumbriculus variegatus* from lake sediments. Ecotoxicol Environ Saf 71:860–868. doi:10.1016/j.ecoenv.2008.01.025
Jensen HF, Holmer M, Dahllöf I (2004) Effects of tributyltin (TBT) on the seagrass Ruppia maritima. Mar Pollut Bull 49:564–573
Jha AN (2004) Genotoxicological studies in aquatic organisms: an overview. Mutat Res 552:1–17. doi:10.1016/j.mrfmmm.2004.06.034
Kaag NHBM, Foekema EM, Scholten MCT, van Straalen NM (1997) Comparison of contaminant accumulation in three species of marine invertebrates with different feeding habits. Environ Toxicol Chem 16:837–842. doi:10.1002/etc.5620160501
Karman CC (2000) The role of time in environmental risk assessment. Spill Sci Technol Bull 6:159–164. doi:10.1016/S1353-2561(00)00071-2
Kilmartin J, Cazabon D, Smith P (1996) Investigations of the toxicity of ivermectin for salmonids. B Eur Assoc Fish Pat 17:107–112
Koelmans AA, Van der Heijde A, Knijff LM, Aalderink RH (2001) Integrated modelling of eutrophication and organic contaminant fate and effects in aquatic ecosystems. A Review. Water Res 35:3517–3536. doi:10.1016/S0043-1354(01)00095-1
Koelmans AA, Jonker MTO, Cornelissen G, Bucheli TD, Van Noort PCM, Gustafsson Ö (2006) Black carbon: the reverse of its dark side. Chemosphere 63:365–377
Koelmans AA, Kaag K, Sneekes A, Peeters ETHM (2009) Triple domain in situ sorption modeling of organochlorine pesticides, polychlorobiphenyls, polyaromatic hydrocarbons, polychlorinated dibenzo-p-dioxins, and polychlorinated dibenzofurans in aquatic sediments. Environ Sci Technol 43:8847–8853. doi:10.1021/es9021188
Koelmans AA, Poot A, Lange HJD, Velzeboer I, Harmsen J, van Noort PCM (2010) Estimation of in situ sediment-to-water fluxes of polycyclic aromatic hydrocarbons, polychlorobiphenyls and polybrominated diphenylethers. Environ Sci Technol 44:3014–3020. doi:10.1021/es903938z
Konstantinou I, Albanis T (2004) Worldwide occurrence and effects of antifouling paint booster biocides in the aquatic environment: a review. Environ Int 30:235–248
Krogh KA, Søeborg T, Brodin B, Halling-Sørensen B (2008) Sorption and mobility of ivermectin in different soils. J Environ Qual 37:2202–2211. doi:10.2134/jeq2007.0592
Langston WJ, Pope ND (1995) Determinants of TBT adsorption and desorption in estuarine sediments. Mar Pollut Bull 31:32–43. doi:10.1016/0025-326X(95)91269-M
Lee RF, Steinert S (2003) Use of the single cell gel electrophoresis/comet assay for detecting DNA damage in aquatic (marine and freshwater) animals. Mutat Res 544:43–64. doi:10.1016/S1383-5742(03)00017-6
Legler J, Van den Brink CE, Brouwer A, Murk AJ, van der Saag PT, Vethaak AD, van der Burg B (1999) Development of a stably transfected estrogen receptor-mediated luciferase reporter gene assay in the human T47D breast cancer cell line. Toxicol Sci 48:55–66. doi:10.1093/toxsci/48.1.55
Leppänen MT, Kukkonen JVK (1998) Relative importance of ingested sediment and pore water as bioaccumulation routes for pyrene to oligochaete (*Lumbriculus variegatus*, Müller). Environ Sci Technol 32:1503–1508. doi:10.1021/es970941k
Levin LA et al (2001) The function of marine critical transition zones and the importance of sediment biodiversity. Ecosystems 4:430–451. doi:10.1007/s10021-001-0021-4
Liebig M et al (2010) Environmental risk assessment of ivermectin: a case study. Integr Environ Assess Manag 6:567–587. doi:10.1002/ieam.96
Lu X, Reible DD, Fleeger JW (2004) Relative importance of ingested sediment versus pore water as uptake routes for PAHs to the deposit-feeding Oligochaete Ilyodrilus templetoni. Arch Environ Contam Toxicol 47:207–214. doi:10.1007/s00244-004-3053-x
Maltby L (2013) Ecosystem services and the protection, restoration, and management of ecosystems exposed to chemical stressors. Environ Toxicol Chem 32:974–983. doi:10.1002/etc.2212

Maltby L, Blake N, Brock TCM, Van den Brink PJ (2005) Insecticide species sensitivity distributions: importance of test species selection and relevance to aquatic ecosystems. Environ Toxicol Chem 24:379–388. doi:10.1897/04-025r.1

Maltby L, Brock TCM, van den Brink PJ (2009) Fungicide risk assessment for aquatic ecosystems: importance of interspecific variation, toxic mode of action, and exposure regime. Environ Sci Technol 43:7556–7563. doi:10.1021/es901461c

Marinković M, Verweij RA, Nummerdor GA, Jonker MJ, Kraak MHS, Admiraal W (2011) Life cycle responses of the midge Chironomus riparius to compounds with different modes of action. Environ Sci Technol 45:1645–1651. doi:10.1021/es102904y

Maund S et al (1997) Development and evaluation of triggers for sediment toxicity testing of pesticides with benthic macroinvertebrates. Environ Toxicol Chem 16:2590–2596. doi:10.1002/etc.5620161222

McIntyre A (1969) Ecology of marine meiobenthos. Biol Rev 44:245–288

McLeod PB, van den Heuvel-Greve MJ, Luoma SN, Luthy RG (2007) Biological uptake of polychlorinated biphenyls by Macoma balthica from sediment amended with activated carbon. Environ Toxicol Chem 26:980–987. doi:10.1897/06-278r1.1

McLeod PB, Luoma SN, Luthy RG (2008) Biodynamic modeling of PCB uptake by Macoma balthica and Corbicula fluminea from sediment amended with activated carbon. Environ Sci Technol 42:484–490. doi:10.1021/es070139a

MEA (2005) Ecosystem and human well-being: synthesis. MEA, Washington, DC

Meador JP, Rice CA (2001) Impaired growth in the polychaete *Armandia brevis* exposed to tributyltin in sediment. Mar Environ Res 51:113–129. doi:10.1016/S0141-1136(00)00033-7

Meador JP, Krone CA, Dyer DW, Varanasi U (1997) Toxicity of sediment-associated tributyltin to infaunal invertebrates: species comparison and the role of organic carbon. Mar Environ Res 43:219–241. doi:10.1016/0141-1136(96)00090-6

Menone ML, Miglioranza KSB, Iribarne O, Aizpún de Moreno JE, Moreno VJ (2004) The role of burrowing beds and burrows of the SW Atlantic intertidal crab *Chasmagnathus granulata* in trapping organochlorine pesticides. Mar Pollut Bull 48:240–247. doi:10.1016/S0025-326X(03)00394-1

Moermond CT, Zwolsman JJ, Koelmans AA (2005) Black carbon and ecological factors affect in situ biota to sediment accumulation factors for hydrophobic organic compounds in flood plain lakes. Environ Sci Technol 39:3101–3109

Morrison HA, Gobas FAPC, Lazar R, Haffner GD (1996) Development and verification of a bioaccumulation model for organic contaminants in benthic invertebrates. Environ Sci Technol 30:3377–3384. doi:10.1021/es960280b

Mulligan CN, Fukue M, Sato Y (2009) Sediments contamination and sustainable remediation. CRC Press, Boca Raton, FL

Murk AJ, Legler J, Denison MS, Giesy JP, van de Guchte C, Brouwer A (1996) Chemical-Activated Luciferase Gene Expression (CALUX): a novel in vitro bioassay for Ah receptor active compounds in sediments and pore water. Fundam Appl Toxicol 33:149–160. doi:10.1006/faat.1996.0152

Nealson KH (1997) Sediment bacteria: who's there, What are they doing, and What's new? Annu Rev Earth Planet Sci 25:403–434. doi:10.1146/annurev.earth.25.1.403

Nendza M (2002) Inventory of marine biotest methods for the evaluation of dredged material and sediments. Chemosphere 48:865–883

Nguyen TH, Goss K-U, Ball WP (2005) Polyparameter linear free energy relationships for estimating the equilibrium partition of organic compounds between water and the natural organic matter in soils and sediments. Environ Sci Technol 39:913–924. doi:10.1021/es048839s

Nienstedt KM et al (2012) Development of a framework based on an ecosystem services approach for deriving specific protection goals for environmental risk assessment of pesticides. Sci Total Environ 415:31–38

OECD (2000a) Test No. 106: Adsorption -- desorption using a batch equilibrium method. OECD, Paris
OECD (2000b) Test No. 216: Soil microorganisms: nitrogen transformation test. OECD, Paris
OECD (2002) Test No. 308: Aerobic and anaerobic transformation in aquatic sediment systems. OECD, Paris
OECD (2004a) Test No. 218: Sediment-water *Chironomid* toxicity using spiked sediment. OECD, Paris
OECD (2004b) Test No. 219: Sediment-water *Chironomid* toxicity using spiked water. OECD, Paris
OECD (2007) Test No. 225: Sediment-water *Lumbriculus* toxicity test using spiked sediment. OECD, Paris
OECD (2010) Test No. 233: Sediment-water *Chironomid* life-cycle toxicity test using spiked water or spiked sediment. OECD, Paris
OECD (2014) Accepted OECD test guideline for water-sediment *Myriophyllum spicatum* toxicity test (Myrio 2-Phase), April 2014. OECD, Paris, http://www.oecd.org/env/ehs/testing/section2effectsonbioticsystems.htm
Palmer MA et al (2000) Linkages between aquatic sediment biota and life above sediments as potential drivers of biodiversity and ecological processes. Bioscience 50:1062–1075. doi:10.1641/0006-3568(2000)050[1062:lbasba]2.0.co;2
Park RA, Clough JS, Wellman MC (2008) AQUATOX: Modeling environmental fate and ecological effects in aquatic ecosystems. Ecol Model 213:1–15. doi:10.1016/j.ecolmodel.2008.01.015
Pastorok RA, Akçakaya R, Regan H, Ferson S, Bartell SM (2003) Role of ecological modeling in risk assessment. Hum Ecol Risk Assess 9:939–972. doi:10.1080/713610017
Pistocchi A, Sarigiannis DA, Vizcaino P (2010) Spatially explicit multimedia fate models for pollutants in Europe: state of the art and perspectives. Sci Total Environ 408:3817–3830. doi:10.1016/j.scitotenv.2009.10.046
Poot A, Jonker MTO, Gillissen F, Koelmans AA (2014) Explaining PAH desorption from sediments using Rock Eval analysis. Environ Pollut 193:247–253. doi:10.1016/j.envpol.2014.06.041
Posthuma L, Suter GWI, Traas TP (2002) Species-sensitivity distributions in ecotoxicology. CRC Press, Lewis Publishers, Boca Raton, FL
Posthuma L, Eijsackers HJP, Koelmans AA, Vijver MG (2008) Ecological effects of diffuse mixed pollution are site-specific and require higher-tier risk assessment to improve site management decisions: a discussion paper. Sci Total Environ 406:503–517
Redman AD, Parkerton TF, Paumen ML, McGrath JA, den Haan K, Di Toro DM (2014) Extension and validation of the target lipid model for deriving predicted no-effect concentrations for soils and sediments. Environ Toxicol Chem 33:2679–2687. doi:10.1002/etc.2737
Rico A, Van den Brink PJ (2015) Evaluating aquatic invertebrate vulnerability to insecticides based on intrinsic sensitivity, biological traits, and toxic mode of action. Environ Toxicol Chem 34:1907–1917. doi:10.1002/etc.3008
Rico A et al (2014) Use, fate and ecological risks of antibiotics applied in tilapia cage farming in Thailand. Environ Pollut 191:8–16. doi:10.1016/j.envpol.2014.04.002
Rico A, Van den Brink PJ, Gylstra R, Focks A, Brock TCM (2015 online). Developing ecological scenarios for the prospective aquatic risk assessment of pesticides. Integrated Environmental Assessment and Management doi: 10.1002/ieam.1718
Rubach MN et al (2011) Framework for traits-based assessment in ecotoxicology. Integr Environ Assess Manag 7:172–186. doi:10.1002/ieam.105
Rykiel EJ Jr (1996) Testing ecological models: the meaning of validation. Ecol Model 90:229–244. doi:10.1016/0304-3800(95)00152-2
Sanco (2002) Working document: guidance document on aquatic ecotoxicology, vol rev. 4 (Final). European Commission, Health and Consumer Protection Directorate General, Ispra

Sanderson H et al (2007) Assessment of the environmental fate and effects of ivermectin in aquatic mesocosms. Aquat Toxicol 85:229–240. doi:10.1016/j.aquatox.2007.08.011

Scheffer M, Beets J (1994) Ecological models and the pitfalls of causality. In: Mortensen E, Jeppesen E, Søndergaard M, Nielsen LK (eds) Nutrient dynamics and biological structure in shallow freshwater and brackish lakes, vol 94, Developments in hydrobiology. Springer, Amsterdam, pp 115–124. doi:10.1007/978-94-017-2460-9_10

Schmolke A, Thorbek P, Chapman P, Grimm V (2010) Ecological models and pesticide risk assessment: current modeling practice. Environ Toxicol Chem 29:1006–1012. doi:10.1002/etc.120

Selck H et al (2012) Explaining differences between bioaccumulation measurements in laboratory and field data through use of a probabilistic modeling approach. Integr Environ Assess Manag 8:42–63. doi:10.1002/ieam.217

Semple KT, Morriss AWJ, Paton GI (2003) Bioavailability of hydrophobic organic contaminants in soils: fundamental concepts and techniques for analysis. Eur J Soil Sci 54:809–818. doi:10.1046/j.1351-0754.2003.0564.x

Seth R, Mackay D, Muncke J (1999) Estimating the organic carbon partition coefficient and its variability for hydrophobic chemicals. Environ Sci Technol 33:2390–2394. doi:10.1021/es980893j

Sidney LA, Diepens NJ, Guo X, Koelmans AA (in prep) Trait-based modelling of bioaccumulation by freshwater benthic invertebrates

Smit MGD, Kater BJ, Jak RG, van den Heuvel-Greve MJ (2006) Translating bioassay results to field population responses using a Leslie-matrix model for the marine amphipod Corophium volutator. Ecol Model 196:515–526

Solomon KR et al (2008) Extrapolation practice for ecological effect and exposure characterization of chemicals. Society of Environmental and Chemistry (SETAC) & CRC Press, Boca Raton, FL

Stronkhorst J, van Hattum B, Bowmer T (1999) Bioaccumulation and toxicity of tributyltin to a burrowing heart urchin and an amphipod in spiked, silty marine sediments. Environ Toxicol Chem 18:2343–2351. doi:10.1002/etc.5620181031

Telfer T, Baird D, McHenery J, Stone J, Sutherland I, Wislocki P (2006) Environmental effects of the anti-sea lice (Copepoda: Caligidae) therapeutant emamectin benzoate under commercial use conditions in the marine environment. Aquaculture 260:163–180

Thain JE, Davies IM, Rae GH, Allen YT (1997) Acute toxicity of ivermectin to the lugworm *Arenicola marina*. Aquaculture 159:47–52. doi:10.1016/S0044-8486(97)00210-X

Thomann RV, Connolly JP, Parkerton TF (1992) An equilibrium model of organic chemical accumulation in aquatic food webs with sediment interaction. Environ Toxicol Chem 11:615–629. doi:10.1002/etc.5620110505

Thomann RV, Mahony JD, Mueller R (1995) Steady state model of biota sediment accumulation factor for metals in 2 marine bivalves. Environ Toxicol Chem 14:1989–1998. doi:10.1897/1552-8618(1995)14[1989:smobsa]2.0.co;2

Van Beelen P, Doelman P (1997) Significance and application of microbial toxicity tests in assessing ecotoxicological risks of contaminants in soil and sediment. Chemosphere 34:455–499

van Beusekom OC, Eljarrat E, Barceló D, Koelmans AA (2006) Dynamic modeling of food-chain accumulation of brominated flame retardants in fish from the Ebro River Basin, Spain. Environ Toxicol Chem 25:2553–2560. doi:10.1897/05-409r.1

Van den Brink PJ, Baveco JM, Verboom J, Heimbach F (2007) An individual-based approach to model spatial population dynamics of invertebrates in aquatic ecosystems after pesticide contamination. Environ Toxicol Chem 26:2226–2236. doi:10.1897/07-022r.1

Van der Ploeg MJC, Baveco JM, Van der Hout A, Bakker R, Rietjens IMCM, Van den Brink NW (2011) Effects of C60 nanoparticle exposure on earthworms (*Lumbricus rubellus*) and implications for population dynamics. Environ Pollut 159:198–203. doi:10.1016/j.envpol.2010.09.003

van Noort PCM, Koelmans AA (2012) Nonequilibrium of organic compounds in sediment–water systems. Consequences for risk assessment and remediation measures. Environ Sci Technol 46:10900–10908. doi:10.1021/es300630t

Van Vlaardingen P, Traas TP, Aldenberg T (2004) ETX2.0 Normal distribution based hazardous concentration and fraction affected. RVIM, Bilthoven

van Wijngaarden RPA, Maltby L, Brock TCM (2015) Acute tier-1 and tier-2 effect assessment approaches in the EFSA Aquatic Guidance Document: are they sufficiently protective for insecticides? Pest Manag Sci 71:1059–1067. doi:10.1002/ps.3937

Vanier C, Planas D, Sylvestre M (2001) Equilibrium partition theory applied to PCBs in macrophytes. Environ Sci Technol 35:4830–4833. doi:10.1021/es001519y

Vermeire TG et al (1997) European Union System for the Evaluation of Substances (EUSES). Principles and structure. Chemosphere 34:1823–1836. doi:10.1016/S0045-6535(97)00017-9

VICH (2004) Environmental impact assessment for veterinary medicinal products—phase II. International cooperation on harmonisation of technical requirements for registration of veterinary products. VICH, London

Wall DH (2004) Sustaining biodiversity and ecosystem services in soils and sediments. Island Press, Washington, DC

Wall DF, Blackburn TH, Brussaard L, Hutchings P, Palmer MA, Snelgrove PV (1997) Linking biodiversity and ecosystem functioning of soils and sediments. Ambio 26:556–562

Weisbrod AV, Woodburn KB, Koelmans AA, Parkerton TF, McElroy AE, Borgå K (2009) Evaluation of bioaccumulation using in vivo laboratory and field studies. Integr Environ Assess Manag 5:598–623. doi:10.1897/ieam_2009-004.1

Weston DP, You J, Harwood AD, Lydy MJ (2009) Whole sediment toxicity identification evaluation tools for pyrethroid insecticides: III. Temperature manipulation. Environ Toxicol Chem 28:173–180. doi:10.1897/08-143.1

# How Important Is Research on Pollution Levels in Antarctica? Historical Approach, Difficulties and Current Trends

**Małgorzata Szopińska, Jacek Namieśnik, and Żaneta Polkowska**

## Contents



## List of Acronyms

| | |
|---|---|
| AFS | Atomic fluorescence spectrometry |
| CCAMLR | The Commission for the Conservation of Antarctic Marine Living Resources |
| CD | Conductometry detector |
| CFCs | Chlorofluorocarbons |
| CHLs | Chlordanes |
| COMNAP | Council of Managers of National Antarctic Program |
| CZE | Capillary zone electrophoresis |

M. Szopińska • J. Namieśnik • Ż. Polkowska (✉)
Department of Analytical Chemistry, Faculty of Chemistry, Gdansk University of Technology, 11/12 Narutowicza St., Gdansk 80-233, Poland
e-mail: szopinska.malgorzata@gmail.com; chemanal@pg.gda.pl; zanpolko@pg.gda.pl



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| | |
|---|---|
| DDD | Dichlorodiphenyldichloroethane |
| DDE | Dichlorodiphenyldichloroethane |
| DDT | Dichlorodiphenyltrichloroethane |
| DLCs | Dioxin-like compounds |
| ECD | Electron capture detector |
| GC-MS | Gas chromatography–mass spectrometry |
| GPC | Gel permeation chromatography |
| HBB | Hexabromobenzene |
| HCB | Hexachlorobenzene |
| HCFCs | Hydrochlorofluorocarbons |
| HCHs | Hexachlorocyclohexanes |
| HPLC | High-performance liquid chromatography |
| IC | Ion chromatography |
| ICP-AES | Inductively coupled plasma atomic emission spectrometry |
| ICP-MS | Inductively coupled plasma mass spectrometry |
| ICP-OES | Inductively coupled plasma optical emission spectrometry |
| IDMS | Isotope dilution mass spectrometry |
| LC-MS/MS | Liquid chromatography with tandem mass spectrometry detection |
| LOD | Limit of detection |
| LOQ | Limit of quantification |
| LRAT | Long-range atmospheric transport |
| NNA | Neuron activation analysis |
| OC | Organochlorine compound |
| OCP | Organochlorine pesticides |
| PAHs | Polycyclic aromatic hydrocarbons |
| PBDEs | Polybrominated diphenyl ethers |
| PCBs | Polychlorinated biphenyls |
| PCDDs | Polychlorinated dibenzodioxins |
| PCDFs | Polychlorinated dibenzofurans |
| PCNs | Polychlorinated naphthalenes |
| PFBS | Perfluorobutane sulfonate |
| PFHxA | Perfluorohexanoic acid |
| PFNA | Perfluorononanoic acid |
| PFOA | Perfluorooctanoic acid |
| PFOS | Perfluorooctanesulfonic acid |
| POPs | Persistent organic pollutants |
| QqQ | Triple quadrupole |
| SFC | Supercritical fluid chromatography |
| SML | Surface microlayer |
| TC | Thermal conductivity |
| TLC | Thin-layer chromatography |
| TOC | Total organic carbon |
| TOF | Time of flight analyzer |
| XRF | X-ray fluorescence |

Highlights

- Scientific interest in the issue of presence of pollutants in Antarctica steadily increasing since 1960.
- In various samples from Antarctica a variety of harmful pollutants were identified.
- The analytic methods, which are dedicated to determine POPs and metals in different matrices, need to be developed.
- Antarctica is prone to storage of POPs, which may also undergo remobilization processes.

## 1 Introduction

The term "*Antarctica*" is used to define both the Antarctica continent itself as well as the Southern Ocean that surrounds the continent and the islands of this ocean. Antarctica is the most isolated continent; however, its specific location does not protect this area from negative impact of human activities (Aronson et al. 2011). A broad belt of the Southern Ocean's waters constitutes a barrier, which makes it difficult to transport pollutants this way. Therefore, volatile and semi-volatile chemical compounds may reach Antarctica together with air masses moving in this direction (long-range atmospheric transport—LRAT) (Corsolini 2009). However, more and more attention has been recently paid to the determination of the size of the locally emitted contamination impact on Antarctic environment (Bengtson Nash et al. 2011).

The first information on the occurrence of anthropogenic pollutants comes from the 1960s and it pertains to the presence of dichlorodiphenyltrichloroethane (DDT) in sea organisms (Bargagli 2008). Further research pertained to chemical composition of samples of water, snow and ice and it included metal and ion determination. Since the 1960s, research on the presences of pollutants from the group of persistent organic pollutants (POPs), e.g. hexachlorobenzene (HCB), hexachlorocyclohexanes (HCHs), aldrin, endrin, heptachlor and other pollutants in samples of living and non-living matter collected in Antarctica has been undertaken (Bargagli 2008; Corsolini 2009).

However, due to difficult climatic conditions, research pertaining to pollution analysis in this area was conducted on irregular basis. In recent decades, there has been a growing interest in the problems of pollutants present in samples from various elements of Antarctica's ecosystem. Figure 1 presents milestones of events influencing the development of research on Antarctica (including ones influenced development of chemical research).

Urbanised areas, especially those with intensive agriculture, as well as tropical and subtropical regions, where spraying is used for disease vector control, are the main sources of POPs and heavy metals in the Southern Hemisphere. The increase in the usage of many POPs has been observed in the 1990s in Asian countries and Southern Pacific islands (Bargagli 2008). Some large amounts of polychlorinated biphenyls (PCBs) used in older electrical devices were also deposited as landfill in some developing countries. The heaviest user of DDT, toxaphene and lindane, has

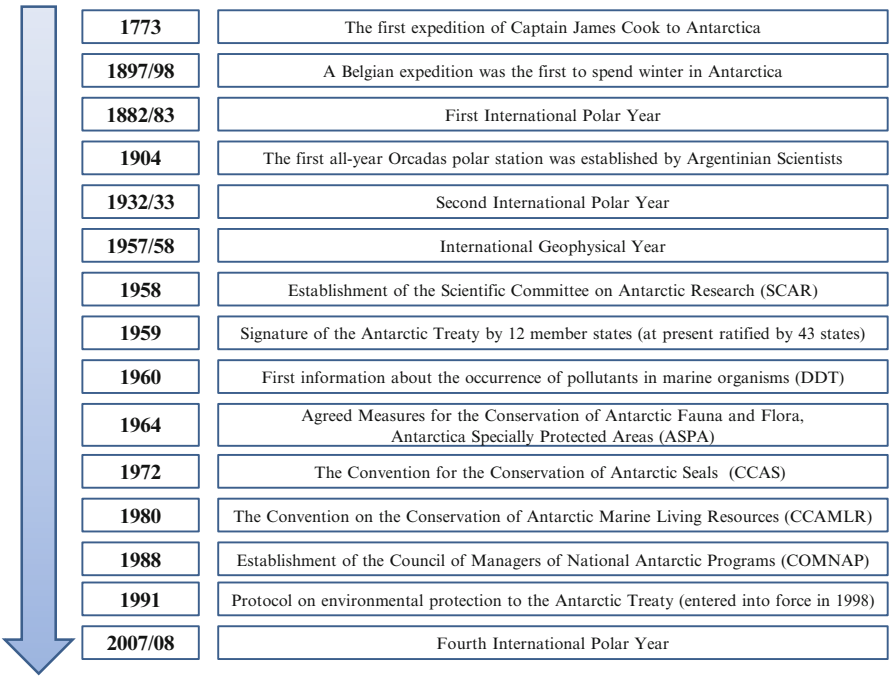


**Fig. 1** Milestones of events connected with the development of Antarctic research (Köler 2013; SCAR Information; Dastidar and Ramachandran 2008; Dodds 2010)

historically been in South America. A comprehensive report by UNEP in 2002 gives more precise data on air levels of POPs in the Southern Ocean and Antarctica (Bargagli 2008).

A critical comparison and discussion of results of the research conducted over decades is not easy, as over a period of more than 50 years, methods and techniques used for research have undergone continuous changes. Moreover, while conducting research on such a complex ecosystem, it is necessary to frequently verify any possible changes by comparing the data acquired during different research projects and at different times. However, this task often cannot be practiced as the results may be achieved with the use of analytical techniques which present extremely different degrees of accuracy and sensitivity (Magi and Tanwar 2014).

The study presents information on the dynamics of the development of polar research (covering main groups of pollutants) both in terms of its methodology and the scope of research on Antarctica (diversity of tested samples and analytes) conducted over the past decades by members of teams working at polar research stations.

## 2 The Presence of Pollutants in Antarctica's Environment

Polar ecosystems consist of several key species. Mutual relationships between individual elements of the environment are closely connected; therefore, the presence of pollutants in one of elements of the ecosystem may have a significant

influence on the functioning of the other ones. To become familiar with the influence of pollutants on the functioning of Antarctica's ecosystem, research is conducted on both abiotic and biological samples.

## *2.1 Abiotic Environment*

Abiotic environmental media (fresh water and seawater, precipitation, glaciers, soils, etc.), as well as all processes and phenomena connected with changes occurring in individual elements of the environment (meteorological, geological, geochemical processes, etc.), play a significant role in transporting pollutants in Antarctica (Cipro et al. 2012). Elements of abiotic environmental media, such as snow, glaciers and polar catchment areas are sources of water for all organisms living in Antarctica. Antarctica's ecosystem has a very simple structure, therefore, even a small amount of pollution present in abiotic elements of nature may constitute a significant hazard for any individual plant and animal species because of absence of advanced detoxification mechanisms (Bengtson Nash et al. 2011).

### 2.1.1 Air

The atmosphere plays an important role in transport of pollutants to polar areas. Over the past decade, a range of research has been conducted to determine mechanisms, which contribute to the presence of pollutants in Antarctica, as well as to distinguish between local sources of pollution and long-range atmospheric transport.

Information about Antarctica's air pollutants mostly comes from research conducted during cruises near Antarctica (Bengtson Nash et al. 2011) and is predominantly based on short-term (weeks–month) atmospheric monitoring (Kallenborn et al. 2013). Some of these data have been included in the assessment of global distribution of numerous POPs. However, due to the limited number of samples and non-continuous measurement periods, it is difficult to compare the results of air sample research conducted in Antarctica with the results of sample research from the Arctic region. A long-term atmospheric pollution monitoring in the polar regions is a significant scientific tool for assessing anthropogenic influences on the environment on a global scale. It enables the control or even changes of international legal regulations (Kallenborn et al. 2013).

The results of research on long-term monitoring of POPs were published in 2013 and focused on the concentrations of long-range transported contaminants (POPs) in the Antarctic environment. The research has revealed that the atmospheric long-range transport of polluted air masses is considered as the main source for the POPs monitored at Norwegian Troll station in Dronning Maud Land (Kallenborn et al. 2013). In the discussion about the presence of more volatile substances in Antarctica, as a source of it, long-range atmospheric transport is considered, while the presence of less volatile substances, which occur occasionally in Antarctic's air,

may rather indicate influence of local sources (Kallenborn et al. 2013). A particular impact of local sources is shown in the analysis of compounds from the polybrominated diphenyl ethers (PBDEs) group. Due to the fact that neither plastics nor PBDE manufacturing occur in Antarctica, the substantial indoor PBDE residues are likely to originate from losses of imported flame retarded plastic and electronic products. There are plenty of electronic devices in the research stations, but at the same time there is not much space for them. Moreover, the material transport to Antarctica is expensive (Hale et al. 2008). The first atmospheric measurement, which was constructed as a part of a new continuous monitoring effort, was presented in one of Australia's all-year research station—Casey Station (66°17′ S 110°3′ E). The results suggest a potential local source of the currently produced, involatile, decabrominated PBDE congener 209, which contributes to PBDE profiles in all the samples (Bengtson Nash et al. 2011).

These discussions prove that it is necessary to take additional precautions in order to stop further deterioration of the pristine air status in Antarctica caused by the human presence in this region.

### 2.1.2 Snow and Ice

In polar areas chemicals like POPs have been observed in seasonal snowpack and in older layers of firn and ice, providing accumulation time series (Herbert et al. 2006b).

During long-range atmospheric transport, pollutants may undergo decomposition and deposition processes, depending on the physicochemical properties of individual compounds.

The mechanisms of exchange of trace organic contaminants between the atmosphere and snow (both falling snow and standing snowpack) depend on the major processes like scavenging (vapour and particle) by falling snow, vapour sorption/desorption to the snow's surface, and diffusion of chemicals both into and out of the snowpack (Herbert et al. 2006b). These processes dictate the quantities of chemical compounds available to meltwater and in deeper areas (permanent snow and ice). Additionally, processes occurring after deposition, e.g. snow settling (fresh snow is gradually transformed into firn and then in a glacier layer, the volume of which becomes gradually reduced) are of importance. The snow-settling process is the first stage, during which compounds, e.g. from the polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) group, are adsorbed on snowflakes. These compounds due to their physicochemical properties are classified as semi-volatile compounds, may become released back to the gaseous phase during seasonal snowmelt or diffused into deeper snow layers (Wania 1997). This process *inter alia* depends on solubility (concentration of a given compound), the snow-air partitioning properties and the temperature gradient. The snow-air partitioning properties not only depend on the vapour pressure but also on the surface properties of the snow flakes/snow pack. These properties largely determine the sorption and diffusion processes (Herbert et al. 2006b).

Based on experimental diffusivities for a volatile tracer of sulfur hexafluoride in snowpack it was concluded that in the low-wind (up to 3 m/s) scenario the migration of sulfur hexafluoride in the snowpack can be largely attributed to diffusive transport, while at high wind speeds (up to 9 m/s) the chemical migration is largely due to advective transport (Albert and Shultz 2002). Snow and firn metamorphism processes depend on the temperature fluctuations. Grain growth may occur, which, in turn, increases the firn permeability. As a result of global migration of a broad range of compounds towards higher latitudes, they become accumulated in polar regions (Kozak et al. 2013). Systematic compound accumulation contributes to the formation of a pollutant reservoir. A large part of the pollutant load is stored in snow and ice. Chemical compounds, which may be trapped in polar areas, can constitute a long-term hazard due to the possibility of their subsequent release into the environment—the so-called reemission into the environment may occur (Herbert et al. 2006a). Quantities of pollutants released during the spring snowmelt could have significant influence on the quantities of pollutants present in both freshwater and marine system (Herbert et al. 2006b). This hypothesis is named "spring pulse" and currently researchers are working on the creation of snowmelt models concerning quantitative transport of pollutants from snow to other abiotic environmental media (Burniston et al. 2007; Herbert et al. 2006b; Wania et al. 1999).

### 2.1.3 Soil and Permafrost

For the study of air transported pollutants, soil samples are worthy of note materials because of their direct contact with the atmosphere. Antarctica's soil may become polluted as a result of wet and dry deposition (LRAT) and accidental release of pollutants into the environment (oil spills) (Curtosi et al. 2007; Webster et al. 2003; Aisable et al. 2004).

The concentration limits of compounds in soil depend on the type of soil. Antarctica's soil variability is mainly due to parent material, differences in land-surface age (range: from a few thousand to millions of years), topographic position and local climate (Aisable et al. 2004).

In general approach to the presence of pollutants in soil, permafrost and an active soil layer play an important role in migration of compounds in soil (Curtosi et al. 2007). An active soil layer and permafrost presence is a unique characteristic of polar areas. It is known that repeated freeze/thaw cycles occur in areas with an active layer of permafrost, as a result of which soil particles may undergo a slow process of screening. Small particles may migrate from the surface layer into deeper layers, while stones have a tendency to migrate from deeper layers to the surface. Pollutants are adsorbed mostly from the surface of particles with a smaller diameter. Research results show that the percentage (quantity) of small particles and their dynamics in the soil matrix are the key factors in determining the fate and degradation of pollutants, e.g. PAHs in Antarctic soil. In this way, thawing of the upper layer of the permafrost, which may be caused by global warming, will have widespread influence on the distribution of pollutants in this environment (Curtosi et al. 2007).

### 2.1.4 Catchment Areas

There are lakes and small streams, which thaw in the summer in small areas of Antarctica which are free from ice. Open water lakes in Antarctica are very rare due to low temperatures. However, the accumulation of pollutants also occurs in lakes and lake sediments. Much higher concentrations (as compared to concentrations of the same analytes in soil samples) of some compounds, e.g. HCH in lake sediments are probably determined by the nature of Antarctic lakes. Antarctic's lakes are formed from melting ice water, which is rich in atmospheric particles (trapped in it during formation) (Fuoco et al. 2009a; Vandal et al. 1998).

Another factor, which influences the level of pollutants in freshwater environment, is the transport of persistent chemicals by seabirds biovector. Higher concentration of POPs has been recorded in aquatic organisms from a seabird-affected lake. This is a proof that seabird-transported contaminants have been entering freshwater and thereby local food webs (Michelutti et al. 2010; Xie and Sun 2008). As long as detailed mechanism of pollution transfer by seabird's vectors are not widely described, further researches should be applied in this direction.

### 2.1.5 Ocean, Seas and Bottom Sediments

Oceans and seas plays a significant role in the circulation and removal of pollutants. Within Antarctica, the Antarctic Convergence Zone (also called the Antarctic Polar Front) is distinguished. It runs between 47°S and 62°S. It separates cold and less saline Antarctic waters from subantarctic waters. The zone may be the barrier for pollutants transported by sea (Bengtson Nash et al. 2011).

Relatively much attention was devoted to research targeted at estimating the degree of exchange of pollutants between the seawater surface (inter-phase) and the atmosphere and the role of seawater in the process of transporting chemical compounds to polar regions. The sea surface consists of layers, out of which the sea surface microlayer (SML) has been researched most broadly (0.1–0.001 mm). This is a place where pollutants, atmospheric particles and microorganisms accumulate. However, the majority of research projects focusing on measurements of pollutant content in SML samples were conducted using samples collected in coastal environments. There is very little data from open ocean samples (Fuoco et al. 2009a).

Another element of abiotic environmental media in the pollutant transportation process is bottom sediments. More hydrophobic organic compounds may undergo sorption on solid particles and microorganisms. Dead particles of organic matter and solid particles settle on the bottom and, thus, pollutants adsorbed on them accumulate in bottom sediments (Boutron et al. 1990). Pollutants present in bottom sediments may be re-emitted as a result of activity of bottom organisms and ocean currents. Thus, the bottom sediments can become secondary source of pollution.

## 2.2 *Biotic Environment*

Anthropogenic pollutants have an adverse effect on living organisms. Antarctic biota (e.g. seals and penguins) are particularly sensitive to contaminants. The natural stress on wildlife in extreme polar environments is often more severe than in temperate regions. Hence Antarctic species can be more vulnerable to the effects of pollutants in comparison with species which come from temperate regions (Schiavone et al. 2009a). Moreover, due to very simple structures of polar ecosystems, relationships between individual organisms are important in terms of pollution transfer. Mutual connections between individual species determine the way, in which pollutants are transported (Cipro et al. 2012).

### 2.2.1 Plants

Mosses and lichens are the main components of the terrestrial flora of Antarctica's ecosystem. Bryophytes are predominantly useful for monitoring the atmospheric pollution (metals and organochlorine compounds) because they have no protective waxy cuticles and no root system (Borghini et al. 2005). The content of pollutants present in samples of these plants largely depends on precipitation. Thus, they can play a very important role of biomonitors, i.e. indicators of long-term pollutant deposition (Fuoco et al. 2009a).

As mentioned above, pollutants present in the air may undergo dry or wet deposition, thus getting into Antarctica's environment. Plants absorb pollutants from the atmosphere (through their above-ground parts, especially leaves) or/and from the soil (through the roots). For compounds with strong hydrophobic properties, transport through solids seems to have little significance. Literature data may be the basis for concluding that the main mechanism of collecting pollutants from the environment is absorption from the surrounding air into the leaf surface of pollutants in the gaseous phase or the solid phase (through particles settled on plant surfaces) (e.g. Borghini et al. 2005; Mão de Ferro et al. 2014; Poblet et al. 1997; Wu et al. 2014; Yogui and Sericano 2008; Yogui et al. 2011). Pollutants get into plants through stomata or leaf epidermis. Furthermore, the process of "assimilating pollutants" into plants is influenced by a range of physicochemical factors (e.g. partial pressure of water vapour, the numerical value of the octanol/water partition coefficient and the water/octanol partition coefficient), environmental factors (e.g. the temperature, precipitation, wind speed) and plant properties (e.g. the species, fat content, leaf morphology) (Yogui and Sericano 2008; Yogui et al. 2011).

### 2.2.2 Crustaceans, Benthic Organisms and Fishes

Antarctica's ecosystem has a very simple structure. Organisms at higher levels of the trophic chain depend on several key species, such as the Antarctic silverfish (*Pleuragramma antarcticum*) and the Antarctic krill (*Euphausia superba*). The

Antarctic silverfish and the Antarctic krill are the main sources of food for many maritime species of birds and mammals. As a result of the mutual relationship between the size of the krill and silverfish populations and the size of the populations of other species, a decrease in the krill and silverfish population size may have a negative impact on the entire environment of Antarctica's marine ecosystem (Corsolini et al. 2002b). As a result of close relationships between individual species, POPs are present in every level of the trophic chain (Corsolini et al. 2002b). The phenomenon of biomagnification plays a more important role than bioaccumulation itself in the case of Antarctic fish. Lower pollutant concentrations are observed in samples of fish, for which krill is the staple food. Values of harmful compound concentrations increase if invertebrates or other fish are the main source of food (Weber and Goerke 2003).

In pelagic fish a downward trend in concentrations of some persistent organic pollutants (e.g. HCB, dieldrin) is visible (Van den Brink et al. 2011). It contrasts distinctly with steady or increasing concentrations levels in benthic organisms. Transfer of contaminants between Antarctic pelagic and benthic food webs is associated with seasonal sea-ice dynamics and thus with different climatic conditions. This fact may hinder the predictability of future trends of emerging compounds in the Antarctic ecosystem (e.g. the brominated compounds). The discrepancy in trends between pelagic and benthic organisms still remains the question whether the total environmental burden of contaminants in the Antarctic ecosystem is declining or increasing (Van den Brink et al. 2011).

### 2.2.3 Seabirds

Marine birds are another link in the food chain, where penguins constitute the most numerous group. They belong to key-species in Antarctica's ecosystem. Penguins feed mainly on krill and also on fish (depending on krill's accessibility). Researchers have reported that predators may be a sink for chemicals (special for volatile and toxic ones) and this may pose an important environmental problem (Corsolini et al. 2007).

Penguins (Adèlie and Emperor) spend their whole life in the Southern Ocean, while marine bird species, such as migrating snow petrel, south polar skua, brown skua are species migrating all over Antarctica. In both cases, results of samples researched from these species could reflect the condition of their ecosystems (Corsolini et al. 2011). The aforementioned bird species rely on all krill species and the Adèlie penguin eats the most krill (Corsolini et al. 2011). The Emperor penguin also eats a lot of fish as well as crustaceans and cephalopods. The south polar skua feeds on penguins' eggs and chicks and it also eats Antarctic silverfish krill (over 80 %). In the nesting season, on the other hand, skuas depend on food found on land. The brown skua also relies on sea food (Corsolini et al. 2011). Moreover, the research results concerning detection of POPs in seabirds' eggs (including penguin and south polar skua eggs) proved the transfer of POPs from mothers to eggs (Corsolini et al. 2002a).

The most important link between Antarctic marine, freshwater and terrestrial ecosystems constitutes seabirds. In fact, they maintain the development of terrestrial flora due to the high amount of nutrients deposited by seabirds on the land (e.g. by guano). Seabirds usually transport loads of pollution. Unfortunately, endocrine mechanisms are still poorly investigated in free-living organisms, despite the fact, that contaminants have endocrine disrupting properties. In the scientific literature there is surprisingly only few data on the effect of age on contaminant levels, despite the fact that long-lived organisms are thought to be highly sensitive to pollution. Therefore, it is not clear if seabirds accumulate POPs with increasing age (Tartu et al. 2015).

Comparing research results concerning pollution in birds' tissues from other areas of the world, shows that POPs concentrations in penguins are relatively low (Corsolini et al. 2007). In relation to species and sex, different chemical accumulation patterns are observed. Penguins are showing low detoxifying capacities and therefore studies on their xenobiotic metabolism should be carried out (Corsolini et al. 2007).

### 2.2.4 Marine Mammals

During the evaluation of contamination presence in the marine mammals' tissues scientists should bear in mind the migratory habits of these organisms. Some species of marine mammals (including cetaceans) exist in Antarctica' seawaters in summer time and then go northward during winter, while other species, e.g. some seals, spend their entire life cycles in the Southern Ocean and on the Antarctic coasts. In migrating organisms what may affect the amount of pollution in Antarctic organisms is the forage or breed during summer, as well as exposition to pollutants in more contaminated areas during winter. Species and individuals staying in anthropized areas during migration contribute to greater exposure to contamination compared with those that stay in Antarctica all year round. Furthermore, pollution (like POPs) accumulation in marine mammals depends on some other factors including metabolism (Corsolini 2009).

Marine mammals differ from the land ones with a high lactation transfer of all lipophilic substances (including pollutants) to young animals (Schiavone et al. 2009a; Trumble et al. 2012). This mostly results from an increased fat content in the mother's milk (Schiavone et al. 2009a). For cetacea and pinnipeds a vast majority (approx. 90 %), of the total amount of chloroorganic pollutants occurring in newborns are transferred in the mother's milk (Cipro et al. 2012). Due to the position of mammals in the trophic chain of the marine environment, a relatively long life and an increased demand for energy, the pinniped species can be treated as an indicator (reference) species for the examination of harmful effects of pollutant bioaccumulation in organisms (Cipro et al. 2012).

Marine mammals have been exposed also *inter alia* to heavy metals. Scientists are devoting particular attention to mercury because of its toxicity as well as the fact that it is widespread within the environment, and can be biomagnified in marine food chains. Very important is also the fact that Hg is available mainly because of human activities (e.g. Jerez et al. 2011). However, data of concentrations of Hg in seals and other vertebrates of Antarctica's are sparse (Szefer et al. 1993). Moreover, most of the attention in marine mammals' research is devoted to the identification of organic contaminants. Some reports lead even to observation of an increasing trend of PCBs and chlorinated pesticides: HCB, HCHs, chlordanes (CHLs), DDTs in minke whales (*Balaenoptera bonaerensis*) feeding on Antarctic krill between 1984/1985 and 1992/1993 (Aono et al. 1997). Concentration of DDTs, PCBs and HCB have been reported in various species of marine mammals during last decades. However, data on the presence of other POPs (including new emerging ones, like poly- and per fluorinated organic compounds (PFCs)), even if it was reported in oceanic and lake water samples (Cai et al. 2012), in marine mammals tissues are still scarce (Corsolini 2009).

Only a few of the hundreds of thousands of different industrial chemicals produced on a world scale have been studied and reported in the Antarctic environment. Antarctica's trophic chains are relatively simple and short and therefore understanding the detailed information on the levels of pollutants in different parts of the environment (including abiotic part) is very important. Animals at the top of the food webs depend on a few key species. Therefore affecting one of these key species could have a devastating impact on the whole ecosystem.

## 3 Types of Pollutants Present in Antarctica's Environment

Anthropogenic pollutants in Antarctica may come from global (LRAT) and local sources. Global sources include industrialised sites situated all over the Southern Hemisphere, from which pollutants are transported to Antarctica by various routes (Bargagli 2008). Local sources, on the other hand, include, amongst other things, scientific activities which are connected with the use of waste incineration plant, fuel consumption, sewage production, developing tourism and related intensification of ship transport (Cincinelli et al. 2009). The most polluted areas include areas around historic bases and polar stations where soil is often polluted by fuel remains, solid waste and household sewage (Negri et al. 2006; Webster et al. 2003). Anthropogenic pollutants are present in various elements of the environment in Antarctica. Because of their specific (also hazardous) properties POPs and heavy metals are described in this article in detail. However, authors do not include any chapter about general sources, properties and toxicity of pollutant groups determined in various types of samples collected from the Antarctic environment. This information has been given in other literature sources (e.g. Aisable et al. 2004; Borghesi et al. 2008; Cincinelli and Dickhut 2011; Corsolini 2009; Fuoco et al. 2012; Houde et al. 2011; Ma et al. 2014; Planchon et al. 2002; Vecchiato et al. 2015).

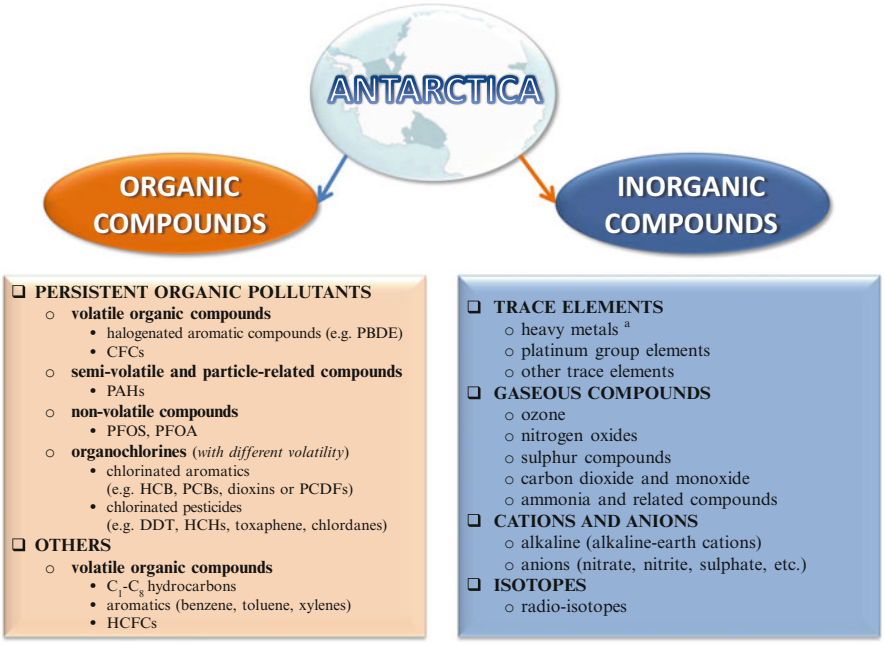


**Fig. 2** The group of chemical compounds identified in Antarctica

Despite the fact that environmental studies represent only a small part of scientific research in Antarctica (Magi and Tanwar 2014), polar explorers are increasingly also interested in chemical research. Figure 2 shows a group of chemical compounds that are of interest to researchers in Antarctica (after Walton et al. 2001).

In the discussion on the presence of organic compounds in the Antarctic environment, scope of interest is mainly focused on POPs like HCB, PCBs, DDTs, PBDE and PAHs. Over the past decades, sporadic research also pertained to identification and determination of compounds such as: CHL, dioxins, dioxin-like compounds (DLCs), PFCs, pesticides (dieldrin, mirex, heptachlor, endosulfan), aliphatic hydrocarbons, n-alkanes and cumulative parameters such as total organic carbon (TOC) in various environmental samples.

The presence of metals in remote Antarctica is not, as it was thought previously, limited only to lead and copper, but also other includes metallic elements, metalloids and radioactive elements, such as: V, Cr, Mn, Zn, Co, Ag, Cd, Ba, Bi, U, Pt, Ir, Rh, Mo, Tl, As, Sb (Hong et al. 2012; Soyol-Erdene et al. 2011).

# 4 Detailed Information Pertaining to Analytical Research in Antarctica

For a long time Antarctica was not available to scientists mainly because of the specificity of its location. Initial research was aimed at getting to know geological properties of the area. With time, also meteorological, magnetic and botanic research was undertaken and in recent years, chemical research was also conducted. The implementation of this research requires enormous involvement and determination on the part of scientists, mostly due to very difficult weather conditions (Köler 2013).

## *4.1 History of Research on the Chemical Composition of Samples from Antarctica*

Research conducted in Antarctica has always been interdisciplinary. One area of research includes actions connected with determining the chemical composition of biotic and abiotic samples. Initially, it was research using classical analytical techniques; however, the scope of determined compounds has been expanded over time. Table 1 presents the historical calendar pertaining to the development of the scope of analytical research of the Antarctic environment conducted up to the end of 1989.[1]

## *4.2 Pollution Concentration Levels Over Decades*

The scope of analytical researches conducted over individual decades is differentiated both in respect of the place of research and types of samples and analytes which are determined in them. Monitoring of the environment allows for reliable observation changes and information contained in publications pertain to individual parts of the Antarctic ecosystem and various groups of pollutants. At present, scientists devote a lot of attention to research on pollutant levels in Antarctica's environment; however, there are still areas which have not been researched in this respect. Figure 3 shows the percentage of most commonly studied regarding the presence of contaminants in the environment of Antarctica up to end of 2014.

In this article, the authors pay particular attention to the research on determination of persistent organic compounds and heavy metals in different samples from

[1] Analytical research is applied in Antarctic since the early 1960s. (that gives 55 years period of research). Hence authors decided to designate first three decades as historic ones (up to the end of 1989). During this period only few data has been published, hence this period is three decades long.

**Table 1** Historical calendar pertaining to the development of the scope of analytical research of the Antarctic environment conducted up to the end of 1989

| Year | Sampling place | Analytes or subject of research | Type of sample | The analytic techniques | Literature |
|---|---|---|---|---|---|
| 1960 | n/a[a] | DDTs | Adelie penguins, crabeater seal | n/a | Bargagli (2008) |
| 1963 | Princess Elizabeth Land | Trace metals: Sr, Br, | Lake water | n/a | Burton (1981) |
| 1964 | South Victoria Land | Element: I | Lake water | n/a | Burton (1981) |
| 1966 | Mc Murdo Dry Valley | Chemical composition ($Cl^-$, $Mg^{2+}$, $Ca^{2+}$,C –biocarbonate ion concentration) temperature, density, solar radiation penetrating the ice, conductivity | Lake water | Classical analytical techniques (titration), selenium photo-electric cell, a bolometer, remote control conductivity probe | House et al. (1966) |
| 1967 | McMurdo Station, Hut Point Peninsula Saddle, Taylor Valley, Ross Ice Shelf, Mt. Discovery | $NO_2$, $SO_2$ aldehydes | Air | Portable air sampling apparatus | Fischer et al. (1967) |
| | South Victoria Land | Trace metals: Mn, Fe, Mo, Pb, Zn, Bi, Rb, Cs | Lake water | n/a | Burton (1981) |
| 1969 | Pacific Ocean | PCBs | Sea birds | n/a | Risebrough et al. (1969) |
| | Interior of The Antarctic Continent | Pollutant lead aerosols, terrestrial dusts and sea salts | Snow strata | n/a | Murozumi et al. (1969) |
| | Plateau Station | DDT | Surface snow | n/a | Peterle (1969) |
| 1972 | Mirny, Vostok | Cl, Na, Mg, K, Ca, Mg, Fe | Surface firn | Atomic absorption, neutron activation | Boutron et al. (1972) |
| | Doumer Island, Antarctic Peninsula | PCBs | Penguin eggs | n/a | Risebrough and Carmlgnani (1972) |
| 1975 | Halley Bay | DDT | Snow | n/a | Peel (1975) |
| 1976 | n/a | DDTs, PCBs | Snow penguin eggs | n/a | Aono et al. (1997), Risebrough et al. (1976) |

(continued)

**Table 1** (continued)

| Year | Sampling place | Analytes or subject of research | Type of sample | The analytic techniques | Literature |
|---|---|---|---|---|---|
| 1978 | East Antarctic, South Polar Station And Dome C | Sulfate $SO_4^{2-}$ | Snow | Classical analytical techniques (titration) | Delmas and Boutron (1978) |
| 1978/1979 | Ross Island and the Wrightand Taylor Valleys | Fe, Hg | Sediments, clays and rock fines | Atomic absorption spectrophotometry | Siegel et al. (1981) |
| 1980 | Mc Mundo | Environmental assessment of Antarctic research | Rocks, ice cores, soil samales, meteorites, certain biota, fossils | n/a | Myers et al. (1980) |
| | King Edward Cove | Aliphatic hydrocarbons, PAHs | Plants, soil, freshwater sediment, zooplankton | Gas chromatography-mass spectrometry (GC-MS) | Platt and Mackie (1980) |
| | James Ross Island | Acidity | Precipitation | pH determination or titration | Delmas and Gravenhorst (1983) |
| 1981 | Signy Island, King Edward Cove | Aliphatic and aromatic hydrocarbons | Marine benthic invertebrates | n/a | Clarke and Law (1981) |
| | Syowa Station | DDTs, PCBs | Fish (whole body) | Gas chromatography—electron capture detector (GC-ECD) | Subramanian et al. (1983) |
| 1982 | The Geographic South Pole | Na, Mg, K, Ca, Fe, Al, Mn, Pb, Cd, Cu, Zn and Ag | Snow layers | Atomic absorption techniques | Boutron (1982) |
| 1983 | n/a | DDTs, PCBs | Fish tissues | n/a | Aono et al. (1997) |
| | Ross Sea | DDTs, PCBs | Weddell seal blubber | n/a | Aono et al. (1997) |
| | East Antarctica | Pb | Snow cores | Isotope dilution mass spectrometry (IDMS) | Boutron and Patterson (1983) |
| 1984 | The Coast On Riiser-Larsenisen Ice Shelf | Ions (for example: $SO_4^{2-}$, $Na^+$) | Snow profiles | n/a | Gjessing (1984) |
| | n/a | DDTs, PCBs | Mink whale liver, Ross seal blubber | n/a | Aono et al. (1997) |

| | | | | | |
|---|---|---|---|---|---|
| 1979 | Areas of the Antarctic ice cap | Heavy metals (Pb, Cd, Cu, Zn, Ag) | Snow | Atomic absorption techniques | Boutron (1979) |
| 1984 | n/a | Trace metals and chlorinated hydrocarbons | Ross seal tissues | Atomic absorption techniques, gas-liquid chromatograph fitted with ECD | McClurg (1984) |
| | East Antarctica | Cd, Cu, Zn, Au, Se, $SO_4^{2-}$ | Prehistoric ice | n/a | Boutron et al. (1984) |
| | n/a | $Na^+$, $NH_4^+$, $K^+$, $Cl^-$, $NO_3^-$, $SO_4^{2-}$ | Snow and ice | Ion chromatography (IC) | Legrand et al. (1984) |
| 1986 | Antarctic Peninsula | Chlorinated hydrocarbon residues (HCB, HCH isomers, p,p′ DDT, DDE, PCB congeners) | Lichen and moss samples | n/a | Bacci et al. (1986) |
| | Adelie Land | $Na^+$, $NH_4^+$, $K^+$, $CI^-$ $NO_3^-$, $SO_4^{2-}$, $Mg^{2+}$ | Precipitation | IC | Legrand and Delmas (1986) |
| | n/a | DDTs, PCBs | Penguin tissues | n/a | Aono et al. (1997) |
| 1987 | Ross Sea, Wilkes Land | Normal alkanes (n-C-$C_{36}$), isoprenoid hydrocarbons (i-$C_{15}$, i-$C_{16}$, i-$C_{18}$, i-$C_{19}$, and i-$C_{20}$) triterpanes ($C_{27}$-$C_{32}$), and ($C_{27}$-$C_{29}$) | Quaternary sediment | n/a | Kvenvolden et al. (1987) |
| | Syowa Station, Antarctica | Heavy metals | Tissue of the Weddell seal | n/a | Yamamoto et al. (1987) |
| | n/a | $NH_4^+$, $F^-$, $COOH^-$, $CHOO^-$, $CH_3SO_3^-$, $F^-$, $NH_4^+$ ions | Ice | IC | Saigne et al. (1987) |
| 1988 | The South Shetland Islands | Pb | Aerosols | IDMS | Völkening et al. (1988) |
| | The Ekstrrm ice shelf, "Georg-von- Neumayer" station | Heavy metals | Surface snow | IDMS, differential pulse anodic stripping voltammetry (DPASV) | Völkening and Heumann (1988) |

(continued)

**Table 1** (continued)

| Year | Sampling place | Analytes or subject of research | Type of sample | The analytic techniques | Literature |
|---|---|---|---|---|---|
| | Weddell Sea, Antarctic Peninsula | $HNO_3$ | Surface snow | IDMS | Neubauer and Heumann (1988) |
| | Sections Of the Byrd Station | Liquid conductivity, acidity, sulfate, nitrate, aluminum, and sodium concentrations | Ice containing tephra (volcanic ash) layers | n/a | Palais (1988) |
| | Vostok Station | $Na^+$, $NH_4^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$, $H^+$, $Cl^-$, $NO_3^-$ $SO_4^{2-}$ | Ice core | n/a | Legrand et al. (1988) |
| | Mc Muurdo Sound | Fatty acids, -alcohols, n-alkanes, PAH | Marine sediments | n/a | Venkatesan (1988) |
| 1989 | n/a | Organochlorine pesticides, PCBs and mercury | Seabird eggs and tissues | n/a | Luke et al. (1989) |
| | The coastal area of Antarctica | $SO_4^{2-}/Na^+$, $SO_4^{2-}/Cl^-$, $SO_4^{2-}/Mg^{2+}$ | Snow | n/a | Gjessing (1989) |
| | Wright Valley, Antarctica | Mn, Fe, Co, Ni, Cu, Cd | Fresh water | n/a | Green et al. (1989) |

[a]no data

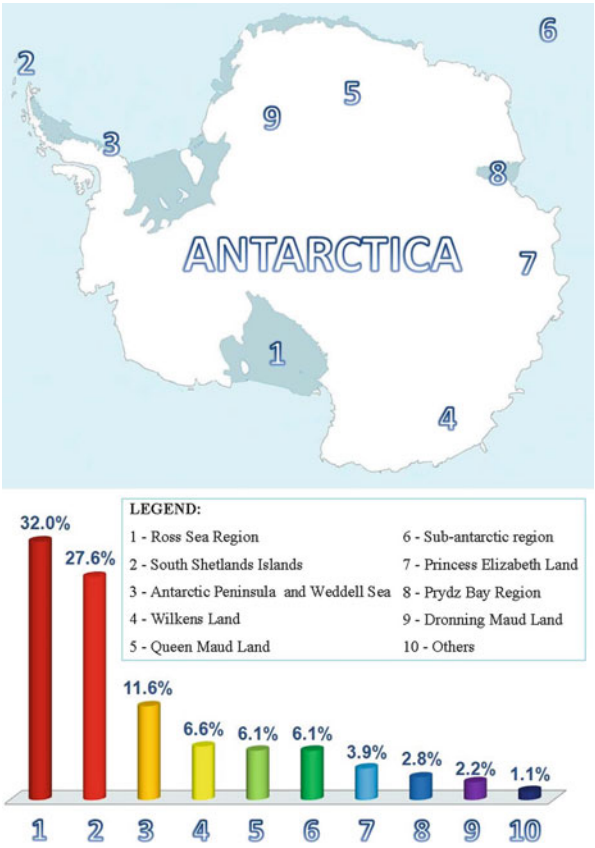


**Fig. 3** The percentage of areas most commonly studied regarding the presence of contaminants up to end of 2014 in the Antarctic environment

Antarctica because of the toxic properties and the threat which is associated with their presence in the polar environment. Table 2 presents general information on xenobiotics determined in samples collected from various parts of the Antarctic ecosystem.

In the discussion pertaining to the presence of pollutants in Antarctica, it is very important to become familiar with accurate levels of concentration present in individual elements of both, biotic and abiotic, environments. Table 3 (A, B, C) data referring to levels of detected contamination present in the whole Antarctic environment and Fig. 4 presents a summary of POPs and heavy metals concentration levels determined in various elements of Antarctica's environments during three time periods (up to end of 2014).

As is showed in Fig. 4 studies on the determination of the pollutants concentrations in biotic and abiotic samples over the decades are irregular. It makes presentation of concentrations trends very difficult. However, as a main source of air contamination the LRAT from Africa, South America or Australia (Negoita et al. 2003) is administered. Nevertheless, the year-round operation of stations

**Table 2** Summary of literature data on results of analytical research on various types of (a) abiotic and (b) biotic samples collected in Antarctica in three time periods

| Abiotic samples | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Type of sample | Time range within which the results were published | Analytes | | | | | | | | | | |
| | | OCP | | | | PCBs | PBDEs | PAHs | PFCs | Metals | Other[b] | Literature |
| | | DDTs | HCHs | HCB | Other[a] | | | | | | | |
| Air | Up to 1989 | x | | | | | | | | | x | Sen Gupta et al. (1996), Fischer et al. (1967) |
| | 1990–1999 | x | x | x | x | x | | x | | x | | Larsson et al. (1992), Kallenborn et al. (1998), Caricchia et al. (1995), Bidleman et al. (1993), Riidlein and Heumann (1995) |
| | 2000–2014 | x | x | x | x | x | x | | | x | x | Cincinelli et al. (2009), Cabrerizo et al. (2013), Galbán-Malagón et al. (2013a, c), Gambaro et al. (2005), Li et al. (2012), Choi et al. (2008), Montone et al. (2003), Baek et al. (2011), Montone et al. (2005), Kallenborn et al. (2013), Dickhut et al. (2005), Ma et al. (2014), Fischer et al. (2002), Sprovieri et al. (2002) |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Snow | Up to 1989 | x | x | | | x | | | | x | x | Kang et al. (2012), Sen Gupta et al. (1996), Delmas and Boutron (1978), Boutron and Patterson (1983), Wania et al. (1998), Boutron et al. (1972), Aono et al. (1997), Risebrough et al. (1976), Völkening and Heumann (1988) |
| | 1990–1999 | | | | | | | | | x | | Suttie and Wolff (1992), Görlach and Boutron (1992), Wolff et al. (1999), Vandal et al. (1995), Capelli et al. (1998). Vandal et al. (1998) |
| | 2000–2014 | | x | x | | x | x | x | x | x | x | Kang et al. (2012), Vecchiato et al. (2015), Fuoco et al. (2012), Nemirovskaya (2006), Antony et al. (2011), Cai et al. (2012), Zoccolillo et al. (2007), Edwards et al. (2001), Planchon et al. (2002), Planchon et al. (2001), Thamban and Thakur (2013), Fortner et al. (2011), Witherow and Lyons (2008), Han et al. (2013), Velde et al. (2005), Burn-Nunes et al. (2011), Vallelonga et al. (2010) |
| Ice | Up to 1989 | | | | | | | | | x | | Boutron et al. (1984) |
| | 1990–1999 | | | | | | | | | x | x | Green et al. (1992), Hong et al. (1998), Vandal et al. (1995) |
| | 2000–2014 | | | | | | | x | | x | | Nemirovskaya (2006), Vallelonga et al. (2010), Jiratu et al. (2009) |

(continued)

**Table 2** (continued)

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Fresh waters | Up to 1989 | x | x | | | | | x | | x | x | Sen Gupta et al. (1996), Burton (1981), Platt and Mackie (1980), Green et al. (1989) |
| | 1990–1999 | | | | | | | | | x | | Vandal et al. (1998) |
| | 2000–2014 | | | | | | | | x | x | x | Cai et al. (2012), Mão de Ferro et al. (2013) |
| Seawater | Up to 1989 | | | | | | | | | | x | Platt and Mackie (1980) |
| | 1990–1999 | | | | | | | | | x | x | Guerra et al. (2013), Stortini et al. (2009), Cripps (1992), Green et al. (1992), Niemistö and Perttilä (1995) |
| | 2000–2014 | x | x | x | | x | | x | x | | x | Cincinelli et al. (2009), Cincinelli et al. (2008), Stortini et al. (2009), Bicego et al. (1996), Galbán-Malagón et al. (2013b), Fuoco et al. (2009b), Zhang et al. (2013), Ahrens et al. (2010), Cai et al. (2012) |
| Polonya water | Up to 1989 | | | | | | | | | | | – |
| | 1990–1999 | x | x | | | x | | | | | | Sen Gupta et al. (1996) |
| | 2000–2014 | | | | | | | | | | | – |
| Sediments | Up to 1989 | | | | | | | x | | x | x | Platt and Mackie (1980), Venkatesan (1988), Merlin et al. (1989), Siegel et al. (1981) |
| | 1990–1999 | x | x | | | x | | | | x | x | Fuoco et al. (1996), Sen Gupta et al. (1996), Risebrough et al. (1990), Green et al. (1992), Vandal et al. (1998), |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | | Yuguang and Junlin (1991), Giordano et al. (1999), Ciaralli et al. (1998), Crespi et al. (1993), Niemistö and Perttilä (1995), Ahn et al. (1996), Alam and Sadiq (1993), Santos et al. (2005), Lenihan (1992) |
| | 2000–2014 | x | x | x | | x | | x | | x | x | Zhang et al. (2013), Klánová et al. (2008), Montone et al. (2001), Curtosi et al. (2007), Dauner et al. (2014), Kim et al. (2006), Negri et al. (2006), Crockett and White (2003), Martins et al. (2010), Siegel et al. (1981), Santos et al. (2007), Ribeiro et al. (2011), Ribeiro et al. (2010), Waheed et al. (2001), Negri et al. (2006), Ianni et al. (2010), Huang et al. (2014), Townsend and Snape (2008), Sun et al. (2013), Vodopivez et al. (2015), Curtosi et al. (2010), Andrade et al. (2001) |
| Soil | Up to 1989 | | | | | | | x | | | x | Platt and Mackie (1980) |
| | 1990–1999 | | x | x | | x | | x | | x | | Aislabie et al. (1999), Mazzera et al. (1999), Kennicutt et al. (1995), |

(continued)

**Table 2** (continued)

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | | Fuoco et al. (1996), Carrasco and Prendez (1991), Bargagli et al. (1995), Bargagli et al. (1999) |
| | 2000–2014 | x | x | x | | x | | x | | x | | Borghini et al. (2005), Klánová et al. (2008), Cabrerizo et al. (2012), Negoita et al. (2003), Curtosi et al. (2007), Kang et al. (2012), Webster et al. (2003), Lu et al. (2012) |
| Biotic samples | | | | | | | | | | | | |
| Type of sample | Time range within which the results were published | Analytes | | | | | | | | | | |
| | | OCP | | | | PCBs | PBDEs | PAHs | PFCs | Metals | Other[d] | Literature |
| | | DDTs | HCHs | HCB | Other[c] | | | | | | | |
| Krill | Up to 1989 | | | | x | | | | | x | x | Platt and Mackie (1980), Bargagli (2008), Moreno et al. (1997) |
| | 1990–1999 | x | x | x | x | x | | | | x | | Sen Gupta et al. (1996), Aono et al. (1997), Bargagli (2008), Petri and Zauke (1993) |
| | 2000–2014 | x | x | x | x | x | x | | | x | | Corsolini et al. (2002a, b), Corsolini et al. (2006), Cincinelli et al. (2009), Cipro et al. (2010), Senthil et al. (2002), Santos et al. (2006) |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Zooplankton and phytoplankton | Up to 1989 | | | | x | | | x | | | x | Platt and Mackie (1980) |
| | 1990–1999 | | | | | | | | | | | – |
| | 2000–2014 | | x | x | | x | | | | x | | Bargagli (2008), Galbán-Malagón et al. (2013b) |
| Benthic organisms | Up to 1989 | | | | x | | | | | | x | Platt and Mackie (1980), Clarke and Law (1981) |
| | 1990–1999 | | | | | | | | | x | | Ahn et al. (1996), Moreno et al. (1997) |
| | 2000–2014 | x | x | x | | x | | x | | x | | Zhang et al. (2013), Hale et al. (2008), Poigner et al. (2013), Vodopivez et al. (2015), Negri et al. (2006), Bargagli (2001), Majer et al. (2014), Bargagli (2008) |
| Fishes | Up to 1989 | x | | | x | x | | x | | | x | Subramanian et al. (1983), Platt and Mackie (1980), Aono et al. (1997) |
| | 1990–1999 | | | | | | | | | x | | Moreno et al. (1997) |
| | 2000–2014 | x | x | x | x | x | | x | | x | | Corsolini et al. (2002a, b), Corsolini et al. (2006), Corsolini (2009), Hale et al. (2008), Borghesi et al. (2009), Borghesi et al. (2008), Weber and Goerke (2003), Lana et al. (2014), Bargagli (2001), Santos et al. (2006) |

(continued)

**Table 2** (continued)

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Seabirds | Up to 1989 | x | | | x | x | | | | x | | Sen Gupta et al. (1996), Risebrough et al. (1969), Aono et al. (1997), Luke et al. (1989), Bargagli (2008) |
| | 1990–1999 | x | x | x | | x | | | | | | Sen Gupta et al. (1996), Court et al. (1997), Aono et al. (1997), Inomata et al. (1996) |
| | 2000–2014 | x | x | x | x | x | x | x | | x | | Corsolini et al. (2006), Corsolini et al. (2011), Schiavone et al. (2009a), Geisz et al. (2008), Cipro et al. (2010), Yogui and Sericano (2009), Taniguchi et al. (2009), Van den Brink et al. (2011), Corsolini et al. (2007), Bustnes et al. (2006), Llorca et al. (2012), Van den Brink et al. (2011), Senthil et al. (2002), Tao et al. (2006), Taniguchi et al. (2009), Brasso and Polito (2013), Santos et al. (2006), Smichowski et al. (2006), Jerez et al. (2013a), Jerez et al. (2011), Bargagli (2001) |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Marine mammals | Up to 1989 | x | | | x | x | | | | x | x | Schiavone et al. (2009a), Aono et al. (1997), Bargagli (2008), Risebrough and Carmlgnani (1972), McClurg (1984), Yamamoto et al. (1987) |
| | 1990–1999 | | | | x | | | | | x | | Aono et al. (1997), Schiavone et al. (2009a), Malcolm et al. (1994), Moreno et al. (1997), Aono et al. (1997), Szefer et al. (1993) |
| | 2000–2014 | x | x | x | x | x | x | | x | x | | Cipro et al. (2012), Schiavone et al. (2009c), Schiavone et al. (2009a), Corsolini et al. (2002a), Trumble et al. (2012), Krahn et al. (2007), Bengtson Nash et al. (2010), Senthil et al. (2002), Tao et al. (2006), Santos et al. (2006) |
| Alge | Up to 1989 | | | | | | | | | | | – |
| | 1990–1999 | | | | | | | | | x | | Moreno et al. (1997) |
| | 2000–2014 | x | | x | | x | | x | | x | | Cabrerizo et al. (2012), Runcie and Riddle (2004), Santos et al. (2006) |
| Antarctic lichens | Up to 1989 | | | | | | | | | | | – |
| | 1990–1999 | | | | | | | | | x | | Poblet et al. (1997), Olech et al. (1998), Upreti and Pandev (1994), Bargagli et al. (1999) |
| | 2000–2014 | x | x | x | | x | x | x | | x | | Cipro et al. (2011), Cabrerizo et al. (2012), Yogui and Sericano (2008), |

(continued)

**Table 2** (continued)

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | | Yogui et al. (2011), Mão de Ferro et al. (2013), Osyczka et al. (2007), Santos et al. (2006) |
| Antarctic mosses | Up to 1989 | | | | | | | | | | | – |
| | 1990–1999 | x | x | x | | x | | | | x | | Focardi et al. (1991), Bargagli et al. (1995) |
| | 2000–2014 | x | x | x | | x | x | x | | x | | Yogui and Sericano (2008), Yogui et al. (2011), Borghini et al. (2005), Cipro et al. (2011), Cabrerizo et al. (2012), Mão de Ferro et al. (2013), Osyczka et al. (2007), Santos et al. (2006) |

[a]Heptachlor epoxide and nanochlors
[b]Sulphate, methyl Hg, n- alkanes, aliphatic hydrocarbons, chlorinated terphenyls, and TOC
[c]Mirex, dieldrin, endosulfan (I/II)
[d]PCNs, PCDDs, PCDFs; sulphate, methyl Hg, n- alkanes, aliphatic hydrocarbons, chlorinated terphenyls, TOC
Authors decided to summary the first three decades of analytical research as historic ones (up to the end of 1989). During this period only few data has been published, hence this period is three decades long. The period between 1990 and 1999 was relatively abundant in terms of applied analytical research, so it has been limited to only one decade. The last period contains years form 2000 up to present times. Authors do not see the need to separate the last decade (incomplete), so this period is 15 years long

**Table 3** Detailed literature data on results of analytical research on (a) main POPs; (b) remaining organic compounds; (c) heavy metals in various types of biotic and abiotic samples collected in Antarctica in three time periods

| Main POPs detected in biotic samples | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Type of sample | Sample | Localization | Range or average concentrations (±standard deviation, if available) | | | | | | | |
| | | | DDTs[a] | PCBs[b] | HCHs[c] | HCB | PBDEs[d] | PAHs | Unit | Literature |
| Data reported in 80th years and earlier | | | | | | | | | | |
| Fish | **Antarctic fishes**; **whole body** (*Pagothenia borchgrevinki*, *Trematomus bernacchii*, *T. hansoni*, *T. Newnesi. T. Borchgrevinki*) | near Syowa Station | 0.03–1.9 | 0.08–0.77 | – | – | – | – | µg/g wet wt | Subramanian et al. (1983) |
| | **Antarctic code**; **flesh** (*Notothenia rossii*) | King Edward Cove | – | – | – | – | – | 0.01–0.5 | ng/g wet wt | Platt and Mackie (1980) |
| | **Antarctic code**; **liver** (*Notothenia rossii*) | | – | – | – | – | – | 0.01–0.11 | ng/g wet wt | |
| Seabirds | **Chinstrap penguin** (*Pygoscelis antarcticus*) | – | 0.63–4.27 | – | – | – | – | – | pg/g | Sen Gupta et al. (1996) |
| | **Macaroni penguin** (*Eudyptes chrysolophus*) | – | 500 | – | – | – | – | – | pg/g | |
| | **Migrating snow petrel** (*Pagodroma nivea*) | – | 600 | – | – | – | – | – | pg/g | |
| Marine mammals | **Crabeater seals** (*Lobodon carcinophagus*) | – | 7–17 | – | – | – | – | – | ng/g | Corsolini (2009) |
| Data reported from 1990 up to 1999 | | | | | | | | | | |
| Crustaceans | **Krill** (*Euphausia superba*) | Dakshin Gangotri, Queen Maud Land | 31.1–44.4 | 146.9–166.2 | 141.3–164.3 | – | – | – | pg/g dry wt | Sen Gupta et al. (1996) |
| | | – | 0.56 | <1.0 | 0.028 | 0.30 | – | – | ng/g wet wt | Aono et al. (1997) |
| Seabirds | **Penguin**; **feathers** | Dakshin Gangotri, Queen Maud Land | 30.8–35.7 | 105.8–113.6 | 103.6–112.8 | – | – | – | pg/g dry wt | Sen Gupta et al. (1996) |
| | **Adélie penguin**; **eggs** (*Pygoscelis adeliea*) | Cape Bird, Ross Island | 12.1–97.4 | 18.7–110.6 | – | 12.5–57.2 | – | – | ng/g dry wt | Court et al. (1997) |
| | **Adélie penguin**; **liver** (*Pygoscelis adeliea*) | | 24.3 ± 12.8 | 618.0 ± 506.0 | – | 15.9 ± 3.9 | – | – | | |
| | **South polar skuas**; **liver** (*Catharacta maccormicki*) | | 263.4 ± 209.2 | 2546.0 ± 1675.0 | – | 49.6 ± 26.0 | – | – | | |
| | **Gentoo penguin**; **fat tissue** (*Pygoscelis papua*)<br>**Adélie penguin**; **fat tissue** (*Pygoscelis adeliea*) | Admiralty Bay, King George Island | 30.8–972.3 | 43.2–1583.6 | <LOD[e]–39.3 | 42.3–1159.7 | – | – | ng/g | Inomata et al. (1996) |

(continued)

**Table 3** (continued)

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|---|---|---|---|---|---|---|---|---|---|---|
| Marine mammals | **Minke whale**; **blubber** (*Balaenoptera Acutorostrata*) | – | 27–380 | 13–210 | 0.67–5.7 | 39–290 | – | – | ng/g wet wt | Aono et al. (1997) |
| Flora | **Antarctic mosses** | Kay Island, Ross Sea and Antarctic Peninsula | 0.2–0.5 | <5–16 | 0.2–1.7 | 0.3–0.8 | – | – | ng/g dry wt | Focardi et al. (1991) |
| Data reported from 2000 up to 2014 | | | | | | | | | | |
| Crustaceans | **Krill** (*Euphausia superba*) | Ross Sea | 0.22–2.30 | 85.27–282.29 | – | 0.2–0.6 | – | – | ng/g wet wt | Corsolini et al. (2002b) |
| | | | 0.07–0.10 | – | 0.28 ± 0.04 | 0.23 ± 0.01 | 0.17–0.23 | – | ng/g wet wt | Corsolini et al. (2006) |
| | | | – | – | 0.001–0.32 | 0.006–0.06 | – | – | ng/g wet wt | Cincinelli et al. (2009) |
| | | | – | 1.9 | – | – | – | – | ng/g wet wt | Corsolini et al. (2002a) |
| | | Admiralty Bay, King George Island | 0.05–0.79 | 4.66–13.6 | – | <LOD–0.06 | – | – | ng/g wet wt | Cipro et al. (2010) |
| Phytoplancton | – | Southern Ocean areas (Weddell, South Scotia, and Bellingshausen Seas) | – | 2.67 ± 0.86–14.07 ± 12.72 | 0.16 ± 0.17–1.81 ± 2.11 | 1.64 ± 2.4–4.34 ± 4.34 | – | – | ng/g dry wt | Galbán-Malagón et al. (2013b) |
| | – | Palmer Station | – | – | 0.45 ± 0.38–1.24 ± 1.65 | 2.9 ± 1.76 | – | – | ng/g lipid wt | Chiuchiolo et al. (2004) |
| Benthic organisms | **Antarctic invertebrates** (*Protelpidia murrayi*, *Peniagone vignoni*, *Bathyplotes natans*, *Molpadia musculus*) | Western Antarctic Peninsula | 0.26 ± 0.15 | 0.84–10.3 | 0.14–0.35 | 0.87 ± 0.34 | – | – | ng/g lipid wt | Zhang et al. (2013) |
| | **Antarctic invertebrates** *clams* (*Laternula elliptica*), *sea stars* (*Odontaster validus*), *sea urchins* (*Sterechinus neumayeri*), *sponges* (*Haliclona sp. and Homaxinella balfourensis*), *proboscis worms* (*Parborlasia corrugatus*) | Mc Murdo Sound | – | – | – | – | – | 356 ± 196 | ng/g lipid wt | Hale et al. (2008) |

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|---|---|---|---|---|---|---|---|---|---|---|
| Fish | **Silverfish**; **larva** (*Pleurgramma antarcticum*) | Ross Sea | 1.51–2.03 | 497.81–509.88 | – | 0.88–4.04 | – | – | ng/g wet wt | Corsolini et al. (2002b) |
| | **Silverfish**; **adults** (*Pleurgramma antarcticum*) | | 0.04–5.70 | 16.2–1050.58 | – | 0.07–14.93 | – | – | | |
| | **Silverfish** (*Pleurgramma antarcticum*) | | – | 138 | – | – | – | – | ng/g wet wt | Corsolini et al. (2002a) |
| | **Rockcod**; **whole body** (*Trematomus bernacchii*) | | 0.02–2.53 | – | 0.03–0.17 | 1.35 ± 1.24 | 0.15– 0.16 | – | ng/g wet wt | Corsolini et al. (2006) |
| | **Rockcod**; **muscle** (*Trematomus bernacchii*) | | 0.11–1.1 | – | 0.03–1.23 | 1.44 ± 0.45 | 0.02–0.06 | – | | |
| | **Rockcod**; (*Trematomus bernacchii*) | | – | – | – | – | – | 1520–1840 | ng/g lipid wt | Hale et al. (2008) |
| | **Antarctic fish** (*Chionodraco hamatus*, *Chaempsocephalus gunnari*,*Gymnoscopelus nicholsi*, *Trematomus eulepidotes*) | | – | – | – | – | 0.001–0.13 | – | ng/g wet wt | Borghesi et al. (2009) |
| | **Crocodile icefish**; **muscle** (*Chionodraco hamatus*) | | – | 0.07–0.95 | – | – | (0.085–0.300) | – | ng/g wet wt; | Borghesi et al. (2008) |
| | **Crocodile icefish**; **liver** (*Chionodraco hamatus*) | | – | 0.75–3.30 | – | – | (0.001–0.320) | – | | |
| | **Emerald rockcod**; **muscle** (*Trematomus bernacchii*) | | – | (0.35–4.20) | – | – | (0.220–0.530) | – | | |
| | **Emerald rockcod**; **liver** (*Trematomus bernacchii*) | | – | (5.20–28) | – | – | (0.500–1.100) | – | | |
| | **Antarctic fish**; **liver** (*Gobionotothen gibberifrons*, *Champsocephalus gunnari*, *Chaenocephalus aceratus*) | Elephant Island, South Shetland Islands | 5–13 | 0.4–2 | – | 15–20 | – | – | ng/g lipid wt | Weber and Goerke (2003) |
| | **Sharp-spined notothen** (*Trematomus pennellii*) | Ross Sea | – | 111–175 | – | – | – | – | ng/g wet wt | Corsolini et al. (2002a) |
| | **Notothenioids fish**; **muscle** (*Trematomus newnesi*, *Notothenia coriiceps*, *Notothenia rossii*) | Potter Cove, King George Island | <LOD–7.31 | <LOQ[f]–8.33 | <LOQ–3.44 | – | <LOQ–8.53 | – | ng/g lipid wt | Lana et al. (2014) |
| | **Notothenioids fish**; **liver** (*Trematomus newnesi*, *Notothenia coriiceps*, *Notothenia rossii*) | | <LOD–10.5 | <LOQ–7.00 | <LOQ–0.99 | – | <LOQ–73.6 | – | ng/g lipid wt | Lana et al. (2014) |
| | **Notothenioids fish**; **gonads** (*Trematomus newnesi*, *Notothenia coriiceps*, *Notothenia rossii*) | | <LOQ–98.8 | <LOQ–46.9 | 2.41–24.2 | – | <LOQ–4.86 | – | ng/g lipid wt | Lana et al. (2014) |
| | **Notothenioids fish**; **gills** (*Trematomus newnesi*, *Notothenia coriiceps*, *Notothenia rossii*) | | <LOQ–43.0 | <LOQ–14.8 | 1.57–9.95 | – | <LOQ–39.8 | – | ng/g lipid wt | Lana et al. (2014) |

(continued)

**Table 3** (continued)

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|---|---|---|---|---|---|---|---|---|---|---|
| Seabirds | **Penguin adèlie**; **eggs** (*Pygoscelis adèliae*) | Ross Sea | 0.31–20.7 | – | 0.05–0.54 | 18.7 ± 8.0 | 0.03–0.65 | – | ng/g wet wt | Corsolini et al. (2006) |
| | | | <LOD–55.80 | 0.03–114.28 | – | 0.12–8.00 | – | – | ng/g wet wt | Corsolini et al. (2011) |
| | | Brainsfield Strait | <LOD–35.13 | 7.26–16.81 | 0.06–1.14 | 5.49–10.56 | – | – | ng/g wet wt | Corsolini et al. (2011) |
| | | King George Island, South Shetland | 23 ± 10 | 12 ± 4 | – | 7.63 ± 1.8 | – | – | ng/g wet wt | Schiavone et al. (2009a) |
| | | Palmer Archipelago | 58.5–755 | – | – | – | – | – | ng/g lipid wt | Geisz et al. (2008) |
| | **Penguin emperor**; **eggs** (*Aptenodytes forsteri*) | Ross Sea | 3.86–10.82 | 2.52–7.69 | – | <LOD–6.57 | – | – | ng/g wet wt | Corsolini et al. (2011) |
| | **Penguins**; **eggs (pooled together)**<br>**Penguins adèlie** (*Pygoscelis adèliae*)<br>**Gentoo penguin** (*Pygoscelis papua*)<br>**Chinstrap penguin** (*Pygoscelis antarcticus*) | Admiralty Bay King George Island | 2.07–38.0 | 2.53–78.7 | <LOD–6.19 | 4.99–39.1 | – | – | ng/g wet wt | Cipro et al. (2010) |
| | **Gentoo penguin**; **eggs** (*Pygoscelis papua*) | Antarctic Peninsula | – | – | – | – | – | 3.03–22.7 | ng/g lipid wt | Yogui and Sericano (2009) |
| | | King George Island, South Shetland | 15 ± 9 | 5 ± 3 | – | 3.7 ± 3.5 | – | – | ng/g wet wt | Schiavone et al. (2009a) |
| | **Chinstrap penguin**; **eggs** (*Pygoscelis antarcticus*) | Antarctic Peninsula | – | – | – | – | – | 3.13–33.0 | ng/g lipid wt | Yogui and Sericano (2009) |
| | | King George Island, South Shetland | 17 ± 15 | 6 ± 4 | – | 3.8 ± 3.7 | – | – | ng/g wet wt | Schiavone et al. (2009a) |
| | **Penguins**; **fat tissue (pooled together)**<br>**Penguins adèlie** (*Pygoscelis adèliae*)<br>**Gentoo penguin** (*Pygoscelis papua*)<br>**Chinstrap penguin** (*Pygoscelis antarcticus*) | King George Island, South Shetland | 193 ± 16 | 256 ± 125 | 12.3 ± 9.1 | 373 ± 177 | – | 1588 ± 654 | ng/g lipid wt | Taniguchi et al. (2009) |
| | **Penguin adèlie**; **fat** (*Pygoscelis adèliae* | Palmer Archipelago | 105–312 | – | – | – | – | – | ng/g lipid wt | Geisz et al. (2008) |
| | **Penguin adèlie**; **preen oil** (*Pygoscelis adèliae*) | Hop Island | – | 1–37 | – | 2–567 | – | – | ng/g lipid wt | Van den Brink et al. (2011) |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | **Penguin adèlie**; **preen oil** (*Pygoscelis adèliae*) | Hop Island | – | 1–37 | – | 2–567 | – | – | ng/g lipid wt | Van den Brink et al. (2011) |
| | **Southern fulmar**; **preen oil** (*Fulmarus glacialoides*) | Hop Island | – | 1–40 | – | 1–314 | – | – | ng/g lipid wt | Van den Brink et al. (2011) |
| | **Penguin blood** (**pooled together**)<br>**Penguins adèlie** (*Pygoscelis adèliae*)<br>**Gentoo penguin** (*Pygoscelis papua*)<br>**Chinstrap penguin** (*Pygoscelis antarcticus* | Admiralty Bay, King George Island | 2.7–16 | 1.5–17 | – | 0.4–20 | 0.0017–1726 | – | ng/g wet wt | Corsolini et al. (2007) |
| | **Migrating snow petrel**; **eggs** (*Pagodroma nivea*) | Ross Sea | 3.64–10.83 | 15.23–22.66 | 0.03–0.37 | 10.43–15.40 | – | – | ng/g wet wt | Corsolini et al. (2011) |
| | **South polar skua**; **eggs** (*Catharacta maccormicki*) | Ross Sea | <LOD–64.75 | 1.69–64.23 | <LOD–0.080 | 9.23–43.39 | – | – | ng/g wet wt | Corsolini et al. (2011) |
| | | Antarctic Peninsula | – | – | – | – | 19.0–558 | – | ng/g lipid wt | Yogui and Sericano (2009) |
| | **South polar skua**; **blood** (*Catharacta maccormicki* | Dronning Maud Land | 0.4–40.9 | 1.0–50.5 | <0.1–6.5 | 0.6–21.2 | – | – | ng/g lipid wt | Bustnes et al. (2006) |
| | **Migrating brown skua**; **eggs** (*Catharacta antartica*) | Brainsfield Strait | 0.09–27.87 | 31.28–68.62 | <LOD–0.04 | 1.80–27.49 | – | – | ng/g wet wt | Corsolini et al. (2011) |
| | **Migrating brown skua**; **fat tissue** (*Catharacta antartica*) | King George Island, South Shetland | 6118 ± 3813 | 19,720 ± 9620 | 1.22–3.11 | 573 ± 278 | – | 3375 ± 1588 | ng/g lipid wt | Taniguchi et al. (2009) |
| | **Antarctic tern**; **fat tissue** (*Sterna vittata*) | King George Island, South Shetland | 524 ± 205 | 613 ± 187 | <0.12–2.60 | 601 ± 256 | – | 5744 ± 2546 | ng/g lipid wt | Taniguchi et al. (2009) |
| | **Blue-eyed shag**; **fat tissue** (*Phalacrocorax Atriceps*) | King George Island, South Shetland | 374 | 282 | 1.33 | 161 | – | 3961 | ng/g lipid wt | Taniguchi et al. (2009) |
| | **Snowy sheathbill**; **fat tissue** (*Chionis alba*) | King George Island, South Shetland | 468 | 297 | <0.12 | 282 | – | 4090 | ng/g lipid wt | Taniguchi et al. (2009) |

(continued)

**Table 3** (continued)

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|---|---|---|---|---|---|---|---|---|---|---|
| Marine mammals | **Southern elephant seal**; **liver** (*Mirounga leonina*) | King George Island, South Shetland | 460 | 150 | – | 2 | – | – | ng/g lipid wt | Cipro et al. (2012) |
| | **Antarctic fur seal**; **liver** (*Arctocephalus gazella*) | Livingston Island, Antarctic Peninsula | <2–2254 ± 3969 | 3 ± 0.8–429 ± 145 | 12 ± 20 | <2 | <0.04–10 ± 18 | – | ng/g lipid wt | Schiavone et al. (2009c) |
| | **Antarctic fur seal pup**; **liver** (*Arctocephalus gazella*) | Livingston Island, South Shetland | 191 ± 106 | 59 ± 43 | – | 2.2 ± 0.88 | – | – | ng/g wet wt | Schiavone et al. (2009a) |
| | **Antarctic fur seal pup**; **muscle** (*Arctocephalus gazella*) | | 103 ± 55 | 33 ± 22 | – | 1.37 ± 0.69 | – | – | | |
| | **Antarctic fur seal**; **fat tissue** (*Arctocephalus gazella*) | King George Island, South Shetland | 168 | 523 | 3.21 | 4.72 | – | – | ng/g lipid wt | Cipro et al. (2012) |
| | **Weddel seal**; **fat tissue** (*Leptonychotes weddelli*) | | 131 | 300 | 2.59 | 5.77 | 2.04 | – | | |
| | **Crabeater seal**; **fat tissue** (*Lobodon carcinophagus*) | | 14.4 | 154 | 0.223 | 7.23 | – | – | | |
| | **Weddel seal**; **blubber** (*Leptonychotes weddelli*) | Terra Nova Bay | 1.5–660 | 395 | – | – | – | | ng/g wet wt | Corsolini et al. (2002a) |
| | | McMurdo Sound | – | 0.52–18 | – | – | 1.2–1.8 | – | | Trumble et al. (2012) |
| | **Killer whales** (*Orcinus orca*) | Ross Sea | – | 1.6 ± 1.1 | – | – | – | – | µg/g lipid wt | Krahn et al. (2007) |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Flora | **Antarctic lichen** (*Usnea spp.*) | King George Island | 0.353 ± 0.04 | 7.76 ± 2.3 | 0.205 ± 0.08 | 0.141 ± 0.10 | 0.236 ± 0.05 | – | ng/g dry wt | Cipro et al. (2011) |
| | **Antarctic lichens** (*Usnea Antarctica*) | Southern Shetlands | 0.003–0.01 | 0.043–0.61 | | 0.002–0.31 | – | 15–40 | ng/g dry wt | Cabrerizo et al. (2012) |
| | **Antarctic lichens** (*Usena aurantiaco-atra*) | Admirality Bay, King George Island, | – | – | – | – | 139 ± 33.6 | – | pg/g dry weight | Yogui and Sericano (2008) |
| | **Antarctic lichens** (*Usnea aurantiaco-atra*) | | – | – | – | – | 262 ± 48.7 | – | | Yogui et al. (2011) |
| | **Antarctic lichens** (*Usnea Antarctica*) | | – | – | – | – | 192 ± 93.9 | – | | Yogui and Sericano (2008) |
| | **Antarctic lichens** (*Usnea aurantiaco-atra*) | | – | – | – | – | 262 ± 48.7 | – | | Yogui et al. (2011) |
| | **Antarctic mosses** (*Sanionia uncinata*) | | – | – | – | – | 818 ± 270 | – | | Yogui and Sericano (2008) |
| | **Antarctic mosses** (*Sanionia uncinata*) | | – | – | – | – | 1022 ± 348 | – | | Yogui et al. (2011) |
| | **Antarctic mosses** (*Syntrichia princeps*) | | – | – | – | – | 718 | – | | |
| | **Antarctic mosses** (*Brachythecium sp.*) | | – | – | – | – | 276 | – | | |
| | **phanerogam** (*Colobanthus quitensis*) | | – | – | – | – | 328 | – | | |
| | **Antarctic mosses** (*Bryum argenteum*, *Pottia heimii*, *Ceratodon purpureus*) | Victoria Land | 0.54–7.9 | 23–34 | 0.18–4.0 | 0.82–1.95 | – | – | ng/g dry wt | Borghini et al. (2005) |
| | **Antarctic mosses** (*Brachitecyum sp. Syntrichia princeps Sanionia uncinata*) | King George Island | <LOQ–1.73 | 7.76–18.6 | <LOQ–1.20 | 0.141–1.06 | 0.276–0.893 | – | ng/g dry wt | Cipro et al. (2011) |
| | **Antarctic mosses** (*Sanionia uncinata.*) | Southern Shetlands | 0.005–0.04 | 0.04–0.76 | – | 0.21–0.12 | – | 4.4–34 | ng/g dry wt | Cabrerizo et al. (2012) |
| | **Hair grass** (*Deschampsia antarctica*) | Southern Shetlands | 0.061–0.09 | 0.39–2.40 | – | 0.080–0.20 | – | 6–10 | ng/g dry wt | Cabrerizo et al. (2012) |
| | **Pearl-wort** (*Colobanthus quitensis*) | | 0.04 | 0.31 | – | 0.04 | – | 9.5 | | |
| | **Green algae** (*Prasiola crispa*) | | 0.08 | 0.86 | – | 0.033 | – | 7 | | |
| | **Red snow algae** | | 0.28 | 3.07 | – | 0.67 | – | 141 | | |
| Main POPs detected in abiotic samples | | | | | | | | | | |
| Type of sample | | Localization | Range or average concentrations (±standard deviation, if available) | | | | | | | |
| | | | DDTs | PCBs | HCHs | HCB | PBDEs | PAHs | UNIT | LIT |
| Data reported in 80th years and earlier | | | | | | | | | | |
| Air | | – | 150 | – | – | – | – | – | $pg/m^3$ | Sen Gupta et al. (1996) |
| Snow | | East Antarctica | – | – | 2300–4900 | – | – | – | pg/L | Kang et al. (2012) |
| | | – | 0.63–4.27 | – | – | – | – | – | | Sen Gupta et al. (1996) |

(continued)

**Table 3** (continued)

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|---|---|---|---|---|---|---|---|---|---|
| Fresh water | – | 1.3–30.7 | – | 1665 | – | – | – | pg/L | Sen Gupta et al. (1996) |
| Sediments | King Edward Cove | – | – | – | – | – | 2–220 | ng/g dry wt | Platt and Mackie (1980) |
| Data reported from 1990 up to 1999 | | | | | | | | | |
| Air | Ross Island | 1.0–2.0 | 12.2 | 25.8 | – | – | – | $pg/m^3$ | Larsson et al. (1992) |
| Air (ambient air) | Signy Island | 0.07–0.40 | 0.02–17 | 22 | – | – | – | $pg/m^3$ | Kallenborn et al. (1998) |
| Air (atmospheric particulates) | Terra Nova Bay | – | – | – | – | – | $<$1.5–689 | $pg/m^3$ | Caricchia et al. (1995) |
| Soil | McMurdo Sound—Dry Valley Region (fuel-oil contaminated area) | – | – | – | – | – | 46–3398 | ng/g dry weight | Aislabie et al. (1999) |
| | McMurdo Station | – | – | – | – | – | 28–27,000 | ppb | Mazzera et al. (1999) |
| | | – | – | – | – | – | 6267–6339 | ppm | Kennicutt et al. (1995) |
| | Victoria Land | – | 60 | – | – | – | – | pg/g dry wt | Fuoco et al. (1996) |
| Sediments | Ross Sea | – | 80 | – | – | – | – | pg/g dry wt | Fuoco et al. (1996) |
| | Winter Quarters Bay | – | 100–1400 | – | – | – | – | ng/g | Risebrough et al. (1990) |
| | Victoria Land | – | 120 | – | – | – | – | pg/g dry wt | Fuoco et al. (1996) |
| | – | 605.03–844.9 | – | 92.9–123.2 | – | – | – | pg/g | Sen Gupta et al. (1996) |
| Seawater | Admiralty Bay, King George Island | – | – | – | – | – | 0.003–0.011 | µg/L | Bicego et al. (1996) |
| Polynya water | Dakshin Gangotri | 24.8–26.5 | 96.8–103.8 | 85.6–90.7 | – | – | – | pg/L | Sen Gupta et al. (1996) |

| Data reported from 2000 up to 2014 | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Air (gase phase) | Western Ross Sea | – | – | 0.1–1.05 | 7.23–20.39 | – | – | pg/m$^3$ | Cincinelli et al. (2009) |
| | Western Antarctic Peninsula | – | – | 0.06–2.98 | 11.9–32.1 | – | – | | Dickhut et al. (2005) |
| | Livingston Island (Antarctica) | – | 4–29 | – | – | – | – | | Cabrerizo et al. (2013) |
| | South Scotia Sea | – | | 1.63 ± 1.52–1.70 ± 2.16 | 49.71 ± 8.19 | – | – | | Galbán-Malagón et al. (2013a) |
| | Weddell | – | | 0.16 ± 0.14–0.87 ± 0.88 | 11.93 ± 15.77 | – | – | | |
| | Livingston Island | – | | 0.79 ± 0.77–2.27 ± 0.68 | 10.30 ± 4.81–11.97 ± 2.67 | – | – | | |
| | Southern Ocean, Antarctic Peninsula | – | 1–70 | – | – | – | – | | Galbán-Malagón et al. (2013c) |
| | Terra Nova Bay | – | <LOD–0.25 | – | – | – | – | | Gambaro et al. (2005) |
| | Southern Ocean | – | – | – | – | – | 0.03–4.58 | ng/m$^3$ | Cabrerizo et al. (2014) |
| Air (aerosol phase) | Southern Ocean, Antarctic Peninsula | – | 0.04–0.4 | – | – | – | – | pg/m$^3$ | Galbán-Malagón et al. (2013c) |
| Air | King George Island | – | 1.66–6.5 | – | – | 0.67–2.98 | – | pg/m$^3$ | Li et al. (2012) |
| | | – | <LOD–117.8 | – | – | – | – | | Choi et al. (2008) |
| | | – | <LOD–33.2 | – | – | – | – | | Montone et al. (2003) |
| | | – | – | 2.5–3.65 | – | – | – | | Baek et al. (2011) |
| | Antarctic Ocean | <2.7–5.2 | <2.3–22.8 | <2.7–4.6 | 3.3–25.3 | – | – | | Montone et al. (2005) |
| | Dronning Maud Land | 0.02–0.20 | – | 0.02–0.46 | 22 | – | – | | Kallenborn et al. (2013) |
| Snow | Dome Fuji, East Antarctica | – | – | 17.5–137.0 | <LOD–182 | – | – | pg/L | Kang et al. (2012) |
| | Victoria Land | – | 110–580 | – | – | 130–340 | 0.65–140 | pg/L | Vecchiato et al. (2015) |
| Snow/firn core | Talos Dome | – | 0.03–0.24 | – | – | – | 0.35–4.6 | ng/L | Fuoco et al. (2012) |

(continued)

**Table 3** (continued)

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Snow-ice cover | Russian Antarctic stations (*Molodezhnaya, Cosmonaut Sea; Progress, Prydz Bay, Commonwealth Sea; and Mirnyi, coastal part of the Davis Sea*) | – | – | – | – | – | <10 | ng/L | Nemirovskaya (2006) |
| Seawater | Western Ross Sea | – | – | 0.61–8.79 | 1.72–16.24 | – | – | pg/L | Cincinelli et al. (2009) |
| | Ross Sea | – | – | – | – | – | 1.21–3.96 | ng/L | Cincinelli et al. (2008) |
| | Ross Sea | – | 23–45 | – | – | – | 2–104 | pg/L | Fuoco et al. (2009b) |
| | Gerlache Inlet sea | – | – | – | – | – | 7.32–553 | ng/L | Stortini et al. (2009) |
| | **Southern Ocean areas (Weddell, South Scotia, and Bellingshausen Seas)** | – | 1.34 ± 0.398–3.727 ± 1.466 | 0.189 ± 0.09–3.132 ± 4.031 | 0.281 ± 0.078–0.976 ± 0.828 | – | – | pg/L | Galbán-Malagón et al. (2013b) |
| Porewater | Western Antarctic Peninsula | 0.11–1.00 | 0.06–3.4 | – | 0.63–6.7 | – | – | pg/L | Zhang et al. (2013) |
| Sediments | Western Antarctic Peninsula | – | 0.003–0.35 | – | – | – | – | ng/g dry wt | Zhang et al. (2013) |
| | James Ross Island | 0.19–1.15 | 0.32–0.83 | 0.14–0.76 | 0.95–4 | – | 1.4–205 | ng/g | Klánová et al. (2008) |
| | Admiralty Bay | – | <0.05–57 | – | – | – | – | ng/g dry wt | Montone et al. (2001) |
| | King George Island, Potter Cove | – | – | – | – | – | 28 ± 3–1908 ± 114 | ng/g dry wt | Curtosi et al. (2007) |
| | | – | – | – | – | – | 12.05–210.02 | ng/g | Dauner et al. (2014) |
| | McMurdo Sound | – | – | – | – | – | 38,326–5024 | ng/g | Kim et al. (2006) |
| | | – | 11–21 | – | – | – | 0.27–0.55 | ng/g | Negri et al. (2006) |
| | Winter Quarters Bay, Mc Murdo Station | – | <LOD–4299 | – | – | – | <LOD–12,848 | ng/g | Crockett and White (2003) |
| Sediment cores | Admiralty Bay, King George Island | – | – | – | – | – | 46.9–454.9 | ng/g | Martins et al. (2010) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Soil | Victoria Land | 0.053–0.086 | 0.36–0.59 | – | 0.034–0.17 | – | – | ng/g dry wt | Borghini et al. (2005) |
| | James Ross Island | 0.51–3.68 | 0.51–1.82 | 0.49–1.34 | 2.41–7.75 | – | 34.9–171 | ng/g | Klánová et al. (2008) |
| | Southern Shetlands | LOQ–0.20 | 0.005–0.15 | – | <LOQ–0.07 | – | 0.16–3718 | ng/g dry wt | Cabrerizo et al. (2012) |
| | East Antarctic coast | 0.11–1.22 | 0.20–0.41 | 0.86–4.69 | – | – | $12 \pm 1$–$1182 \pm 113$ | ng/g dry wt | Negoita et al. (2003) |
| | | – | – | 0.09–40.1 | 0.02–25.28 | – | – | ng/g | Kang et al. (2012) |
| | Potter Cove, Jubany Station | – | – | – | – | – | 19–42 | ng/g dry wt | Curtosi et al. (2007) |

[a]DDTs: p,p'-DDE; o,p'-DDT; p,p'-DDD; p,p'-DDT

[b]PCBs: congeners (penta-CB: 99, 101, 105, 118; hexa-CB: 128, 138, 146, 149, 151, 153, 156; hepta-CB: 170, 171, 174, 177, 180, 183, 187; octa-CB: 194, 195, 199; nona-CB:206; deca-CB: 209)

[c]HCHs: α-HCH; β-HCH; γ-HCH

[d]PBDEs: BDE-47; BDE-99; BDE-100 and others congeners (nos: 28,153, 154, 183)

[e]LOD—limit of detection

[f]LOQ—limit of quantification

**Table 3b** Detailed literature data on results of analytical research on (a) main POPs; (b) remaining organic compounds; (c) heavy metals in various types of biotic and abiotic samples collected in Antarctica in three time periods

| Various chemical compounds identified in biotic samples | | | | | | |
|---|---|---|---|---|---|---|
| Type of sample | | Compound groups/ determined compounds | | Range or average concentrations (±standard deviation, if available) | Unit | Literature |
| Data reported in 80th years and earlier | | | | | | |
| Crustances | **Krill** (*Euphausia superba*) | Hydrocarbons | n-alkanes | 0.5 | µg/g wet wt | Platt and Mackie (1980) |
| Benthic organisms | **Bivalve** (*Yoldia eightsii*) | Hydrocarbons | n-alkanes | 0.4 | | |
| Fish | **Antarctic code**; **flesh** (*Notothenia rossii*) | Hydrocarbons | n-alkanes | 0.05 | | |
| | **Antarctic code**; **liver** (*Notothenia rossii*) | Hydrocarbons | n-alkanes | 1.9 | | |
| Marine mammals | **Crabeater seal**; **tissues** (*Lobodon carcinophagus*) | DLCs | PCDFs | 3.7–6.1 | pg/g lw | Schiavone et al. (2009c) |
| | **Minke whale**; **blubber** (*Balaenoptera Acutorostrata*) | OCP | CHLs[g] | 9.6–59 | ng/g wet wt | Aono et al. (1997) |
| Flora | **terristial plants** (*Tortula robusta*, *Rostkovia magellanica*, *Festuca contracta Poa flabellata*, *Acaena magellanica*) | Hydrocarbons | n-alkanes | 15.7–420.5 | µg/g wet wt | Platt and Mackie (1980) |
| Data reported from 1990 up to 1999 | | | | | | |
| Crustances | **Krill** (*Euphausia superba*) | OCP | CHLs | 68 | pg/g wt wt | Aono et al. (1997) |
| Marine mammals | **Minke whale**; **blubber** (*Balaenoptera Acutorostrata*) | OCP | CHLs | 18–75 | ng/g wet wt | Aono et al. (1997) |
| | **Antarctic fur seal**; **tissues** (*Arctocephalus gazella*) | Dioxins | PCDDs | 15.7 | pg/g wet wt | Schiavone et al. (2009c) |
| | | DLCs | PCDFs | 7 | | |
| Data reported from 2000 up to 2014 | | | | | | |
| Crustances | **Krill** (*Euphausia superba*) | OCP | Chlordanes[h] | <LOD–0.13 | ng/g wet wt | (Cipro et al. (2010) |
| | | | Drins[i] | <LOD–0.54 | | |
| | | Dioxin | total PCDD/DFs | 27 | pg/g | Senthil et al. (2002) |

| | | | | | | |
|---|---|---|---|---|---|---|
| Fish | **Antarctic fishes**; **muscle** (*Chionodraco Hamatus*, *Trematomus Bernacchii*) | Dioxins | PCDDs | 2.69–5.8 | pg/g wet wt | Borghesi et al. (2008) |
| | | DLCs | PCDFs | 1.53–1.68 | | |
| | **Antarctic fishes**; **liver** (*Chionodraco Hamatus*, *Trematomus Bernacchii*) | Dioxins | PCDDs | 4.6–4.94 | | |
| | | DLCs | PCDFs | 1.25–2.3 | | |
| | **Antarctic fishes**; (*Trematomus pennelli*, *Chionodrodraco hamatus*) | Dioxin | Total PCDD/DFs | 11–17 | pg/g | Senthil et al. (2002) |
| | **Emerald rockcod**; (*Trematomus bernacchii*) | OCP | CHLs | $2.61 \pm 2.07$ | ng/g wet wt | Corsolini (2009) |
| | **Antarctic fishes**; **liver** (*Champsocephalus gunnari*, *Gobiontothen gibberifrons*, *Chanocephelus aceratus*) | OCP | Mirex | 1–7 | ng/g lipid wt | Weber and Goerke (2003) |
| Seabirds | **Pinguin**; **dung** (*Pygoscelis papua*) | Surfactants | PFCs[j] | 0.63–603 | ng/g | Llorca et al. (2012) |
| | **Pinguin**; **muscle tissues** (*Pygoscelis papua*) | Surfactants | PFCs | <LOQ[f]–2.28 | ng/g | Llorca et al. (2012) |
| | **Penguin**; **preen oil** (*Pygoscelis adeliae*) | OCP | Dieldrin | 2–24 | ng/g lipid wt | Van den Brink et al. (2011) |
| | **Penguins**; **fat tissue** (*Pygoscelis adeliae*, *Pygoscelis papua*, *Pygoscelis antarctica*) | OCP | Dieldrin | $47.1 \pm 12.4$ | ng/g lipid wt | Cipro et al. (2012); Cipro et al. (2010); Corsolini et al. (2007); Senthil et al. (2002), Tao et al. (2006); Taniguchi et al. (2009) |
| | | | Mirex | $26.4 \pm 20.2$ | | |
| | | | Dieldrin | $26.4 \pm 19.1$ | | |
| | | | Mirex | $90.6 \pm 70.6$ | | |
| | **Penguin**; **blood** (*Pygoscelis adeliae*) | Surfactants | PFOS | <0.1 | ng/ml | |
| | **Penguin**; **blood** (*Pygoscelis adeliae*, *Pygoscelis papua Pygoscelis antarctica*) | Dioxins | PCDDs | 0.7–103 | pg/g wet wt | |
| | | DLCs | PCDFs | 0.8–194 | | |

(continued)

**Table 3b** (continued)

| | | | | | | |
|---|---|---|---|---|---|---|
| | **Penguin**; **eggs** (*Pygoscelis adeliae*, *Pygoscelis papua Pygoscelis antarctica*) | Surfactants | PFOS | <0.1–8.8 | ng/g | |
| | | OCP | Chlordanes | 0.32–7.57 | ng/g wet wt | |
| | | | Mirex | 0.67–6.37 | | |
| | | | Drins | 0.06–35.8 | | |
| | **Penguin**; **eggs** (*Pygoscelis adeliae*) | Dioxins | eoni PCDD/DFs | 23 | pg/g | |
| | **South polar skua**; **blood** (*Catharacta maccormicki*) | Surfactants | PFOS | <0.24–1.36 | ng/ml | |
| | **South polar skua**; **egg** (*Catharacta maccormicki*) | Surfactants | PFOS | 2.08–3.12 | ng/g | |
| | **Brown skua**; **fat tissue** (*Catharacta Antarctica*) | OCP | Chlordanes | 977 ± 445 | ng/g lipid wt | |
| | | | Oxychlordane | 408 ± 169 | | |
| | | | Dieldrin | 254 ± 158 | | |
| | | | Mirex | 2210 ± 1590 | | |
| | **Antarctic tern**; **fat tissue** (*Sterna vittata*) | OC | Chlordanes | 80.6 ± 47.1 | | |
| | | | Oxychlordane | 44.2 ± 21.0 | | |
| | | | Dieldrin | <0.48–23.0 | | |
| | | | Mirex | 260 ± 58 | | |
| | **Blue-eyed shag**; **fat tissue** (*Phalacrocorax Atriceps*) | OCP | Chlordanes | 3.05 | | |
| | | | Oxychlordane | <0.24 | | |
| | | | Dieldrin | <0.48 | | |
| | | | Mirex | 89.2 | | |
| | **Snowy sheathbill**; **fat tissue** (*Chionis alba*) | OCP | Chlordanes | 468 | | |
| | | | Oxychlordane | 63.3 | | |
| | | | Dieldrin | 22.4 | | |
| | | | Mirex | 149 | | |

| | | | | | | |
|---|---|---|---|---|---|---|
| | **Whitechinned petrel**; **pectoral muscle** (*Procellaria aequioctialis*) | surfactants | PFOS | 1.2–2.0 | ng/g | Llorca et al. (2012) |
| | **Southern fulmar**; **preen oil** (*Fulmarus glacialoides*) | OCP | Dieldrin | 1–38 | ng/g lipid wt | Van den Brink et al. (2011) |
| Marine mammals | **Seals**; **tissues** (**muscle**, **blubber**, **fur**) | OCP | Drins | 18.4–82.4 | ng/g lipid wt | Cipro et al. (2012); Bengtson Nash et al. (2010); Schiavone et al. (2009a, c); Corsolini et al. (2002b) |
| | **Antarctic fur seal** (*Arctocephalus gazella*) | | Endosulfan (I/II) | 2.09–21.15 | | |
| | **Other seal spiecies** (*Leptonychotes weddelli*, *Lobodon carcinophagus*) | | Mirex | 5.53–17.0 | | |
| | | | Chlordanes | 9.5–78.2 | | |
| | | – | PCNs | 0.01–3.08 | | |
| | | Dioxins | PCDDs | 3.5–53.6 | ng/g wet wt | |
| | | DLCs | PCDFs | 8.5–96.4 | | |
| | | Surfactants | PFCs | <0.4–2.0 | ng/g | |
| | **Seals**; **liver** | Pesticides OCP | Drins | 6.88 | ng/g lipid wt | |
| | **Southern elephant seal** (*Mirounga leonine*) | | Endosulfan (I/II) | 2.72 | | |
| | **Antarctic fur seal** (*Arctocephalus gazella*) | | Mirex | 16.2 | | |
| | | | Chlordanes | 37.7 | | |
| | | Dioxins | PCDDs | 10.6 | ng/g wet wt | |
| | | DLCs | PCDFs | 153.7 | | |
| | | Surfactants | PFCs | <0.4–12.6 | ng/g | |
| | **Weddell seal**; **liver** (*Leptonichotes weddelli*) | Dioxin | total PCDD/DFs | 8.9 | pg/g | Senthil et al. (2002) |
| | **Southern elephant seal**; **blood** (*Mirounga leonine*) | PFCs | PFOS | <0.08–3.52 | ng/ml | Tao et al. (2006) |

(continued)

**Table 3b** (continued)

| Various chemical compounds identified in abiotic samples | | | | | |
|---|---|---|---|---|---|
| Type of sample | Compound groups/determined compounds | | Range or average concentrations (± standard deviation, if available) | Unit | Literature |
| Data reported in 80th years and earlier | | | | | |
| Snow | – | Sulphate | 50–100 | ng/g | Delmas and Boutron (1978) |
| Soil | Hydrocarbons | n-alkanes | 0.6 | µg/g | Platt and Mackie (1980) |
| Freshwater sediments | Hydrocarbons | n-alkanes | 0.9–1.7 | | |
| Seawater | Hydrocarbons | n-alkanes | 5.8 | | |
| Data reported from 1990 up to 1999 | | | | | |
| Air | OCP | Heptachlor epoxide | 0.52 | $pg/m^3$ | Bidleman et al. (1993); Kallenborn et al. (1998) |
| | | Chlordanes + nanochlors | 1.8 | | |
| | | Chlordanes | 0.04–0.9 | | |
| Seawater | Hydrocarbons | n-alkanes | 2.6–7.6 | µg/L | Guerra et al. (2013) |
| | | n-alkanes | 353–968 | ng/L | Stortini et al. (2009) |
| | | n-alkanes | 2.6–7.6 | µg/L | Cripps (1992) |
| Seawater (particulate matter) | Hydrocarbons | Aliphatic hydrocarbons | 0.07–0.17 | µg/L | Green et al. (1992) |
| Marine sediment | OC | Chlorinated terphenyls | 30–1200 | ng/g | Risebrough et al. (1990) |
| | Hydrocarbons | Aliphatic hydrocarbons | 45–48 | µg/g | Green et al. (1992) |
| | Organic carbon | TOC | 0.34 | g % | Vandal et al. (1998) |
| Sea ice | Hydrocarbons | Aliphatic hydrocarbons | 1.9–12.5 | $mg/m^2$ | Green et al. (1992) |

| Data reported from 2000 up to 2014 | | | | | |
|---|---|---|---|---|---|
| Air (gase phase) | Pesticides | Heptachlor | <1–19.1 | pg/m$^3$ | Dickhut et al. (2005) |
| | | Heptachlor epoxide | <0.3–20.7 | | |
| Air | – | Chlorinated paraffin | 3.7–20.8 | pg/m$^3$ | Ma et al. (2014) |
| | Pesticides | Aldrin and dieldrin | 12.2–88.5 | pg/m$^3$ | Baek et al. (2011) |
| | Hydrocarbons | Akryl nitrates | <LOD–1.11 | ppt(v) | Fischer et al. (2002) |
| Snow | Organic carbon | TOC | 88–928 | µg/L | Antony et al. (2011) |
| | Surfactants | PFCs | 1129.2–2491.3 | pg/L | Cai et al. (2012) |
| | Hydrocarbons | Chlorinated hydrocarbons | <LOD–380 | µg/g | Zoccolillo et al. (2007) |
| Fresh water | Surfactants | PFCs | 2121.8–5767.9 | pg/L | Cai et al. (2012) |
| Surface water | Surfactants | PFCs | <3.0–51 | pg/L | Ahrens et al. (2010) |
| Seawater | Surfactants | PFCs | 531.9–15,284 | pg/L | Cai et al. (2012) |
| Sediments | Hydrocarbons | n-alkanes | 0.03–0.41 | µg/g | Dauner et al. (2014) |
| Marine sediments | Hydrocarbons | n-alkanes | 1.1–2.1 | µg/g | Negri et al. (2006) |
| | | Total hydrocarbons | 81–144 | | |

[a]CHLs: oxychlordane + cis-chlordane + trans-nonachlor + cis − nonachlor
[b]Chlordanes: heptachlor + epoxides + oxychlordane + α-and β-chlordane
[c]LOD—limit of detection
[d]Drins: aldrin + endrin + dieldrin + isodrin
[e]PFCs: PFHxA, PFOA, PFNA, PFBS, PFOS
[f]LOQ—limit of quantification

**Table 3c** Detailed literature data on results of analytical research on (a) main POPs; (b) remaining organic compounds; (c) heavy metals in various types of biotic and abiotic samples collected in Antarctica in three time periods

| Heavy metals in biotic samples | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Type of sample | Sample | Localization | Range or average concentrations (±standard deviation, if available) | | | | | | | | | | Unit | Literature |
| | | | Fe | Cd | Co | Cr | Cu | Hg | Mn | Ni | Pb | Zn | | |
| Data reported in 80th years and earlier | | | | | | | | | | | | | | |
| Crustaceans | **Krill** (*Euphausia superba*) | Antarctic Scotia Sea | – | 0.85 | – | – | – | <0.1 | – | – | – | – | µg/g dry wt | Bargagli (2008) |
| | **Others** (*T. gaudichaudii*) | – | – | 18.7–52.6 | 28.1–31.1 | – | – | – | – | – | – | – | µg/g dry wt | Moreno et al. (1997) |
| Seabirds | **Penguin**; **liver** (*Pygoscelis adeliae*) | Southern Ocean | – | 13.0 | – | – | – | 0.2 | – | – | – | – | µg/g dry wt | Bargagli (2008) |
| Marine mammals | **Seal**; **liver** (*Ommatophoca rossi*) | | – | 110 ± 88 | – | – | – | 4.6 ± 4.3 | – | – | – | – | | |
| | **Whale**; **liver** (*Balaenoptera acutorosyrata*) | | – | 45 ± 26 | – | – | – | 0.21 ± 0.1 | – | – | – | – | | |
| Data reported from 1990 up to 1999 | | | | | | | | | | | | | | |
| Crustaceans | **Krill** (*Euphausia superba*) | Southern Ocean | – | 0.29 | – | – | – | 0.025 | – | – | – | – | µg/g dry wt | Bargagli (2008) |
| | **Other** (*Glyptonotus antarcticus Waldeckia obese*) | Antarctic Ocean | – | 0.98–1.89 | – | – | 72.80–165.0 | – | – | – | – | 60.60–335.0 | µg/g dry wt | Petri and Zauke (1993) |
| Benthic organisms | **Bivalve**; **digestive glands** (*Laternula elliptica*) | King George Island | 2003 | 11.5 | 2.84 | 2.9 | 38.1 | – | 18.6 | 6.27 | 5.49 | 153 | µg/g dry wt | Ahn et al. (1996) |
| | **Bivalve**; **gonad** (*Laternula elliptica*) | | 1832 | 4.75 | 1.48 | 1.7 | 15.0 | – | 30.1 | 4.47 | 2.15 | 84.9 | | |
| | **Bivalve**; **girls** (*Laternula elliptica*) | | 1998 | 7.21 | 2.71 | 2.9 | 21.4 | – | 44.7 | 6.16 | 2.77 | 206 | | |
| | **Bivalve**; **kidney** (*Laternula elliptica*) | | 4318 | 41.9 | 5.74 | 4.7 | 33.3 | – | 190 | 21 | 37.7 | 1687 | | |
| | **Bivalve**; **muscle** (*Laternula elliptica*) | | 800 | 3.9 | 2.28 | 1.69 | 50 | – | 102 | 2.74 | 1.35 | 115 | | |
| | **Invertebrates** (*Parborlasia corrugatus Anthozoa Nacella concinna Trophon, Waldeckia obesa Glyptonotus antarcticus Odontaster validus Neomilaster georgianus Sterechinus*) | Antarctic Paninsula | – | 0.20–15.60 | – | – | 0.3–49.70 | – | – | – | – | 4.23–46.12 | µg/g wet wt | Moreno et al. (1997) |

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Fish | **Notothenia; muscle** (*Notothenia coriceps*) | Antarctic Peninsula | – | <0.05 | – | – | 0.04–0.5 | 0.01–0.10 | – | – | – | 1.00–6.70 | µg/g wet wt | Moreno et al. (1997) |
| Marine mammals | **Antarctic fur seal; liver** (*Arctocephalus gazella*) | Bird Island, South Georgia; Sub-Antarctic | 0.1 | 350 | – | 1 | 263 | 215 | – | – | – | 384 | ng/g dry wt | Malcolm et al. (1994) |
| | | Antarctic Peninsula | – | 1.90–3.50 | – | – | 11.90–16.20 | 4.10–7.60 | – | – | – | 25.30–38.40 | µg/g wet wt | Moreno et al. (1997) |
| | **Antarctic fur seal; muscle** (*Arctocephalus gazella*) | Antarctic Peninsul | – | <0.05 | 1.10–1.50 | – | – | <0.05 | – | – | – | 12.70–25.70 | µg/g wet wt | Moreno et al. (1997) |
| | **Antarctic fur seal; kidnay** (*Arctocephalus gazella*) | | – | 3.70–5.90 | 8.40–22.30 | – | – | 0.20–0.30 | – | – | – | 23.80–38.90 | | |
| | **Antarctic fur seal; fat** (*Arctocephalus gazella*) | | – | <0.05 | 0.20–0.60 | – | – | <0.05 | – | – | – | 3.20–8.40 | | |
| | **Crabeater seal; muscle** (*Lobodon carcinophagus*) | | – | – | – | – | – | 0.27–6.2 | – | – | – | – | µg/g dry weight | Szefer et al. (1993) |
| | **Crabeater seal; liver** (*Lobodon carcinophagus*) | | – | – | – | – | – | 1.7–16.3 | – | – | – | – | | |
| | **Crabeater seal; kidney** (*Lobodon carcinophagus*) | | – | – | – | – | – | 1.7–2.5 | – | – | – | – | | |
| | **Leopard seal; muscle** (*Hydrurga leptonyx*) | | – | – | – | – | – | 1.06–3.22 | – | – | – | – | | |
| | **Leopard seal; liver** (*Hydrurga leptonyx*) | | – | – | – | – | – | 8.78–18.1 | – | – | – | – | | |
| | **Leopard seal; kidney** (*Hydrurga leptonyx*) | | – | – | – | – | – | 4.64–6.05 | – | – | – | – | | |
| | **Weddell seal; muscle** (*Leptonychotes weddelii*) | | – | – | – | – | – | 1.18–3.61 | – | – | – | – | | |
| | **Weddell seal; liver** (*Leptonychotes weddelii*) | | – | – | – | – | – | 21.1–48.8 | – | – | – | – | | |
| | **Weddell seal; kidney** (*Leptonychotes weddelii*) | | – | – | – | – | – | 9.67–15.9 | – | – | – | – | | |
| | **Southern elephant seal; muscle** (*Mirounga leonine*) | | – | 0.05–0.12 | – | – | 0.57–0.68 | 0.17–0.19 | – | – | – | 24.37–28.58 | µg/g wet wt | Moreno et al. (1997) |
| | **Southern elephant seal; skin** (*Mirounga leonine*) | | – | <0.05 | – | – | 0.49–0.52 | 0.09–0.14 | – | – | – | 25.07–30.72 | | |
| | **Southern elephant seal; fat** (*Mirounga leonine*) | | – | <0.05 | – | – | 0.54–1.46 | <0.05 | – | – | – | 0.30–0.84 | | |
| | **Minke whale; blubber** (*Balaenoptera Acutorostrata*) | – | 262.88–2050 | 0.03–0.28 | – | 1.4–8.9 | 1.63–93 | 0.08–0.43 | 6.77–443 | 0.7–9.5 | 0.6–19.8 | 3.64–104 | ng/g wet wt | Aono et al. (1997) |

(continued)

**Table 3c** (continued)

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Flora | **Algae** (*Desmarestia sp., Durvillea Antarctica, Adenocystis sp., Ascoseyra sp., Cytosphaera sp., Iridaea sp., Leptosomia simplex st.*) | Antarctic Peninsula | – | 0.05–2.02 | – | – | 0.10–4.32 | – | – | – | – | 2.12–27.31 | µg/g dry wt | Moreno et al. (1997) |
| | **Antarctic mosses** (*B. argentatum, B pseudotriquwtrum, Ceratodon purpureus Pottia heimii*) | Edmonson Point | – | 0.10–0.92 | – | – | – | 0.05–0.15 | – | – | 0.3–1.4 | – | µg/g dry wt | Bargagli et al. (1995) |
| | **Antarctic lichens** (*Usena auranticoatra*) | King George Island | 262.88–1364.8 | <LOD[a]–0.015 | – | – | 1.63–5.79 | – | 6.77–39.16 | – | <LOD–2.76 | 3.64–17.92 | µg/g dry wt | Poblet et al. (1997) |
| | | | – | – | – | – | – | – | – | – | 3–39 | – | ppm | Olech et al. (1998) |
| | **Antarctic lichens** (*Usena antarctica*) | King George Island | 283.37–1115.1 | <LOD–0.03 | – | – | 2.17–9.49 | – | 15.65–56.03 | – | <LOD–2.85 | 5.52–21.43 | µg/g dry wt | Poblet et al. (1997) |
| | | | – | – | – | – | – | – | – | – | 4–160 | – | ppm | Olech et al. (1998) |
| | **Antarctic lichens** (*Usena decussata*) | Trishvil Hill base, East Antarctica | 4966–12,760 | – | – | 4.2–3.36 | 45–93 | – | – | – | 5.66–19.8 | – | µg/g dry wt | Upreti Pandev (1995) |
| | | Victoria Land | 802 ± 402 | 0.21 ± 0.11 | – | 1.3 ± 0.6 | 5.3 ± 5.1 | – | 11.8 ± 3.9 | – | 0.54 ± 0.34 | 18.6 ± 4.1 | µg/g dry wt | Bargagli et al. (1999) |
| Data reported from 2000 up to 2014 | | | | | | | | | | | | | | |
| Zooplankton | **Whole body amphipoda** (*Paramoera orrug*) | Windmill Island | – | 7.2 ± 2.7 | – | – | – | 0.07 ± 0.03 | – | – | – | – | µg/g dry wt | Bargagli (2008) |
| | **Whole pooled across species** | Windmill Island | – | 3.4 ± 2.3 | – | – | – | 0.07 ± 0.03 | – | – | – | – | | |
| Crustaceans | **Krill** (*Euphausia superba*) | Admiralty Bay | 72 | – | – | – | – | 34.6* | – | – | – | 50.2 | µg/g; *ng/g | Santos et al. (2006) |
| | **Pooled across species** (*Bovallia gigantea Cheirimedon femoratus Gondogeneia antarctica*) | | 388–1108 | – | – | – | – | 35.0–37.0 | – | – | – | 62.1–84.1 | | |

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|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Benthic organisms | **Porifera**; **whole pooled across species** | Windmill Island | – | 26.4 ± 14.8 | – | – | – | 0.08 ± 0.05 | – | – | – | – | µg/g dry wt | Bargagli (2008) |
| | **Molluscs** (*Nacella conccina*) | Admirality Bay | 2756 | – | – | – | – | 26.1* | – | – | – | 64.4 | µg/g; *ng/g | Santos et al. (2006) |
| | **Bivalve**; **tissue** (*Laternula elliptica*) | McMurdo Sound | – | 5–57 | – | – | 4.2–543 | 0.1–21 | – | – | 0.3–6.4 | 48–419 | µg/g dry wt | Negri et al. (2006) |
| | **Bivalve**; **hemolymph** (*Laternula elliptica*) | King George Island | 5.6–458 | – | – | – | – | – | 0.1–4.0 | – | – | – | mmol/l | Poigner et al. (2013) |
| | **Bivalve**; **digestive gland** (*Laternula elliptica*) | King George Island | 981–2000 | – | – | – | – | – | 3.3–18.6 | – | – | – | µg/g dry wt | Poigner et al. (2013) |
| | | Potter Cove | 541–1413 | 6–22 | – | 0.5–9.4 | 52–108 | – | 4.6–15.1 | – | 0.4–2.5 | 105–133 | µg/g dry wt | Vodopivez et al. (2015) |
| | **Bivalve**; **gill** (*Laternula elliptica*) | King George Island | 350–2060 | – | – | – | – | – | 4.2–44.7 | – | – | – | µg/g dry wt | Poigner et al. (2013) |
| | | Potter Cove | 600–3150 | 1.5–5.1 | – | 0.5–2.3 | 6.2–31.8 | – | 9–67 | – | 0.19–1.16 | 84–139 | µg/g dry wt | Vodopivez et al. (2015) |
| | **Bivalve**; **mantle tissue** (*Laternula elliptica*) | King George Island | 119–9200 | – | – | – | – | – | 1.42–700 | – | – | – | µg/g dry wt | Poigner et al. (2013) |
| | **Bivalve**; **kidney** (*Laternula elliptica*) | Potter Cove | 900–1000 | 88–183 | | 0.5–2.8 | 21.5 | | 106–410 | | 29–489 | 1300–4500 | µg/g dry wt | Vodopivez et al. (2015) |
| | **Bivalve**; **digestive gland** (*Adamussium colbecki*) | Terra Nova Bay | – | 55.7 ± 27 | – | – | – | 0.35 ± 0.08 | – | – | – | – | µg/g dry wt | Bargagli (2001) |
| | **Bivalve**; **digestive gland** (*Neobuccinum eatoni*) | | – | 227 ± 65 | – | – | – | 0.24 ± 0.1 | – | – | – | – | | |
| | **Sponge tissue** (*Homaxinella balfourensis*, *Mycale acerata*, *Sphaerotylus antarcticus*) | McMurdo Sound | – | 7.8–57 | – | – | 2.3–25.3 | – | – | – | <0.2–22.4 | 16–135 | µg/g dry wet | Negri et al. (2006) |
| | **Whole tissue** (*Himantothallus grandifolius Gondogeneia orrugates Sterechinus neumayeri Nacella concinna Amphioplus acutus Paraserolis polita Bovalia gigantean*, *Parborlasia orrugates*) | Admiralty Bay, King George Island, | – | 0.25–21.5 | – | – | 1.0–119.12 | – | – | 0.37–8.28 | <0.6–9.31 | 2.5–353.91 | µg/g dry wt | Majer et al. (2014) |

(continued)

**Table 3c** (continued)

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|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Whole holothuroidea pooled across species** | Windmill Island | – | 7.7 ± 3.8 | – | – | – | 0.23 ± 0.09 | – | – | – | – | µg/g dry wt | Bargagli (2008) |
| | **Asteroidean; arms** (*Odontaster validus*) | | – | 13.6 ± 1.8 | – | – | – | 0.11 ± 0.06 | – | – | – | – | | |
| | **Echinoidea; soft tissued** (*Sterechinus neumayeri*) | | – | 13.0 ± 4.8 | – | – | – | 0.1 ± 0.06 | – | – | – | – | | |
| | **Whole Polychaeta** (*Harmothor spinosa*) | | – | 6.8 ± 0.6 | – | – | – | 0.07 ± 0.02 | – | – | – | – | | |
| Fish | **Emerald rock cod; muscle** (*Trematomus Bernacchii*) | Terra Nova Bay | – | 0.04 ± 0.02 | – | – | – | 0.83 ± 0.65 | – | – | – | – | µg/g dry wet | Bargagli (2001) |
| | **Crocodile icefish; muscle** (*Chionodraco Hamatus*) | | – | 0.03 ± 0.02 | – | – | – | 0.44 ± 0.31 | – | – | – | – | | |
| | **Emerald rock cod; liver** (*Trematomus Bernacchii*) | | – | 9.9 ± 5.8 | – | – | – | 0.46 ± 0.25 | – | – | – | – | | |
| | **Crocodile icefish; liver** (*Chionodraco Hamatus*) | | – | 2.9 ± 0.8 | – | – | – | 0.19 ± 0.12 | – | – | – | – | | |
| | **Myctophid fish; liver** (*Gymnoscopelus piabilis*) | | – | 28 ± 17 | – | – | – | – | – | – | – | – | | |
| | **Myctophid fish; kidney** (*Gymnoscopelus piabilis*) | | – | 16 ± 8 | – | – | – | – | – | – | – | – | | |
| | **Myctophid fish; muscle** (*Gymnoscopelus piabilis*) | | – | <0.1 | – | – | – | 0.31 ± 0.13 | – | – | – | – | | |
| | **dusky rockcod** (*Trematomus newnesi*) | Admiralty Bay | 24 | – | – | – | – | 16.0* | – | – | – | 99.1 | µg/g; *ng/g | Santos et al. (2006) |
| | **Fish** (*Notothenia spp.*) | | 78 | – | – | – | – | 16.3* | – | – | – | 64.6 | | |
| Seabirds | **Penguin Adèlie** (*Pygoscelis adeliae*) | King George Island | – | – | – | – | – | 0.11 ± − 0.22 | – | – | – | – | ppm | Brasso and Polito (2013) |
| | | Ross Sea | – | – | – | – | – | 0.53 ± 0.08 | – | – | – | – | | |
| | **Penguin Adèlie; eggs** (*Pygoscelis adeliae*) | Admiralty Bay | – | – | – | – | – | 5.0* | – | – | – | 8.3 | µg/g; *ng/g | Santos et al. (2006) |
| | **Penguin Adèlie; kidney** (*Pygoscelis adeliae*) | Potter Cove, King George Island | – | 339 ± 12* | 143 ± 5* | – | 1.6 ± 0.12 | 146 ± 4* | 9.4 ± 0.2 | – | 144 ± 7* | – | µg/g; *ng/g dry wt | Smichowski et al. (2006) |
| | | South Shetland Islands | 327.03 ± 112.89 | 0.20 ± 0.15 | – | 0.21 ± 0.13 | 11.85 ± 3.69 | – | 11.18 ± 6.12 | 0.01 ± 0.0 | 0.05 ± 0.12 | 85.74 ± 19.49 | µg/g dry wt | Jerez et al. (2013a) |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Penguin Adèlie; liver** (*Pygoscelis adeliae*) | Potter Cove, King George Island | – | 102 ± 7* | 68 ± 6* | – | 18 ± 1 | 269 ± 10* | 10.0 ± 0.2 | – | 202 ± 9* | – | µg/g; *ng/g dry wt | Smichowski et al. (2006) |
| | | South Shetland Islands | 1364.01 ± 351.09 | 0.06 ± 0.05 | – | 0.12 ± 0.06 | 92.06 ± 74.53 | – | 12.01 ± 5.80 | 0.01 ± 0.01 | 0.04 ± 0.07 | 133.88 ± 71.42 | µg/g dry wt | Jerez et al. (2013a) |
| | **Penguin Adèlie; muscle** (*Pygoscelis adeliae*) | Potter Cove, King George Island | – | <0.07* | 677 ± 32* | – | 6.4 ± 0.4 | – | 1.5 ± 0.1 | – | 121 ± 7* | | µg/g; *ng/g dry wt | Smichowski et al. (2006) |
| | | South Shetland Islands | 154.97 ± 66.71 | 0.01 ± 0.02 | – | 0.46 ± 0.23 | 5.52 ± 1.97 | – | 1.13 ± 0.40 | 0.04 ± 0.03 | 0.04 ± 0.10 | 104.34 ± 49.70 | µg/g dry wt | Jerez et al. (2013a) |
| | **Penguin Adèlie; bone** (*Pygoscelis adeliae*) | South Shetland Islands | 277.18 ± 135.74 | 0.01 ± 0.004 | – | 1.06 ± 0.77 | 57.81 ± 35.82 | – | 10.57 ± 8.76 | 0.41 ± 0.41 | 0.04 ± 0.10 | 227.01 ± 121.11 | µg/g dry wt | Jerez et al. (2013a) |
| | **Penguin Adèlie; feathers** (*Pygoscelis adeliae*) | Antarctic Peninsula | 59.74 ± 45.26 | 0.04 ± 0.02 | – | 6.37 ± 5.6 | 13.41 ± 2.6 | – | 1.3 ± 1.16 | 0.55 ± 0.55 | 0.64 ± 1.09 | 82.45 ± 13.10 | µg/g dry wt | Jerez et al. (2011) |
| | | Terra Nova Bay | – | – | – | – | – | 0.82 ± 0.13 | – | – | – | – | | Bargagli (2001) |
| | | Admiralty Bay | 87 | – | – | – | – | 1401.4* | – | – | – | 61.5 | µg/g; *ng/g | Santos et al. (2006) |
| | | South Shetland Islands | 79.80 ± 62.22 | 0.13 ± 0.08 | – | 0.18 ± 0.12 | 13.32 ± 8.22 | – | 2.01 ± 0.52 | 0.05 ± 0.03 | 0.24 ± 0.38 | 61.11 ± 20.30 | µg/g dry wt | Jerez et al. (2013a) |
| | **Chinstrap penguin; kidney** (*Pygoscelis antarctica*) | South Shetland Islands | 397.49 ± 82.35 | 0.54 ± 0.29 | – | 0.75 ± 0.54 | 13.64 ± 2.28 | – | 10.19 ± 2.63 | 0.08 ± 0.06 | 0.14 ± 0.02 | 92.83 ± 32.19 | µg/g dry wt | Jerez et al. (2013a) |
| | **Chinstrap penguin; liver** (*Pygoscelis antarctica*) | South Shetland Islands | 2075.44 ± 1745.28 | 0.11 ± 0.08 | – | 1.11 ± 0.95 | 95.10 ± 48.67 | – | 11.42 ± 3.24 | 0.07 ± 0.07 | 0.18 ± 0.02 | 132.20 ± 64.40 | µg/g dry wt | Jerez et al. (2013a) |
| | **Chinstrap penguin; muscle** (*Pygoscelis antarctica*) | South Shetland Islands | 328.59 ± 102.73 | 0.01 ± 0.01 | – | 1.49 ± 0.55 | 6.82 ± 1.20 | – | 2.55 ± 1.53 | 1.83 ± 2.67 | 0.20 ± 0.06 | 105.08 ± 55.41 | µg/g dry wt | Jerez et al. (2013a) |
| | **Chinstrap penguin; bone** (*Pygoscelis antarctica*) | South Shetland Islands | 117.49 ± 40.10 | 0.004 ± 0.001 | – | 0.20 ± 0.12 | 0.71 ± 0.36 | – | 12.50 ± 2.13 | 3.82 ± 2.52 | 0.14 ± 0.02 | 235.01 ± 40.62 | µg/g dry wt | Jerez et al. (2013a) |
| | **Chinstrap penguin; feathers** (*Pygoscelis antarctica*) | South Shetland Islands | 173.86 ± 173.09 | 0.02 ± 0.03 | – | 0.68 ± 0.49 | 18.57 ± 2.78 | – | 2.25 ± 3.17 | 0.13 ± 0.10 | 0.06 ± 0.04 | 94.99 ± 5.29 | µg/g dry wt | Jerez et al. (2013a) |
| | | Antarctic Peninsula | 164.26 ± 149.75 | 0.1 ± 0.05 | – | 8.08 ± 9.10 | 19.23 ± 3.65 | – | 3.26 ± 2.68 | 1.18 ± 1.1 | 1.76 ± 1.74 | 97.27 ± 21.35 | µg/g dry wt | Jerez et al. (2011) |
| | **Gentoo penguin; kidney** (*Pygoscelis papua*) | South Shetland Islands | 302.35 ± 103.68 | 0.20 ± 0.05 | – | 0.21 ± 0.14 | 14.26 ± 4.33 | – | 7.54 ± 3.47 | 0.06 ± 0.05 | 0.0008 | 125.43 ± 12.60 | µg/g dry wt | Jerez et al. (2013a) |
| | **Gentoo penguin; liver** (*Pygoscelis papua*) | South Shetland Islands | 854.55 ± 136.61 | 0.08 ± 0.04 | – | 0.18 ± 0.08 | 142.40 ± 63.85 | – | 10.51 ± 3.74 | 0.01 ± 0.01 | 0.0008 | 152.91 ± 45.53 | µg/g dry wt | Jerez et al. (2013a) |

(continued)

**Table 3c** (continued)

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|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Gentoo penguin**; **muscle** (*Pygoscelis papua*) | South Shetland Islands | 180.07 ± 81.65 | 0.01 ± 0.01 | – | 0.94 ± 0.56 | 4.43 ± 1.46 | – | 1.46 ± 0.43 | 0.04 ± 0.01 | 0.0008 | 106.60 ± 37.42 | µg/g dry wt | Jerez et al. (2013a) |
| | **Gentoo penguin**; **bone** (*Pygoscelis papua*) | South Shetland Islands | 154.13 | 0.001 | – | 0.57 | 0.79 | – | 11.01 | 3.37 | 0.19 | 184.11 | µg/g dry wt | Jerez et al. (2013a) |
| | **Gentoo penguin**; **feathers** (*Pygoscelis papua*) | Antarctic Peninsula | 77 ± 134.55 | 0.03 ± 0.04 | – | 2.71 ± 3.13 | 16.44 ± 3.16 | – | 1.8 ± 1.28 | 0.57 ± 0.35 | 0.51 ± 0.46 | 85.12 ± 14.84 | µg/g dry wt | Jerez et al. (2011) |
| | | South Shetland Islands | 42.85 ± 37.05 | 0.06 ± 0.04 | – | 0.13 ± 0.06 | 6.87 ± 1.54 | – | 0.95 ± 0.69 | 0.01 ± 0.01 | 0.87 ± 0.86 | 80.59 ± 10.85 | µg/g dry wt | Jerez et al. (2013a) |
| | | Admiralty Bay King George Island | 434 | – | – | – | – | 540.9* | – | – | – | 90.7 | µg/g; *ng/g | Santos et al. (2006) |
| | **Snow petrel**; **feathers** (*Pagodroma nivea*) | Terra Nova Bay | – | – | – | – | – | 0.5 ± 0.18 | – | – | – | – | µg/g dry wt | Bargagli (2001) |
| | **Kelp gull**; **feathers** (*Larus dominicanus*) | Admiralty Bay King George Island | 291 | – | – | – | – | 2426.6* | – | – | – | 93.5 | µg/g; *ng/g | Santos et al. (2006) |
| | **South polar skua**; **feathers** (*Catharacta maccormicki*) | Terra Nova Bay | – | – | – | – | – | 2.91 ± 1.93 | – | – | – | – | µg/g dry wt | Bargagli (2001) |
| | **South polar skua**; **liver** (*Catharacta maccormicki*) | | – | 35 ± 16 | – | – | – | 3.1 ± 2.1 | – | – | – | – | | |
| Marine mammals | **Weddell seal**; **hair** (*Leptonychotes weddelli*) | Admiralty Bay King George Island | 1450 | – | – | – | – | 2060.7* | – | – | – | 137.6 | µg/g; *ng/g | Santos et al. (2006) |
| Flora | **Thallus** | Windmill Islands | 138 ± 247 | 7.5 ± 8.6 | – | 1.4 ± 0.7 | 3.2 ± 1.5 | – | 6.3 ± 3.2 | 1.8 ± 1 | 6.2 ± 6.3 | 72 ± 33 | µg/g dry wt | Runcie and Riddle (2004) |
| | **macroalge** (*Himmantothallus grandifolius*) | | | | | | | | | | | | | |
| | **Thallus** | | 109 ± 38 | 3.1 ± 0.4 | – | 1.9 ± 0.6 | 19.3 ± 1.5 | 0.09 ± 0.04 | 5.9 ± 1.7 | 1.9 ± 0.4 | 8.3 ± 4.4 | 79 ± 27 | | |
| | **macroalge** (*Iridaea cordata*) | | | | | | | | | | | | | |
| | **Algae** (*Palmaria decipiens Macrocystis spp. Desmarestia spp.*) | Admiralty Bay | 460–4450 | – | – | – | – | (20.4–47.6)* | – | – | – | 27.7–39.6 | µg/g; *ng/g | Santos et al. (2006) |
| | **Phytoplankton** | Windmill Islands | – | 2.1 ± 0.9 | – | – | – | 0.07 ± 0.01 | – | – | – | – | µg/g dry wt | Bargagli (2008) |
| | *pooled across species* | | | | | | | | | | | | | |

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|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Antarctic lichens** (*Usnea sphacelata*, *Usnea sphacelata*) | Deception Island | – | 0.01–0.02 | – | – | 3.2–4 | – | – | – | 0.1–0.7 | – | µg/g | Mão de Ferro et al. (2013) |
| | **Antarctic mosses** (*Polytrichum strictum*, *Sanionia georgicouncinata*) | | – | 0.17–0.23 | – | – | 42–65 | – | – | – | 3.1–4.5 | – | | |
| | **Antarctic mosses** (*Sanionia uncinata*) | King George Island | – | – | 3 ± 1 | 4 ± 1–9 ± 2 | 6 ± 1–19 ± 3 | – | 160 ± 17–390 ± 40 | – | 4 ± 1–19 ± 3 | 25 ± 4–41 ± 7 | µg/g dry wt | Osyczka et al. (2007) |
| | **Antarctic lichens** (*Usnea antarctica*, *Usnea aurantiacoatra*) | | – | – | 2 ± 1 | 2 ± 1–9 ± 2 | 2 ± 1–98 ± 12 | – | 13 ± 2–180 ± 16 | – | 1 ± 1–6 ± 1 | 19 ± 3–35 ± 6 | | |
| | **Antarctic mosses** (*Bryum spp. Polytrichum spp.*) | Admiralty Bay | 3040–4348 | – | – | – | – | (23.1–39.5)* | – | – | – | 18.1–28.0 | µg/g; *ng/g | Santos et al. (2006) |
| | **Antarctic lichens** (*Usnea spp.*) | King George Island | 139 | – | – | – | – | 36.3* | – | – | – | 5.6 | | |
| | **Poaceae** (*Deschampsia antarctica*) | | 610 | – | – | – | – | 67.7* | – | – | – | 44.2 | | |

| Heavy metals in abiotic samples | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Type of sample | Localization | Range or average concentrations (± standard deviation, if available) | | | | | | | | | | Unit | Lit |
| | | Fe | Cd | Co | Cr | Cu | Hg | Mn | Ni | Pb | Zn | | |
| Data reported in 80th years and earlier | | | | | | | | | | | | | |
| Fresh water (lakes) | South Victoria Land | 640–1480 | – | 348 | – | 220 | – | 23–8760 | 1800 | <30[3] | 150 | µg/L | Burton (1981) |
| | Vestfold Hills | – | 5.3 | – | – | 14.3 | – | – | – | 4.4 | – | | |
| | Lutzow-Holm Bay | 65–220 | 0.2–5.3 | – | – | 3.5–8.8 | – | 3–12 | – | 1.2–4.9 | 7–118 | | |
| Snow | Queen Maud Land | (0.5–1.5) × $10^3$ | <0.2–3 | – | 0.8–15 | <11–30 | – | – | 4.8–40 | 3–40 | 30–500 | pg/g | Völkening and Heumann (1988) |
| Sediments | Ross Sea | – | – | – | 47.0 | 25 | – | – | 23.0 | 15.0 | 50 | µg/g | Merlin et al. (1989) |
| | McMurdo Area | 241–808 | – | – | – | – | $14 \times 10^6$–$79 \times 10^6$ | – | – | – | – | mmol/kg | Siegel et al. (1981) |

(continued)

**Table 3c** (continued)

| Data reported from 1990 up to 1999 | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Air (aerosol particles) | Antarctic Ocean | 502–9550 | 1.3–41.6 | – | 16–218 | – | – | – | 78–224 | 14.2–75.8 | – | pg/m$^3$ | Riidlein and Heumann (1995) |
| Snow and firn | Dolleman Island | – | 0.08 | – | – | 4 | – | – | – | – | 0.4 | µg/g | Suttie and Wolff (1992) |
| | Adelie Land | – | 0.3 | – | – | 5 | – | – | – | – | 4 | µg/g | Görlach and Boutron (1992) |
| | Coats Land; Queen Maud Land | – | 0.1 | – | – | 3.5 | – | – | – | – | 1.5 | µg/g | Wolff et al. (1999) |
| Surface snow | Dome C | – | – | – | – | – | 0.13–0.50 | – | – | – | – | pg/g | Vandal et al. (1995) |
| Snow pit | Victoria Land | – | – | – | – | – | 0.07–0.71 | – | – | – | – | pg/g | Capelli et al. (1998) |
| Precipitation (snow) | Lake Hoare | – | – | – | – | – | 0.5–5 | – | – | – | – | pM | Vandal et al. (1998) |
| Fresh water | | – | – | – | – | – | 3.3–6.8 | – | – | – | – | | |
| Seawater | Weddel Sea | – | 45–102 | – | – | 162–358 | – | – | – | 87–461 | – | ng/L | Niemistö and Perttilä (1995) |
| Glacial streams | Lake Hoare | – | | – | – | – | 2.7–4.8 | – | – | – | – | pM | Vandal et al. (1998) |
| Ice cores | Law Dome | – | 0.11–0.63 | – | – | 0.06–0.45 | – | – | – | 0.58–4.5 | 0.42–<100 | pg/g | Hong et al. (1998) |
| | Dome C | – | – | – | – | – | 0.19–2.21 | – | – | – | – | pg/g | Vandal et al. (1995) |
| Soil | Antarctic Peninsula | – | 1.0–8.0 | 1.2–28 | 17–86 | 63–570 | – | 329–1138 | 2.9–47 | <14–82 | 40–1301 | µg/g | Carrasco and Prendez (1991) |
| | northern Victoria Land | 12,760–48,540 | 0.05–0.37 | – | 8–68 | 7–37 | 0.01–0.09 | 77–1356 | 3–29 | 4.5–36 | 29–121 | µg/g | Bargagli et al. (1995) |
| | Victoria Land | 3.16 ± 0.67 | 0.21 ± 0.19 | – | 56.8 ± 27.0 | 38.0 ± 42.0 | – | 546 ± 156 | – | 11.3 ± 7.05 | 1.9 ± 21.8 | µg/g dry wt | Bargagli et al. (1999) |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sediment | Chinese Great Wall station | – | – | – | 16–23 | – | – | – | – | – | 41–73 | µg/g | Yuguang and Junlin (1991) |
| | Terra Nova Bay | 37 300 ± 14 400 | 1.96 ± 3.89 | – | 48.1 ± 9.2 | – | – | 915 ± 350 | 16.1 ± 2.7 | 23.5 ± 20.1 | 100 ± 24.5 | µg/g | Giordano et al. (1999) |
| | Terra Nova Bay | 1.64 | – | – | 20.3 | – | – | 359 | 6.3 | 20.7 | 42 | µg/g | Ciaralli et al. (1998) |
| | Italian station, Terra Nova Bay | – | – | – | 21–328 | – | – | – | – | – | – | µg/g | Crespi et al. (1993) |
| | Weddel Sea | – | 0.04–0.72 | – | 91–146 | 31–44 | 0.014–0.044 | 464–660 | 53–63 | 7–9 | 78–89 | ng/g | Niemistö and Perttilä (1995) |
| | King George Island | 2.42 | – | – | 7.6 | 77 | – | 640 | 15.4 | 8.7 | 69 | µg/g | Ahn et al. (1996) |
| | | 2.37 | – | – | 2.6 | 52 | – | 280 | 11.5 | 121.0 | 74 | µg/g | Alam and Sadiq (1993) |
| | | 6.28 | – | – | – | 68 | – | – | 41.3 | 14.9 | 60 | µg/g | Santos et al. (2005) |
| | McMurdo Station | – | – | – | – | 11 | – | – | 68.0 | 7.0 | 32 | µg/g | Lenihan (1992) |
| Volcanic rocks | King George Island | 2.79 | – | – | – | 111 | – | 1500 | 12.5 | 7.7 | 66 | µg/g | Santos et al. (2005) |
| Data reported from 2000 up to 2014 | | | | | | | | | | | | | |
| Air | Terra Nova Bay | – | – | – | – | – | 0.29–2.3 | – | – | – | – | ng/m$^3$ | Sprovieri et al. (2002) |
| Fresh water | Deception Island | – | 0.019 | – | – | 0.078 | – | – | – | 0.049 | – | µg/L | Mão de Ferro et al. (2013) |
| Snow | Princess Elizabeth Land | – | – | – | – | – | – | – | – | 503–1158 | – | pg/g | Edwards et al. (2001) |
| | Ross Sea | – | – | – | – | – | – | – | – | 749–982 | – | | |
| | Dumont d'Urville Sea | – | – | – | – | – | – | – | – | 42–85 | – | | |
| | Prydz Bay | – | – | – | – | – | – | – | – | 376–727 | – | | |
| | Coats Land | – | 0.03–0.8 | 0.1–1.2 | 0.09–7.3 | 0.7–11.9 | – | 0.03–26 | – | 0.1–10.3 | 0.2–10.8 | pg/g | Planchon et al. (2002) |
| | | – | – | – | 0.1–5.2 | 0.7–12 | – | 0.3–25 | – | 0.1–10 | – | pg/g | Planchon et al. (2001) |

(continued)

**Table 3c** (continued)

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Surface snow | Ingrid Christensen Coast, East Antarctica | 0.23–2.88 | – | 0.01–0.18 | 0.04–0.55 | 0.14–4.6 | – | 0.04–1.66 | – | – | 1.31–14.45 | µg/L | Thamban and Thakur (2013) |
| Snow pit | Antarctic Taylor Valley glaciers (Commonwealth, Canada, Howard) | – | <0.057–0.53 | – | – | <0.56–190 | – | – | – | 0.029–13 | – | nM | Fortner et al. (2011) |
| | Glacier, Taylor Valley, Victoria Land | – | – | – | – | – | 0.3–40 | – | – | – | – | pg/g | Witherow and Lyons (2008) |
| | Dome Fuji | – | – | – | – | – | <0.32–2.93 | – | – | – | – | pg/g | Han et al. (2013) |
| | Victoria Land | – | – | – | – | – | – | – | – | 1.5–21.2 | – | pg/g | Velde et al. (2005) |
| Firn core | Victoria Land | – | – | – | – | – | – | – | – | 1.1–10.3 | – | pg/g | Velde et al. (2005) |
| Ice core | Law Dome; Wilkes Land | – | – | – | – | – | – | – | – | 0.08–5.2 | – | pg/g | Burn-Nunes et al. (2011) |
| | | – | – | – | – | – | – | – | – | 0.5–124 | – | nM | Edwards et al. (2006) |
| | | – | – | – | – | – | – | – | – | 0.21–7.00 | – | pg/g | Vallelonga et al. (2002) |
| | Dome C | – | – | – | – | – | <1–65 | – | – | – | – | pg/g | Jiratu et al. (2009) |
| | | – | – | – | – | – | – | – | – | 0.36–13.4 | – | pg/g | Vallelonga et al. (2010) |
| Sediments | Ferraz station, The King George Island | 6.15 | – | – | 40 | 44 | – | 442 | 5.1 | 11.5 | 52 | µg/g | Santos et al. (2005) |
| | | – | – | – | 25–52 | – | – | – | – | – | 87–134 | µg/g | Santos et al. (2007) |
| | Admirality Bay | – | 0.4–0.9 | – | 7–12 | 47–84 | – | – | 3–10 | 3–11 | 44–89 | µg/g | Ribeiro et al. (2011) |
| | | – | – | – | – | 80–91 | – | – | – | – | 50–57 | µg/g | Ribeiro et al. (2010) |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Princess Regnheld Coast | – | – | – | 40–342 | – | – | – | – | – | 26–134 | µg/g | Waheed et al. (2001) |
| | McMurdo Sound | – | 0.03–0.46 | – | – | 0.9–100 | <0.001–0.087 | – | – | 0.34–12.5 | 17–156 | ng/g | Negri et al. (2006) |
| | Ross Sea | – | 0.1–1.6 | – | 12–97 | 10–38 | – | – | 10–46 | 4–20 | 52–144 | µg/g | Ianni et al. (2010) |
| | Amanda Bay, East Antarctic | – | – | – | – | 22.3–35.3 | 55.5–281* | – | – | 20.5–23.8 | 138–652 | µg/g, *ng/g | Huang et al. (2014) |
| | Antarctic Station, Casey | – | – | – | – | – | – | – | – | 5–26 | – | µg/g | Townsend and Snape (2008) |
| | Prydz Bay | – | 0.254–0.421 | – | – | – | – | – | – | – | 34.6–96.6 | µg/g | Sun et al. (2013) |
| | Potter Cove | 32,800–34,100 | 0.56–0.69 | – | 4.2–6.5 | 54–82 | – | 690–700 | – | 4.9–5.8 | 52–63 | µg/g | Vodopivez et al. (2015) |
| | | 19,665 | 0.25 | – | 7.0 | 103 | – | 798 | – | 7.6 | 56 | | Curtosi et al. (2010) |
| | | 5.15–21.39 | – | – | 4.11–8.11 | 73.37–156.3 | – | 0.79–1.13* | – | 2.29–5.52 | 44–96–63.02 | µg/g; *mg/g | Andrade et al. (2001) |
| Soils | near Lake Vanda | 1.00 | – | – | – | 28 | – | 104 | 11.2 | 3.9 | 24 | µg/g | Webster et al. (2003) |
| | Fildes Peninsula, King George Island, | 43,255–70,534 | 0.04–0.34 | – | 17.10–64.90 | 51.10–176.50 | 0.0081–0.0601* | 449–1401 | 7.18–25.03 | 2.76–60.52 | 41.57–80.65 | µg/g, *ng/g | Lu et al. (2012) |
| Volcanic rocks | The King George Island | 2.92 | – | – | – | – | – | 1100 | 60.7 | – | – | µg/g | Machado et al. (2001) |

[e]LOD—limit of detection

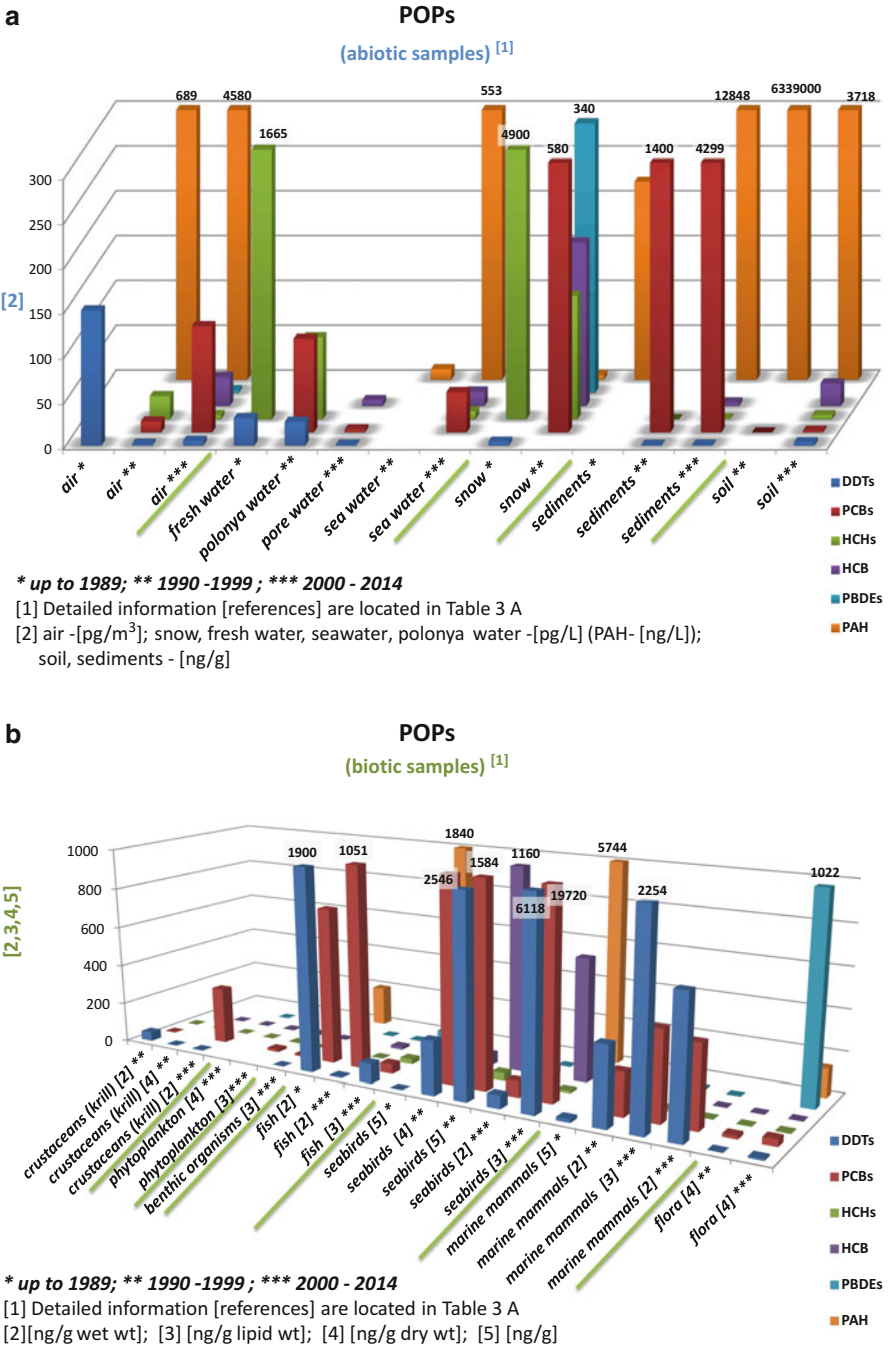
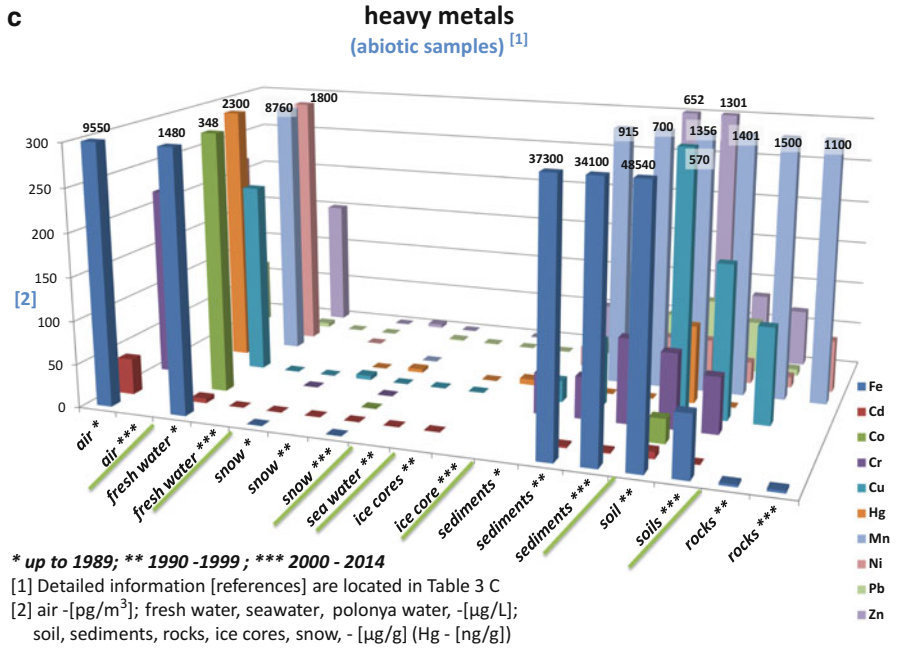


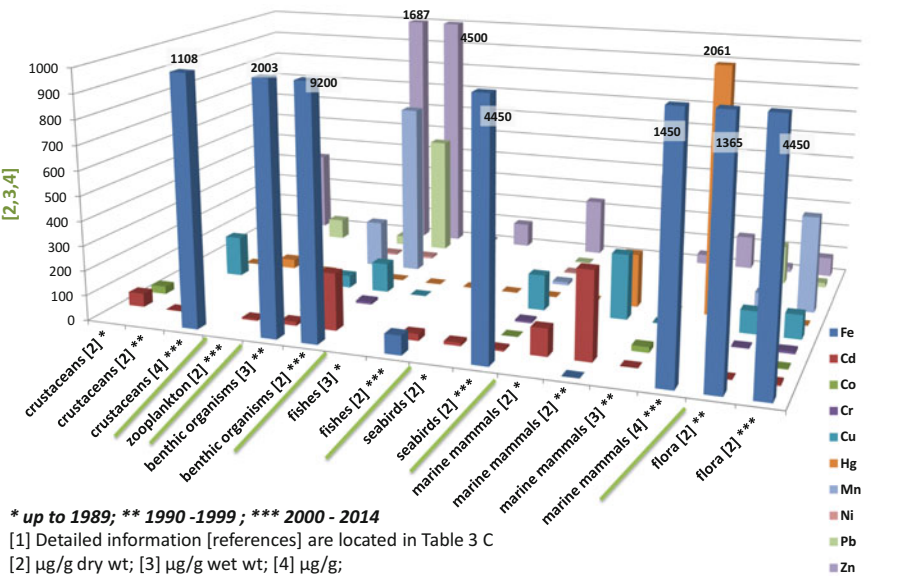

**Fig. 4** Contamination concentration levels during three time periods: (a) POPs in abiotic samples, (b) POPs in biotic samples, (c) heavy metals in abiotic samples, (d) heavy metals in biotic samples




** up to 1989; ** 1990 -1999 ; *** 2000 - 2014*

[1] Detailed information [references] are located in Table 3 C

[2] air -[pg/m$^3$]; fresh water, seawater, polonya water, -[µg/L]; soil, sediments, rocks, ice cores, snow, - [µg/g] (Hg - [ng/g])




** up to 1989; ** 1990 -1999 ; *** 2000 - 2014*

[1] Detailed information [references] are located in Table 3 C

[2] µg/g dry wt; [3] µg/g wet wt; [4] µg/g;

**Fig. 4** (continued)

and activities of tourists and scientists can result in the detectable contaminants (PBDE, PFAS) in most stations' areas in Antarctica (Cai et al. 2012). Every part of the abiotic environment (as well as Antarctica's atmosphere and reservoirs: soil and snow) are currently closely coupled. These parts, affecting each other, have a tendency for re-volatilization of POPs to the atmosphere. These are so called secondary sources of pollution. However it is not known to what extent this remobilization is a part of a seasonal cycle with volatilization during summer and deposition during winter (Cabrerizo et al. 2013). Glacial melt may carry pollutants to nearby lakes and the adjacent coastal marine areas, thereby spreading the contamination and increasing its impacts (Majer et al. 2014). Glacier meltwater can be a current source of pollution to Antarctica's marine food web as a result of an unexpected consequence of climate change (Geisz et al. 2008). Therefore the monitoring and remediation of this scenario is essential. The active layer/permafrost transition zone was revealed to be a low-permeability barrier to downward migration of chemical compounds (Curtosi et al. 2007). Near Antarctica's stations exhibiting PAHs contamination in soils, this behaviour highlights the risk for coastal marine environments (Curtosi et al. 2007). An analysis of stations' emissions and transect sampling of abiotic matrices are carried out. The research provides indication as to the significance of research stations as local sources of POPs contamination (Bengtson Nash et al. 2010). Only few studies have determined PCB and organochlorine pesticides (OCP) concentrations in sediments in Antarctica (Zhang et al. 2013). Pollution in marine sediments are the end result of a long term accumulation and this is not directly correlating with activities on land. Unfortunately, pollutants in sediments will persist for many years to come (Kim et al. 2006), hence it is necessary to control the levels of pollution in every part of abiotic environment including sediments.

Referring to abiotic research the monitoring programs need to be extended to facility points far from major bases, assessing the extent of contamination in order to prevent local pollution episodes. This kind of studies should verify the hypothesis of a decline of PCBs in the last decade in Antarctica (Vecchiato et al. 2015).

In the discussion of biological research, what is important is using organisms for monitoring. Atmospheric monitoring of POPs using conventional instrumental methods is expensive and difficult. Scientists can overcome this limitation using biomonitoring methods and thereby provide reliable information assessing the impact of pollutants on the biota and various ecosystems. Most popular in Antarctica is using mosses to define the relationship between the concentrations of POPs in Antarctic environment and in the atmosphere (Wu et al. 2014). It should be noted, based on PBDEs studies, that mosses can accumulate more POPs than lichens (Yogui et al. 2011).

Equally important is the transport of pollution between organisms. Collected data can be useful to notice that the high concentrations of POPs encountered in the brown skua is certainly correlated to its migratory habits as well as its high trophic level position (Taniguchi et al. 2009). A useful tool to trace migration behaviour of seabirds and marine mammals can be the research of POPs levels in tissues (Kallenborn et al. 2013). Moreover, the transfer of contaminants between

Antarctica's pelagic and benthic organisms is associated with seasonal sea-ice dynamics (Van den Brink et al. 2011). The concentrations of organochlorines in penguin eggs may be toxicologically insignificant, but more studies are needed to assess the real health risks associated with these levels of pollutants because Antarctica's seals and penguins are more sensitive to contaminants than those living in temperate regions (Schiavone et al. 2009b).

In a comprehensive approach to the issue of the presence of pollutants in Antarctica, it is also very important to become familiar with accurate levels of heavy metals in this environment. In a discussion of heavy metals in abiotic environment, the geochemical characteristics of the area should be further investigated, in particular, the transport of metals as particulate or soluble fraction from the terrestrial to the marine environment (Vodopivez et al. 2015). Based on lead isotopic data, Southern South America is an important source of dust deposited in Antarctica's ice (Vallelonga et al. 2010). Moreover, based on results of research on ice cores, anthropogenic activities have become the most important source of heavy metals in Antarctica (Yin et al. 2006). Antarctica is a kind of a sink for heavy metals (e.g. Hg). Considering long atmospheric lifetime and the ability to deposit and be re-emit from soil and oceans, the ability of heavy metals to bioaccumulate suggests that their deposition would indeed have a serious effect for environment (Sprovieri et al. 2002).

Referring to heavy metals present in biological samples, particular attention should be paid to the biomagnification process which depends upon the food web (high trophic level animals have a higher content than lower trophic level ones) (Moreno et al. 1997). The presence of potentially toxic elements (such as Cd and Hg) in penguins suggest, that the accumulation of elements depends on the geochemical characteristics of the area, age of individuals and also on their diet (mainly krill) (Smichowski et al. 2006). Moreover, the results of research indicated, that a slight increase in Mn and Cr levels in Antarctica could be related mainly to human presence (usage of combustibles and oil contamination). Other studies indicate common sources of pollution (such as Cr, Ni, Pb, Mn, Cd or As), which are correlated with anthropogenic activities (plane and ship trips related to the tourism industry) (Jerez et al. 2013a). Feathers can be an important identifiers of the absorbed heavy metals (e.g. Pb) in penguins (Jerez et al. 2013b). For a better understanding of spatio-temporal trends feathers of Antarctic penguins, put together with other penguin tissues, are useful tools for long-term monitoring of trace elements in Antarctic marine environment (Jerez et al. 2011).

Furthermore mercury and its transformation products (e.g. methylmercury), because of their high bioaccumulation properties, should be investigated more precisely. A quantitative understanding of pathways and mechanisms that affect the transport of mercury from sources to ecosystems as well as the conversion of mercury to methylmercury, and their bioaccumulation in food webs are fundamental to evaluating and managing human and wildlife health risks in a local and global scale (Driscoll et al. 2013). The observations that have been made in polar marine ecosystems showed progressive increase in mercury concentrations in the food web (Bargagli et al. 1998). The role of Antarctic coastal ecosystems as sink in the global

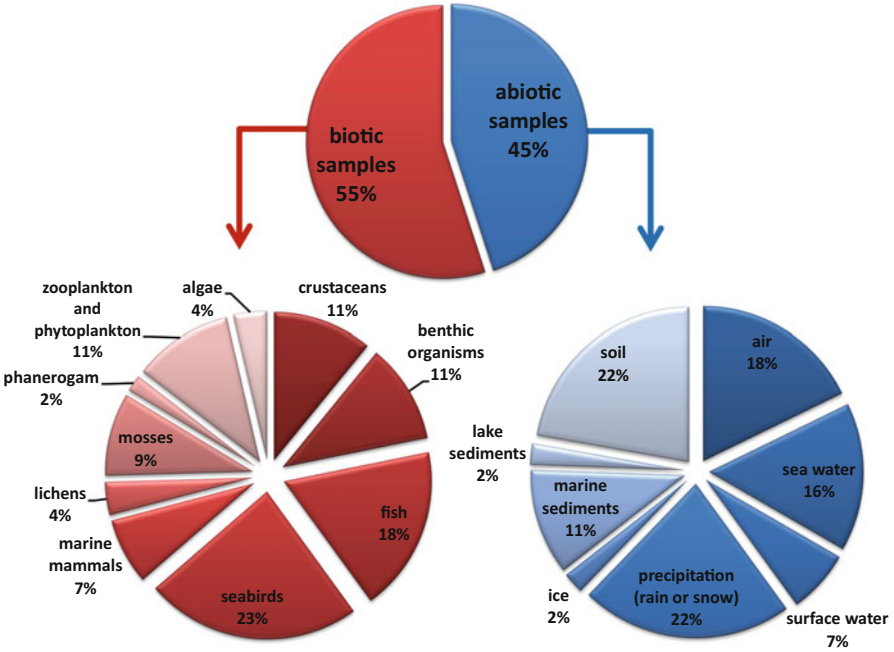



**Fig. 5** Classification of analytical research according to types of environmental samples collected in the years 2000–2014

mercury cycle can be enhanced by the global warming and the possible change in the ice coverage together with increasing anthropogenic emissions of gaseous mercury in countries of the Southern Hemisphere (Bargagli et al. 2007). It clearly demonstrates the need for understanding how climatic variability and anthropogenic disturbances (e.g., increases of population, perturbations to food chains, changes in other air pollutants) affect mercury and methylmercury concentrations in Antarctic ecosystems (Driscoll et al. 2013; Bargagli 2008). Research data on pollutant levels has been enhanced during last two decades. Figure 5 presents information on the proportion of various types of analytical research in a general number of studies aimed at getting to know the degree of pollution of the Antarctica's environment during the last two decades.

The most popular research locations were the areas of the Antarctic Peninsula (including South Shetland Islands) and Ross Sea. A little more attention (55 % of contemporary research) is paid to tests of biological samples, mostly due to the interest in the actual influence of pollutants on Antarctica's ecosystem and becoming familiar with new directions of pollutant movement in the food web. Research on the chemical composition of inorganic samples (45 % of contemporary research), is equally important, as elements of abiotic environmental media are the first link in the pollutant movement process in Antarctica.

## 4.3 Analytical Techniques in the Study of the Antarctic Environment

Together with the development of science and instruments, various analytical procedures and techniques were used in analytical practice to test environmental samples (abiotic and biotic) collected in Antarctica.

Nowadays, Antarctica's researchers have gained access to many different analytical techniques of scope detection, power and robustness, which they couldn't even dream of some decades ago (Caroli 2001). For the chemical elements they can use: atomic absorption spectrometry (AAS) with flame or electrothermal (another name—graphite furnace (GF)) atomisation, inductively coupled plasma—atomic emission spectrometry (ICP-AES), inductively coupled plasma—optical emission spectrometry (ICP-OES), atomic fluorescence spectrometry (AFS), mass spectrometry (MS) with different ionization sources (e. g. ICP), X-ray fluorescence spectrometry (XRF), neutron activation analysis (NAA), ion-selective electrodes and isotope dilution mass spectrometry (IDMS). For organic substances, depending on properties of organic substances, analysts can choose one of the following techniques: gas chromatography (GC), high performance liquid chromatography (HPLC), thin layer chromatography (TLC), supercritical fluid chromatography (SFC) and gel permeation chromatography (GPC) with several detection systems (electron capture (EC), flame ionization (FI)), thermal conductivity (TC), flame photometry (FP), infrared spectroscopy (IR), UV absorption spectrophotometry, fluorescence (F), capillary zone electrophoresis (CZE) and MS (Caroli 2001). To determine ionic compound concentration the analysts use ion chromatography (IC) with various types of detection (e.g. conductometry detector (CD), ICP).

Applications with impressively high-resolution and full scan performances were made possible by modern instrumental configuration, that is hybrid mass spectrometers. Quantification of highly polar organic pollutants without derivatization, lower than the ppt level (nanogram per liter or per kilogram of matrix) in environmental samples, is possible by the use of tandem mass spectrometry combined with liquid chromatography. The measurement of emerging contaminants in environmental analysis are performed using the achievements of liquid chromatography—mas spectrometry (LC-MS) like the more recent advancements in triple quadrupole (QqQ), linear ion trap, time of flight analyzer (TOF) and Orbitrap mass spectrometers (Magi and Tanwar 2014).

Generally, the analysts are warned of pushing the instrumental method beyond its intrinsic limits, in terms of limits of detection, optimal working range and applicability to specific groups of substances. Otherwise, the rapid increase in the overall uncertainty associated with the experimental date will be observed soon (Caroli 2001).

Polar regions are an excellent place to study some natural phenomena as well as historical trends mostly due to the large distance between them and anthropogenic emissions sources. The concentration of micro-constituents or micro-pollutants in

polar regions is rather low and therefore it is necessary to develop some analytical methods of high sensitivity.

The chemical specification of such a variety of samples requires scientific experience and skills from different areas of science. The wide choice of analytical techniques, from the classical to the most innovative ones, which are available nowadays, offers the scientists an opportunity to face challenging qualitative and quantitative determinations. What is more, some more precise chemical information can be achieved by developing hyphenated methodologies, which means the combination of different instrumental techniques (Magi and Tanwar 2014).

Nowadays the most useful analytical tool seems to be the mass spectrometry, which was designed for determining a wide range of compounds present in environmental samples. In combination with such techniques as gas or liquid chromatography, it creates the possibility of specifying the organic (GC-MS, LC-MS) as well as inorganic compounds (ICP-MS) with a large degree of sensitivity and selectivity. Another advantage of such an analytical solution is the fact that MS provides more chemical information using a minimum amount of sample than any other analytical method (Gasparics and Marıa 2000; Magi and Tanwar 2014; Planchon et al. 2001).

Determination of organic contaminants in various matrices is usually performed using chromatographic techniques (Płotka et al. 2013). Actual trend in chromatography is development of multidimentional approaches (e.g. Ouyang et al. 2015; Seeley and Seeley 2013). Multidimensional chromatography is a technique for isolating and identifying volatile (GC) and semi-volatile (GC and LC) organic compounds present in complex mixtures during one analytical cycle. Hence this techniques coupled with mass spectrometry can provide an important tool in a future monitoring of organic chemicals in Antarctica. Therefore, because of a low concentration of chemical compounds in complex matrices (feathers, leathers and internal organs of organisms) (Magi and Tanwar 2014), Antarctica poses a real challenge of developing innovative analytical approaches as well as improving MS instrument performances.

## *4.4 Impact of Research Station Activities on Pollution Levels*

Research stations are and will be an inseparable element of the Antarctic environment. Individual polar stations have a different nature. A detailed description of the operations of polar stations is presented in Table 4. The influence that each station can have on Antarctic environment is related with length of time it has been operated or/and number of people present at station etc. This information is given regularly each year by Council of Managers of National Antarctic Program (COMNAP) on its webpage (e.g. COMNAP Information). It is also important that the development of research (the use of the station and the construction of new facilities) should not additionally contribute to environmental pollution. There are numerous ways of operating stations without polluting the environment. The

**Table 4** Characteristics of polar stations operating in Antarctica (SCAR Information)

| Division according to the infrastructure | |
|---|---|
| Type of infrastructure | Description |
| Station | – consists of durable buildings and mechanical services, |
| | – buildings are equipped with power supply and water and sewage systems |
| Camp | – more basic and less durable sleeping facilities are situated at the camp (tents, shelters), |
| | – these places are often used only for a few seasons, |
| Refuge | – has a permanent nature, |
| | – usually small and easy to install single huts |
| Airfield | – infrastructure (camp or shelter) is situated near the airport, it is usually connected with it, |
| | – not distinguished according to the size |
| Depot | – for storing food, fuel and other things |
| Division according to the specificity of operations | |
| Specificity of operations | Description |
| Year-round | – operate both in summer and in winter |
| Seasonal | – operate in summer |
| Closed | – the facility does not exist any more |
| Temporarily closed | – the facility has been closed on a temporary basis, ready to be re-opened, if necessary |
| Closed stations | – stations closed for an indefinite period of time |
| | – the facility can be renovated and/or re-used at any time |

Princess Elisabeth Antarctica Station is an example of a station that virtually has no impact on the environment. At this station, electricity is produced using photovoltaic panels, solar collectors and wind turbines. The use of renewable sources of energy in Antarctica in the twenty-first century should not be a sign of modernity in this area, but a necessity. Reduction of potential anthropogenic pollution sources to a minimum allows to obtain reliable research results, in particular in research on long-range atmospheric transport of pollutants (Polar Foundation Information). The results of work on the design process of a photovoltaic (PV)-wind power system were recently published. This system could be installed in very challenging ambient conditions. This work has been done in the French-Italian Antarctic Base (Concordia Base). Work in this scope should be continued in other polar bases. Pollution can affect important research activities in this area (e.g. astronomical observations, studies of physics of atmosphere and Earth science). The ambient conditions significantly affect the quality of the research results. Usage of renewable energy leads to reduce usage of diesel generator and thereby leads to preserve an ecosystem, which is mandatory for heritage of the humanity (Boccaletti et al. 2014).

## 5 Summary and Conclusions

The environment of polar regions is characterised by the lowest pollution levels in the world. However, the growing number of studies on the presence of a broad range of chemical compounds in various elements of the Antarctic environment may indirectly indicate the scale of the problem of growing symptoms of global human influence in this area.

Over the past decade, the scope of tested samples has been extended; however, the type of pollutants identified in individual samples (in the years 2000–2014) differs from the previous decades, *inter alia* is enhanced to new emerging pollutants. Most of the information about the presence of pollutants in biotic samples pertains to samples of Antarctic mosses krill, molluscs and invertebrates, various fish species and maritime birds—mostly penguins. Research of biotic samples have a special value as more and more attention is devoted to the phenomenon of bioaccumulation and its consequences within one plant or animal species as well as to biomagnification in the food chain. Research data about pollutants detected in abiotic samples are also important mainly due to direct and continuous contact with Antarctic biota.

A significant part of research is targeted at the occurrence of POPs compounds in the environment (Fuoco et al. 2009a, b). A possibly exhaustive list of information pertaining to POPs present in Antarctica's environment is possible only for several groups of compounds (HCB, PCB, DDTs, PBDE and PAHs). Their presence may largely result from the activity of research stations and the development of tourism. Over the past decades, sporadic research also pertained to identification and determination of compounds, such as: CHL, dioxins, DLC, PFCs, pesticides (dieldrin, mirex, heptachlor, endosulfan), aliphatic hydrocarbons, n-alkanes and cumulative parameters such as TOC in various environmental samples. In the future emerging pollutants exhibiting characteristics of persistence comparable to POPs should also be considered in long term monitoring.

Heavy metals are global pollutants and can reach almost any location on Earth. They come from natural, volcanic or geological sources, or as a result of anthropogenic activities. Accordingly with increasing human presence in Antarctic region the presence of metals in this area is becoming an issue that needs to be more investigated. Especially issues like: understanding of pathways and mechanisms that affect the transport of mercury from sources to ecosystems, the conversion of mercury to methylmercury, and its bioaccumulation state in food webs should be continuously studied.

Regrettably, data on pollutants in Antarctica's environment are dispersed in many magazines. It is worth mentioning that over the years different methods of POPs quantification have been used. Often information is scarce or lacking on the biology of the sampled species (age, sex, nutritional status, reproductive status, etc.). This makes data difficult to compare (Trumble et al. 2012). The fact that research results are presented in various units (g/g wet wt, g/g dry wt., etc.) is a further inconvenience, as it also makes it difficult to compare results of studies

conducted in various areas of Antarctica. To overcome this problem, some of scientists have presented their results expressed in multiple units (Court et al. 1997; Yogui et al. 2011); unfortunately very few researchers have done so.

Research on the influence of research stations on the pollution levels in the surrounding environment is also important. Detailed research in this areas leads to differentiate sources of pollutants between influence of local sources and global sources (LRAT). Additionally polar stations should implement usage of renewable energy in whole possible areas. This kind of solution of energy production leads to reduced usage of diesel generators and thereby lead preservation of the polar ecosystem.

The analysis of available information allows for concluding that human activity on a local and global scale leads to affecting and/or degradation of Antarctic ecosystems. The basic direction for contemporary Antarctic research pertaining to pollutants should be:

- carrying out the long term atmospheric monitoring for main POPs and new emerging pollutants coupled with meteorological data,
- carrying out the long-term monitoring of man-made chemicals (as well as new emerging pollutants monitoring) in Antarctic abiotic environment and endemic species in order to follow the future trends of global contamination,
- the detailed description of remobilization processes and "second sources" (e.g. melting glaciers) of pollutant in polar areas,
- the enlargement of research using non-invasive samples (like feathers and preen oil) as a useful tool to POPs and heavy metals monitoring,
- the determination of reaction and tolerance individual pollution levels for Antarctica's fauna and flora towards individual anthropogenic chemicals (examination of the toxicological sensitivity of Antarctic key species),
- the detailed description of environmental fate (including biotic and abiotic environment) and negative effects on Antarctic ecosystem of anthropogenic compounds,
- the development of innovative analytical approaches improving the limits of detection of chemical compounds in various abiotic and biological matrices.

## References

Ahn I-Y, Lee SH, Kimt KT, Shim JH, Kim D-Y (1996) Baseline heavy metal concentrations in the Antarctic clam, Laternula elliptica in Maxwell Bay, King George Island, Antarctica. Mar Pollut Bull 32:59–598

Ahrens L, Xie Z, Ebinghaus R (2010) Distribution of perfluoroalkyl compounds in seawater from Northern Europe, Atlantic Ocean, and Southern Ocean. Chemosphere 78:1011–1016

Aisable J, Balks M, Foght J, Waterhouse A (2004) Hydrocarbon spills on Antarctic soils: effects and management. Environ Sci Technol 38:1265–1274

Aislabie J, Balks M, Astori N, Stevenson G, Symons R (1999) Polycyclic aromatic hydrocarbons in fuel-oil contaminated soils, Antarctica. Chemosphere 39:2201–2207

Alam IA, Sadiq M (1993) Metal concentrations in antarctic sediment samples collected during the Trans-Antarctica 1990 expedition. Mar Pollut Bull 26:523–527
Albert MR, Shultz EF (2002) Snow and firn properties and air–snow transport processes at Summit, Greenland. Atmos Environ 36:2789–2797
Andrade S, Poblet A, Scagliola M, Vodopivez C, Curtosi A, Pucci A, Marcovecchio J (2001) Distribution of heavy metals in surface sediments from an Antarctic marine ecosystem. Environ Monit Assess 66:147–158
Antony R, Mahalinganathan K, Thamban M, Nair S (2011) Organic carbon in Antarctic snow: spatial trends and possible sources. Environ Sci Technol 45:9944–9950
Aono S, Tanabe S, Fujise Y, Kat H, Tatsukawa R (1997) Persistent organochlorines in minke whale (Balaenoptera acutorostrata) and their prey species from the Antarctic and the North Pacific. Environ Pollut 98:81–89
Aronson RB, Thatje S, Mc Clintock JB, Hughes K (2011) Anthropogenic impacts on marine ecosystems in Antarctica. Ann N Y Acad Sci 1223:82–107
Bacci E, Calamari D, Gaggi C, Fanelli R, Focardi S, Morosini M (1986) Chlorinated hydrocarbons in lichen and moss samples from the Antarctic Peninsula. Chemosphere 15:747–754
Baek S-Y, Choi S-D, Chang Y-S (2011) Three-year atmospheric monitoring of organochlorine pesticides and polychlorinated biphenyls in Polar Regions and the South Pacific. Environ Sci Technol 45:4475–4482
Bargagli R, Brown DH, Nelli L (1995) Metal biomonitoring with mosses: procedures for correcting for soil contamination. Environ Pollut 89:169–175
Bargagli R (2008) Environmental contamination in Antarctic ecosystems. Sci Total Environ 400:212–226
Bargagli R, Monaci F, Bucci C (2007) Environmental biogeochemistry of mercury in Antarctic ecosystems. Soil Biol Biochem 39(1):352–360
Bargagli R, Sanchez-Hernandez JC, Martella L, Monaci F (1998) Mercury, cadmium and lead accumulation in Antarctic mosses growing along nutrient and moisture gradients. Polar Biol 19:316–322
Bargagli R, Sanchez-Hernandez JC, Monaci F (1999) Baseline concentrations of elements in the Antarctic macrolichen Umbilicaria decussata. Chemosphere 38:475–487
Bargagli R (2001) Trace metals in Antarctic organisms and the development of circumpolar biomonitoring networks. Rev Environ Contam Toxicol 171:53–110
Bengtson Nash M, Xiao H, Schlabach M, King C, Stark JS, Hung H (2011) Contaminant profiles of air and soil around Casey station, Antarctica; Discerning local and distant contaminant sources, Society for Environmental Toxicology and Chemistry (SETAC) Europe Proceedings, 21. http://milano.setac.eu/?contentid=291. Accessed 28 Oct 2015
Bengtson Nash S, Rintoul SR, Kawaguchi S, Staniland I, Hoff J, Tierney M, Bossi R (2010) Perfluorinated compounds in the Antarctic region: ocean circulation provides prolonged protection from distant sources. Environ Pollut 158:2985–2991
Bicego MC, Weber RR, Goncalves Ito RR (1996) Aromatic hydrocarbons on surface waters of Admiralty Bay, King George Island, Antarctica. Mar Pollut Bull 32:549–553
Bidleman TF, Walla MD, Roura R, Carr E, Schmidt S (1993) Organochlorine pesticides in the atmosphere of the Southern Ocean and Antarctica. Mar Pollut Bull 26:258–262
Boccaletti C, Felice P, Santini E (2014) Integration of renewable power systems in an Antarctic Research Station. Renew Energ 62:582–591
Borghesi N, Corsolini S, Focardi S (2008) Levels of polybrominated diphenyl ethers (PBDEs) and organochlorine pollutants in two species of Antarctic fish (Chionodraco hamatus and Trematomus bernacchii). Chemosphere 73:155–160
Borghesi N, Corsolini S, Leonards P, Brandsma S, Boer J, Focardi S (2009) Polybrominated diphenyl ether contamination levels in fish from the Antarctic and the Mediterranean Sea. Chemosphere 77:693–698
Borghini F, Grimalt JO, Sanchez-Hernandez JC, Bargagli R (2005) Organochlorine pollutants in soils and mosses from Victoria Land (Antarctica). Chemosphere 58:271–278
Boutron CF, Patterson CC (1983) The occurrence of lead in Antarctic recent snow, firn deposited over the last two centuries and prehistoric ice. Geochim Cosmochim Acta 47:1355–1368

Boutron C (1979) Alkali and alkaline earth enrichments in aerosols deposited in Antarctic snow. Atmos Environ (1967) 13:919–924
Boutron C, Echevin M, Lorius C (1972) Chemistry of polar snows. Estimation of rates of deposition in Antarctica. Geochim Cosmochim Acta 36:1029–1041
Boutron C, Leclerc M, Risler N (1984) Atmospheric trace elements in antarctic prehistoric ice collected at a coastal ablation area. CACGP Symposium on Tropospheric Chemistry with Emphasis on Sulphur and Nitrogen Cycles and the Chemistry of Clouds and Precipitation. Atmos Environ (1967) 18:1947–1953
Boutron C (1982) Atmospheric trace metals in the snow layers deposited at the South Pole from 1928 to 1977. Atmos Environ (1967) 16:2451–2459
Boutron CF, Bolshov MA, Koloshnikov VG, Patterson CC, Barkov NI (1990) Direct determination of lead in vostok antarctic ancient ice by laser excited atomic fluorescence spectrometry. Atmos Environ 24:1797–1800
Brasso RL, Polito MJ (2013) Trophic calculations reveal the mechanism of population-level variation in mercury concentrations between marine ecosystems: case studies of two polar seabirds. Mar Pollut Bull 75:244–249
Burniston DA, Strachan WJM, Hoff JT, Wania F (2007) Changes in surface area and concentrations of semivolatile organic contaminants in aging snow. Environ Sci Technol 41:4932–4937
Burn-Nunes LJ, Vallelonga P, Loss RD, Burton GR, Moy A, Curran M, Rosman KJR (2011) Seasonal variability in the input of lead, barium and indium to Law Dome, Antarctica. Geochim Cosmochim Acta 75:1–20
Burton HR (1981) Chemistry, physics and evolution of Antarctic saline lakes. Hydrobiologia 82:339–362
Bustnes JO, Tveraa T, Henden JA, Janssen K, Skaare JU (2006) Organochlorines in Antarctic and Arctic Avian top predators: a comparison between the South Polar Skua and two species of Northern Hemisphere Gulls. Environ Sci Technol 40:2826–2831
Cabrerizo A, Dachs J, Barceló D, Jones KC (2012) Influence of organic matter content and human activities on the occurrence of organic pollutants in Antarctic soils, lichens, grass, and mosses. Environ Sci Technol 46:1396–1405
Cabrerizo A, Dachs J, Barceló D, Jones KC (2013) Climatic and biogeochemical controls on the remobilization and reservoirs of persistent organic pollutants in Antarctica. Environ Sci Technol 47:4299–4306
Cabrerizo A, Galbán-Malagón C, Del Vento S, Dachs J (2014) Sources and fate of polycyclic aromatic hydrocarbons in the Antarctic and Southern Ocean atmosphere. Global Biogeochem Cycles 28:1424–1436
Cai M, Yang H, Xie Z, Zhao Z, Wang F, Lu Z, Sturm R, Ebinghaus R (2012) Per- and polyfluoroalkyl substances in snow, lake, surface runoff water and coastal seawater in Fildes Peninsula, King George Island, Antarctica. J Hazard Mater 209–210:335–342
Capelli R, Minganti V, Chiarini C, Pellegrini R (1998) Mercury in snow layers from the Antarctica. Int J Environ Anal Chem 71:289–296
Caricchia AM, Chiavarini S, Cremisini C, Morabito R, Perini A, Pezza M (1995) Determination of PAH in atmospheric particulates in the area of the Italian base in Antarctica: report on monitoring activities during the last three scientific expeditions. Environ Pollut 87:345–356
Caroli S (2001) Environmental chemistry in Antarctica: the quest for accuracy. In: Caroli S, Cescon P, Walton DWH (eds) Environmental contamination in Antarctica. The challenge to analytical chemistry. Elsevier, Amsterdam, pp 1–32
Carrasco MA, Prendez M (1991) Element distribution of soils of continental Chile and the Antarctic Peninsula. Projection to atmospheric pollution. Water Air Soil Pollut 57–58:713–722
Chiuchiolo AL, Dickhut RM, Cochran MA, Ducklow HW (2004) Persistent organic pollutants at the base of the Antarctic marine food web. Environ Sci Technol 38(13):3551–3557
Choi S-D, Baek S-Y, Chang Y-S, Wania F, Ikonomou MG, Yoon Y-J, Hong S (2008) Passive air sampling of polychlorinated biphenyls and organochlorine pesticides at the Korean Arctic and

Antarctic research stations: implications for long-range transport and local pollution. Environ Sci Technol 42:7125–7131
Ciaralli L, Giordano R, Lombardi G, Beccaloni E, Sepe A, Costantini S (1998) Antarctic marine sediments: distribution of element and textural characters. Microchem J 59:77–88
Cincinelli A, Dickhut RM (2011) Levels and trends of organochlorine pesticides (OCPS) in Antarctica. Environ Res J 5(4):523–545
Cincinelli A, Martellini T, Bittoni L, Russo A, Gambaro A, Lepri L (2008) Natural and anthropogenic hydrocarbons in the water column of the Ross Sea (Antarctica). J Mar Syst 73:208–220
Cincinelli A, Martellini T, Del Bubba M, Lepri L, Corsolini S, Borghesi N, King MD, Dickhut RM (2009) Organochlorine pesticide air–water exchange and bioconcentration in krill in the Ross Sea. Environ Pollut 157:2153–2158
Cipro CVZ, Bustamante P, Taniguchi S, Montone RC (2012) Persistent organic pollutants and stable isotopes in pinnipeds from King George Island, Antarctica. Mar Pollut Bull 64:2650–2655
Cipro CVZ, Taniguchi S, Montone RC (2010) Occurrence of organochlorine compounds in Euphausia superba and unhatched eggs of Pygoscelis genus penguins from Admiralty Bay (King George Island, Antarctica) and estimation of biomagnification factors. Chemosphere 78:767–771
Cipro CVZ, Yogui GT, Bustamante P, Taniguchi S, Sericano JL, Montone RC (2011) Organic pollutants and their correlation with stable isotopes in vegetation from King George Island, Antarctica. Chemosphere 85:393–398
Clarke A, Law R (1981) Aliphatic and aromatic hydrocarbons in benthic invertebrates from two sites in Antarctica. Mar Pollut Bull 12:10–14
COMNAP Information (2015).https://www.comnap.aq/Information/SitePages/Home.aspx. Accessed 18 Sep 2015
Corsolini S, Borghesi N, Ademollo N, Focardi S (2011) Chlorinated biphenyls and pesticides in migrating and resident seabirds from East and West Antarctica. Environ Int 37:1329–1335
Corsolini S, Borghesi N, Schiamone A, Focardi S (2007) Polybrominated diphenyl ethers, polychlorinated dibenzo-dioxins, -furans, and -biphenyls in three species of Antarctic Penguins. Environ Sci Pollut Res 14:421–429
Corsolini S, Covaci A, Ademollo N, Focardi S, Schepens P (2006) Occurrence of organochlorine pesticides (OCPs) and their enantiomeric signatures, and concentrations of polybrominated diphenyl ethers (PBDEs) in the Adelie penguin food web, Antarctica. Environ Pollut 140:371–382
Corsolini S, Kannan K, Imagawa T, Focardi S, Giesy J (2002a) Polychloronaphtalenes and other dioxin-like compounds in Arctic and Antarctic marine food webs. Environ Sci Technol 36:3490–3496
Corsolini S, Romeo T, Ademollo N, Greco S, Focardi S (2002b) POPs in key species of marine Antarctic ecosystem. Microchem J 73:187–193
Corsolini S (2009) Industrial contaminants in Antarctic biota. J Chromatogr A 1216:598–612
Court GS, Davis LS, Focardi S, Bargargli R, Fossi C, Leonzio C, Marili L (1997) Chlorinated hydrocarbons in the tissues of South Polar Skuas (Catharacta maccormicki) and Adélie Penguins (Pygoscelis adeliea) from Ross Sea, Antarctica. Environ Pollut 97:295–301
Crespi VC, Genova N, Tositti L, Tubertini O, Bettoli G, Oddone M, Meloni S, Berzero A (1993) Trace elements distribution in Antarctic sediments by neutron activation analysis. J Rad Nucl Chem 168:107–114
Cripps GC (1992) The extent of hydrocarbon contamination in the marine environment from a research station in the Antarctic. Mar Pollut Bull 25:288–292
Crockett AB, White GJ (2003) Mapping sediment contamination and toxicity in winter quarters bay, McMurdo station, Antarctica port station for the United States Antarctic Program (USAP), and is located Ad-Jacent to Winter Quarters Bay (WQB), a small embayment on Ross Island. Environ Monit Assess 85:257–275

Curtosi A, Pelletier E, Vodopivez CL, Mac Cormack WP (2007) Polycyclic aromatic hydrocarbons in soil and surface marine sediment near Jubany Station (Antarctica). Role of permafrost as a low-permeability barrier. Sci Total Environ 383:193–204

Curtosi A, Pelletier E, Vodopivez C, Louis R, Mac Cormack WP (2010) Presence and distribution of some persistent toxic substances in sediments and marine organisms of Potter Cove, Antarctica. Arch Environ Contam Toxicol 59:582–592

Dastidar PG, Ramachandran S (2008) Intellectual structure of Antarctic science: a 25-years analysis. Scientometrics 77:389–414

Dauner ALL, Hernández E, MacCormack WP, Martins CC (2014) Molecular characterization of anthropogenic sources of sedimentary organic matter from Potter Cove, King George Island, Antarctica. Sci Total Environ 502:408–416

Delmas RJ, Gravenhorst G (1983) Background precipitation acidity. In: Acid deposition. Commission of the Communities, Brussels, pp 82–107

Delmas R, Boutron C (1978) Sulfate in Antarctic snow: spatio-temporal distribution, Sulfur in the Atmosphere Proceedings of the International Symposium Held in Dubrovnik. Yugoslavia, 7–14 Sep 1977, pp 723–728

Dickhut RM, Cincinelli A, Cochran M, Ducklow HW (2005) Atmospheric concentrations and air-water flux of organochlorine pesticides along the Western Antarctic Peninsula. Environ Sci Technol 39:465–470

Dodds K (2010) Governing Antarctica: contemporary challenges and the enduring legacy of the 1959 Antarctic Treaty. Global Policy 1:108–115

Driscoll CT, Mason RP, Chan HM, Jacob DJ, Pirrone N (2013) Mercury as a global pollutant: sources, pathways, and effects. Environ Sci Technol 47:4967–4983

Edwards R, Sedwick P, Land E (2001) Iron in East Antarctic snow: implications for atmospheric iron deposition and algal production in Antarctic waters. Geophys Res Lett 28:3907–3910

Edwards R, Sedwick P, Morgan V, Boutron C (2006) Iron in ice cores from Law Dome: a record of atmospheric iron deposition for maritime East Antarctica during the Holocene and Last Glacial Maximum. Geochem Geophy Geosy 7:1–15

Fischer WH, Lodge JP, Wartburg AF, Pate JB (1967) Estimation of some atmospheric trace gases in Antarctica. Environ Sci Technol 78:1967–1969

Fischer R, Weller R, Jacobi H-W, Ballschmiter K (2002) Levels and pattern of volatile organic nitrates and halocarbons in the air at Beumayer Station (70°S), Antarctic. Chemosphere 48:981–992

Focardi S, Gaggi C, Chemello G, Bacci E (1991) Organochlorine residues in moss and lichen samples from two Antarctic areas. Polar Record 27:241–244

Fortner SK, Lyons BW, Olesik JW (2011) Eolian deposition of trace elements onto Taylor Valley Antarctic glaciers. Appl Geochem 26:1897–1904

Fuoco R, Capodaglio R, Muscatello B, Radaelli M (2009a) Persistent organic pollutants (POPs) in the Antarctic environment. A review of findings. The SCAR Action Group on Environmental Contamination in Antarctica. http://www.iau.gub.uy/medioambiente/docs-mamb/Otros-docs/POPs_in_Antarctica.pdf. Accessed 28 Oct 2015

Fuoco R, Colombini MP, Ceccarini A, Abete C (1996) Polychlorobiphenyls in Antarctica. Microchem J 54:384–390

Fuoco R, Giannarelli S, Onor M, Ghimenti S, Abete C, Termine M, Francesconi S (2012) A snow/firn four-century record of polycyclic aromatic hydrocarbons (PAHs) and polychlorobiphenyls (PCBs) at Talos Dome (Antarctica). Microchem J 105:133–141

Fuoco R, Giannarelli S, Wei Y, Ceccarini A, Abete C, Francesconi S, Termine M (2009b) Persistent organic pollutants (POPs) at Ross Sea (Antarctica). Microchem J 92:44–48

Galbán-Malagón C, Cabrerizo A, Caballero G, Dachs J (2013a) Atmospheric occurrence and deposition of hexachlorobenzene and hexachlorocyclohexanes in the Southern Ocean and Antarctic Peninsula. Atmos Environ 80:41–49

Galbán-Malagón CJ, Del Vento S, Berrojalbiz N, Ojeda M-J, Dachs J (2013b) Polychlorinated biphenyls, hexachlorocyclohexanes and hexachlorobenzene in seawater and phytoplankton from the Southern Ocean (Weddell, South Scotia, and Bellingshausen Seas). Environ Sci Technol 47:5578–5587

Galbán-Malagón CJ, Del Vento S, Cabrerizo A, Dachs J (2013c) Factors affecting the atmospheric occurrence and deposition of polychlorinated biphenyls in the Southern Ocean. Atmos Chem Phys 13:12029–12041

Gambaro A, Manodori L, Zangrando R, Cincinelli A, Capodaglio G, Cescon P (2005) Atmospheric PCB concentrations at Terra Nova Bay. Environ Sci Technol 39:9406–9411

Gasparics T, Marıa R (2000) Determination of trace elements in Antarctic krill samples by inductively coupled atomic emission and graphite furnace atomic absorption spectrometry. Microchem J 67:279–284

Geisz HN, Dickhut RM, Cochran MA, Fraser WR, Ducklow HW (2008) Melting glaciers: a probable source of DDT to the Antarctic Marine Ecosystem. Environ Sci Technol 42:3958–3962

Giordano R, Lombardi G, Ciaralli L, Beccaloni E, Sepe A, Ciprotti M, Costantini S (1999) Major and trace elements in sediments from Terra Nova. Sci Total Environ 227:29–40

Gjessing Y (1989) Excess and deficit of sulfate in polar snow. Atmos Environ 23:155–160

Gjessing Y (1984) Marine and non-marine contribution to the chemical composition of snow at the Riiser-Larsenisen Ice Shelf in Antarctica. Atmos Environ (1967) 18:825–830

Görlach U, Boutron CF (1992) Variations in heavy metals concentrations in Antarctic snows from 1940 to 1980. J Atmos Chem 14:205–222

Green G, Skerratt JH, Leeming R, Nichols PD (1992) Hydrocarbon and coprostanol levels in seawater, sea-ice algae and sediments near Davis station in eastern Antarctica: a regional survey and preliminary results for a field fuel spill experiment. Mar Pollut Bull 25:293–302

Green WJ, Ferdelman GF, Canfield DE (1989) Metal dynamics in Lake Vanda (Wright Valley, Antarctica). Chem Geol 76:85–94

Guerra MBB, Neto EL, Prianti MTA, Pereira-Filho ER, Schaefer CEGR (2013) Post-fire study of the Brazilian Scientific Antarctic Station: toxic element contamination and potential mobility on the surrounding environment. Microchem J 110:21–27

Hale RC, Kim SL, Harvey E, Guardia MJ, Mainor TM, Bush EO, Jacobs EM (2008) Antarctic research bases: local sources of polybrominated diphenyl ether (PBDE) flame retardants. Environ Sci Technol 42:1452–1457

Han Y, Huh Y, Hong S, Hur S, Motoyama H (2013) Evidence of air-snow mercury exchange recorded in the snowpack at Dome Fuji. Antarctica. Geosci J 18:105–113

Herbert BMJ, Halsall CJ, Jones KC, Kallenborn R (2006a) Field investigation into the diffusion of semi-volatile organic compounds into fresh and aged snow. Atmos Environ 40:1385–1393

Herbert BMJ, Villa S, Halsall CJ (2006b) Chemical interactions with snow: understanding the behavior and fate of semi-volatile organic compounds in snow. Ecotox Environ Safe 63:3–16

Hong S, Boutron CF, Edwards R, Morgan V (1998) Heavy metals in Antarctic Ice from Law Dome: initial results. Environ Res A 78:94–103

Hong S, Soyol-Erdene T-O, Hwang HJ, Hong SB, Hur SD, Motoyama H (2012) Evidence of global-scale As, Mo, Sb, and Tl atmospheric pollution in the Antarctic Snow. Environ Sci Technol 46:11550–11557

Houde M, De Silva AO, Muir DC, Letcher RJ (2011) Monitoring of perfluorinated compounds in aquatic biota: an updated review. Environ Sci Technol 19:7962–7973

House DA, Hoare RA, Popplewell KB, Henderson RA, Prebble WM, Wilson AT (1966) Chemistry in the Antarctic. J Chem Educ 43:502–505

Huang T, Sun L, Wang Y, Chu Z, Qin X, Yang L (2014) Transport of nutrients and contaminants from ocean to island by emperor penguins from Amanda Bay, East Antarctic. Sci Total Environ 468–469:578–583

Ianni C, Magi E, Soggia F, Rivaro P, Frache R (2010) Trace metal speciation in coastal and off-shore sediments from Ross Sea (Antarctica). Microchem J 96:203–212

Inomata ONK, Montone RC, Lara WH, Weber RR, Toledo HHB (1996) Tissue distribution of organochlorine residues – PCBs and pesticides – in Antarctic penguins. Antarct Sci 8:253–255

Jerez S, Motas M, Benzal J, Diaz J, Barbosa A (2013a) Monitoring trace elements in Antarctic penguin chicks from South Shetland. Mar Pollut Bull 69:67–75

Jerez S, Motas M, Benzal J, Diaz J, Vidal V, D'Amico V, Barbosa A (2013b) Distribution of metals and trace elements in adult and juvenile penguins from the Antarctic Peninsula area. Environ Sci Pollut Res Int 20:3300–3311

Jerez S, Motas M, Palacios MJ, Valera F, Cuervo JJ, Barbosa A (2011) Concentration of trace elements in feathers of three Antarctic penguins: geographical and interspecific differences. Environ Pollut 159:2412–2419

Jiratu P, Gabrielli P, Marteel A, Plane JMC, Planchon FAM, Gauchard PA, Ferrari CP, Boutron CF, Adams FC, Hong S, Cescon P, Barbante C (2009) Atmospheric depletion of mercury over Antarctica during glacial periods. Nat Geosci 2:505–508

Kallenborn R, Breivik K, Eckhardt S, Lunder CR, Manø S, Schlabach M, Stohl A (2013) Long-term monitoring of persistent organic pollutants (POPs) at the Norwegian Troll station in Dronning Maud Land, Antarctica. Atmos Chem Phys Discuss 13:6219–6246

Kallenborn R, Oehme M, Wynn-Williams DD, Schlabach M, Harris J (1998) Ambient air levels and atmospheric long-range transport of persistent organochlorines to Signy Island, Antarctica. Sci Total Environ 220:167–180

Kang J-H, Son M-H, Hur SD, Hong S, Motoyama H, Fukui K, Chang Y-S (2012) Deposition of organochlorine pesticides into the surface snow of East Antarctica. Sci Total Environ 433:290–295

Kennicutt M II, McDonald S, Sericano J (1995) Human contamination of the marine environment - Arthur Harbor and McMurdo Sound, Antarctica. Environ Sci Technol 29:1279–1287

Kim M, Kennicutt MC, Qian Y (2006) Molecular and stable carbon isotopic characterization of PAH contaminants at McMurdo Station, Antarctica. Mar Pollut Bull 52:1585–1590

Klánová J, Matykiewiczová N, Mácka Z, Prosek P, Láska K, Klán P (2008) Persistent organic pollutants in soils and sediments from James Ross Island, Antarctica. Environ Pollut 152:416–423

Köler P (2013) Stulecie zdobycia południowego bieguna ziemi. Kwart Hist Nauki Tech 58:57–75, http://cejsh.icm.edu.pl/cejsh/element/bwmeta1.element.cejsh-11f2d66e-c096-4c87-9b37-327c9f94f8d7. Accessed 29 Oct 2015

Kozak K, Polkowska Ż, Ruman M, Kozioł K, Namieśnik J (2013) Analytical studies on the environmental state of the Svalbard archipelago - critical source of information about anthropogenic global impact. Trends Anal Chem 50:107–126

Krahn MM, Hanson MB, Baird RW, Boyer RH, Burrows DG, Emmons CK, Ford JKB, Jones LL, Noren DP, Ross PS, Schorr GS, Collier TK (2007) Persistent organic pollutants and stable isotopes in biopsy samples (2004/2006) from southern resident killer whales. Mar Pollut Bull 54:1903–1911

Kvenvolden KA, Rapp JB, Golan-Bac M, Hostettler FD (1987) Multiple sources of alkanes in Quaternary oceanic sediment of Antarctica. Org Geochem 11:291–302

Lana NB, Berton P, Covaci A, Ciocco NF, Barrera-Oro E, Atencio A, Altamirano JC (2014) Fingerprint of persistent organic pollutants in tissues of Antarctic notothenioid fish. Sci Tot Environ 499:89–98

Larsson P, Järnmark C, Södergren A (1992) PCBs and chlorinated pesticides in the atmosphere and aquatic organisms of Ross Island, Antarctica. Mar Pollut Bull 25:281–287

Legrand BMR, Delmas RJ (1986) Relative contributions of tropospheric and stratospheric sources to nitrate in Antarctic snow. Tellus 38B:236–249

Legrand M, Angelis M, Delmas RJ (1984) Ion chromatographic determination of common ions at ultratrace levels in Antarctic snow and ice. Anal Chim Acta 156:181–192

Legrand MR, Lorius C, Barkov NI, Petrov VN (1988) Vostok (Antarctica) ice core: atmospheric chemistry changes over the last climatic cycle (160,000 years). Atmos Environ (1967) 22:317–331

Lenihan HS (1992) Benthic marine pollution around McMurdo Station, Antarctica: a summary of findings. Mar Pollut Bull 25:318–323

Li Y, Geng D, Liu F, Wang T, Zhang Q, Jiang H (2012) Study of PCBs and PBDEs in King George Island, Antarctica, using PUF passive air sampling. Atmos Environ 51:140–145

Llorca M, Farré M, Tavano MS, Alonso B, Koremblit G, Barceló D (2012) Fate of a broad spectrum of perfluorinated compounds in soils and biota from Tierra del Fuego and Antarctica. Environ Pollut 163:158–166

Lu Z, Cai M, Wang J, Yang H, He J (2012) Baseline values for metals in soils on Fildes Peninsula, King George Island, Antarctica: the extent of anthropogenic pollution. Environ Monit Assess 184:7013–7021

Luke BG, Johnstone GW, Woehler EJ (1989) Organochlorine pesticides, PCBs and mercury in antarctic and subantarctic seabirds. Chemosphere 19:2007–2021

Ma X, Zhang H, Zhou H, Na G, Wang Z, Chen C, Chen J (2014) Occurrence and gas/particle partitioning of short- and medium-chain chlorinated paraffins in the atmosphere of Fildes Peninsula of Antarctica. Atmos Environ 90:10–15

Machado A, Lima EF, Chemale F Jr, Liz JD, Avila JN (2001) Química mineral de rochas vulcânicas da Península Fildes (Ilha Rei George), Antártica. Revista Brasileira de Geociências 31:299–306 (in Portuguese)

Magi E, Tanwar S (2014) "Extreme Mass Spectrometry": the role of mass spectrometry in the study of the Antarctic Environment. J Mass Spectrom 49:1071–1085

Majer AP, Petti MAV, Corbisier TN, Ribeiro AP, Theophilo CYS, Ferreira PADL, Figueira RCL (2014) Bioaccumulation of potentially toxic trace elements in benthic organisms of Admiralty Bay (King George Island, Antarctica). Mar Pollut Bull 79:321–325

Malcolm HM, Boyd IL, Osborn D, French MC, Freestone P (1994) Trace metals in Antarctic fur seal (Arctocephalus gazella) livers from Bird Island, South Georgia. Mar Pollut Bull 28:375–380

Mão de Ferro A, Mota AM, Canário J (2014) Pathways and speciation of mercury in the environmental compartments of Deception Island, Antarctica. Chemosphere 95:227–233

Mão de Ferro A, Mota AM, Canário J (2013) Sources and transport of As, Cu, Cd and Pb in the environmental compartments of Deception Island, Antarctica. Mar Pollut Bull 77:341–348

Martins CC, Bícego MC, Rose NL, Taniguchi S, Lourenço R, Figueira RCL, Montone RC (2010) Historical record of polycyclic aromatic hydrocarbons (PAHs) and spheroidal carbonaceous particles (SCPs) in marine sediment cores from Admiralty Bay, King George Island, Antarctica. Environ Pollut 158:192–200

Mazzera D, Hayes T, Lowenthal D, Zielinska B (1999) Quantification of polycyclic aromatic hydrocarbons in soil at McMurdo Station, Antarctica. Sci Total Environ 229:65–71

McClurg TP (1984) Trace metals and chlorinated hydrocarbons in Ross seals from Antarctica. Mar Pollut Bull 15:384–389

Merlin OH, Salvador GL, Vitturi LM, Pistolato M, Rampazzo G (1989) Preliminary results on trace element geochemistry of sediments from the Ross Sea, Antarctica. Boll Oceanol Teor Applic 7:97–108

Michelutti N, Blais JM, Mallory ML, Brash J, Thienpont J, Kimpe LE, Douglas MSV, Smol JP (2010) Trophic position influences the efficacy of seabirds as metal biovectors. Proc Natl Acad Sci U S A 107:10543–10548

Montone RC, Taniguchi S, Weber RR (2003) PCBs in the atmosphere of King George Island, Antarctica. Sci Tot Environ 308:167–173

Montone RC, Taniguchi S, Weber RR (2001) Polychlorinated biphenyls in marine sediments of Admiralty Bay, King George Island. Mar Pollut Bull 42:611–614

Montone RC, Weber RR, Taniguchi S (2005) PCBs and chlorinated pesticides (DDTs, HCHs and HCB) in the atmosphere of the southwest Atlantic and Antarctic oceans. Mar Pollut Bull 50:778–782

Moreno JEA, Gerpe MS, Moreno VJ, Vodopivez C (1997) Heavy metals in Antarctic organisms. Polar Biol 17:131–140

Murozumi M, Chow TJ, Patterson C (1969) Chemical concentrations of pollutant lead aerosols, terrestrial dusts and sea salts in Greenland and Antarctic snow strata. Geochim Cosmochim Acta 33:1247–1294

Myers CE, Hatcher RF, Tucker RC, Waugh NS (1980) Environmental assessment of Antarctic research. Environ Sci Technol 14(6):668–672
Negoita TG, Covaci A, Gheorghe A, Schepens P (2003) Distribution of polychlorinated biphenyls (PCBs) and organochlorine pesticides in soils from the East Antarctic coast. J Environ Monit 5:281–286
Negri A, Burns K, Boyle S, Brinkman S, Webster N (2006) Contamination in sediments, bivalves and sponges of McMurdo Sound, Antarctica. Environ Pollut 143:456–476
Nemirovskaya I (2006) Organic compounds in the snow-ice cover of eastern Antarctica. Geochem Int 44:825–834
Neubauer J, Heumann KG (1988) Nitrate trace determinations in snow and firn core samples of ice shelves at the Weddell Sea, Antarctica. Atmos Environ (1967) 22:537–545
Niemistö L, Perttilä M (1995) Trace elements in the Weddell Sea water and sediments in the continental shelf area. Chemosphere 31:3643–3650
Olech M, Kwiatek WM, Dutkiewicz EM (1998) Lead pollution in the Antarctic Region. X-Ray Spectrom 27:232–235
Osyczka P, Dutkiewicz EM, Olech M (2007) Trace elements concentrations in selected moss and lichen species collected within Antarctic research stations. Pol J Ecol 55:39–48
Ouyang X, Leonards P, Legler J, van der Oost R, de Boer J, Lamoree M (2015) Comprehensive two-dimensional liquid chromatography coupled to high resolution time of flight mass spectrometry for chemical characterization of sewage treatment plant effluents. J Chrom A 1380:139–145
Palais JM (1988) Chemical composition of ice containing tephra layers in the Byrd Station ice core, Antarctica. Quatern Res 30:315–330
Peel DA (1975) Organochlorine residues in Antarctic snow. Nature 254:324–325
Peterle TJ (1969) DDT in Antarctic snow. Nature 224:620
Petri G, Zauke CP (1993) Trace metals in crustaceans, in the Antarctic Ocean. Ambio 22:529–536
Planchon FAM, Boutron CF, Barbante C, Wolff EW, Cozzi G, Gaspari V, Cescon P (2001) Ultrasensitive determination of heavy metals at the sub-picogram per gram level in ultraclean Antarctic snow samples by inductively coupled plasma sector field mass spectrometry. Anal Chim Acta 450:193–205
Planchon FAM, Boutron CF, Barbante C, Cozzi G, Gaspari V, Wolff EW, Ferrari CP, Cescon P (2002) Short-term variations in the occurrence of heavy metals in Antarctic snow from Coats Land since the 1920s. Sci Tot Environ 300:129–142
Platt HM, Mackie PR (1980) Distribution and fate of aliphatic and aromatic hydrocarbons in Antarctic fauna and environment. Helgoländer Meeresunters 33:236–245
Płotka J, Tobiszewski M, Sulej AM, Kupska M, Górecki T, Namieśnik J (2013) Green chromatography. J Chrom A 1307:1–20
Poblet A, Andrade S, Scagliola M, Vodopivez C, Curtosi A, Pucci A, Marcovecchio J (1997) The use of epilithic Antarctic lichens (Usnea aurantiacoatra and U. antartica) to determine deposition patterns of heavy metals in the Shetland Islands, Antarctica. Sci Total Environ 207:187–194
Poigner H, Monien P, Monien D, Kriews M, Brumsack HJ, Wilhelms-Dick D, Abele D (2013) Influence of the porewater geochemistry on Fe and Mn assimilation in Laternula elliptica at King George Island (Antarctica). Estuar Coast Shelf Sci 135:285–295
Polar Foundation Information (2014) http://www.polarfoundation.org. Accessed 12 Jan 2014
Ribeiro AP, Figueira RCL, Martins CC, Silva CRA, França EJ, Bícego MC, Mahiques MM, Montone RC (2010) Arsenic, copper and zinc in marine sediments from the proximity of the Brazilian Antarctic base, Admiralty Bay, King George Island, Antarctica. Annual Activity Report 137–140
Ribeiro AP, Figueira RCL, Martins CC, Silva CRA, França EJ, Montone RC (2011) Arsenic and trace metal contents in sediment profiles from the Admiralty Bay. Mar Pollut Bull 62:192–196
Riidlein N, Heumann KG (1995) Size fractionated impactor sampling of aerosol particles over the Atlantic Ocean from Europe to Antarctica as a methodology for source identification of Cd, Pb, Tl, Ni, Cr, and Fe. J Anal Chem 352:748–755

Risebrough RW, Reiche P, Olcott HS (1969) Current progress in the determination of the polychlorinated biphenyls. Bull Environ Contam Toxicol 4:192–201
Risebrough RW, Carmlgnani GM (1972) Chlorinated hydrocarbons in Antarctic birds. In: Parker BC (ed) Proceedings of the colloquium. Conservation problems in Antarctica. Allen Press, Lawrence, KS, pp 63–78
Risebrough RW, Walker W, Schmidt TT, Lappe BW, Connors CW (1976) Transfer of chlorinated biphenyls to Antarctica. Nature 264:738–739
Risebrough RW, Lappe BW, Younghans-Haug C (1990) PCB and PCT contamination in Winter Quarters Bay, Antarctica. Mar Pollut Bull 21:523–529
Santos IR, Silvafilho EV, Schaefer C, Maria S, Silva CA, Gomes V, Passos MJ, Van Ngan P (2006) Baseline mercury and zinc concentrations in terrestrial and coastal organisms of Admiralty Bay, Antarctica. Environ Pollut 140:304–311
Runcie JW, Riddle MJ (2004) Metal concentrations in macroalgae from East Antarctica. Mar Pollut Bull 49:1109–1126
Saigne C, Kirchner S, Legrand M (1987) Ion-chromatographic measurements of ammonium, fluoride, acetate, formate and methanesulphonate ions at very low levels in antarctic ice. Anal Chim Acta 203:11–21
Santos IR, Fávaro DIT, Schaefer CERG, Silva-Filho EV (2007) Sediment geochemistry in coastal maritime Antarctica (Admiralty Bay, King George Island): evidence from rare earths and other elements. Mar Chem 107:464–474
Santos IR, Silva-Filho EV, Schaefer CEGR, Albuquerque-Filho MR, Campos LS (2005) Heavy metal contamination in coastal sediments and soils near the Brazilian Antarctic Station, King George Island. Mar Pollut Bull 50:185–194
SCAR Information (2014) http://www.scar.org/information/. Accessed 13 Feb 2014
Schiavone A, Corsolini S, Borghesi N, Focardi S (2009a) Contamination profiles of selected PCB congeners, chlorinated pesticides, PCDD/Fs in Antarctic fur seal pups and penguin eggs. Chemosphere 76:264–269
Schiavone A, Corsolini S, Kannan K, Tao L, Trivelpiece W, Torrens D Jr, Focardi S (2009b) Perfluorinated contaminants in fur seal pups and penguin eggs from South Shetland, Antarctica. Sci Tot Environ 407:3899–3904
Schiavone A, Kannan K, Horii Y, Focardi S, Corsolini S (2009c) Occurrence of brominated flame retardants, polycyclic musks, and chlorinated naphthalenes in seal blubber from Antarctica: comparison to organochlorines. Mar Pollut Bullet 58:1415–1419
Seeley JV, Seeley SK (2013) Multidimensional gas chromatography: fundamental advances and new applications. Anal Chem 85:557–578
Sen Gupta R, Sarkar A, Kureishey W (1996) PCBs and organochlorine pesticides in krill and water from Antarctica. Deep-Sea Res II 43:119–126
Senthil K, Kannan K, Corsolini S (2002) Polychlorinated dibenzo-p-dioxins, dibenzofurans and polychlorinated biphenyls in polar bear, penguin and south polar skua. Environ Pollut 119:151–161
Siegel SM, Siegel BZ, McMurtry G (1981) Antarctic iron-mercury abundance ratios: evidence for mercury depletion in an active volcanic zone. Water Air Soil Pollut 15:465–469
Smichowski P, Vodopivez C, Muñoz-Olivas R, Gutierrez MA (2006) Monitoring trace elements in selected organs of Antarctic penguin (Pygoscelis adeliae) by plasma-based techniques. Microchem J 82:1–7
Soyol-Erdene T-O, Huh Y, Hong S, Hur SD (2011) A 50-year record of platinum, iridium, and rhodium in Antarctic Snow: volcanic and anthropogenic sources. Environ Sci Technol 45:5929–5935
Sprovieri F, Pirrone N, Hedgecock IM, Stevens RK (2002) Intensive atmospheric mercury measurements at Terra Nova Bay in Antarctica during November and December 2000. J Geophys Res 107:1–9
Stortini AM, Martellini T, Del Bubba M, Lepri L, Capodaglio G, Cincinelli A (2009) N-Alkanes, PAHs and surfactants in the sea surface microlayer and sea water samples of the Gerlache Inlet sea (Antarctica). Microchem J 92:37–43

Subramanian BR, Tanabe S, Hidaka H, Tatsukawa R (1983) DDTs and PCB isomers and congeners in Antarctic Fish. Arch Environ Contam Toxicol 12:621–626

Sun W, Hu C, Weng H, Han Z, Shen C, Pan J (2013) Sources and geographic heterogeneity of trace metals in the sediments of Prydz Bay, East Antarctica. Polar Res 32:1–9

Suttie ED, Wolff EW (1992) Seasonal input of heavy metals to Antarctic snow. Tellus 44B:351–357

Szefer P, Czarnowski W, Pempkowiak J, Holm E (1993) Mercury and major essential elements in seals, penguins, and other representative fauna of the Antarctic. Arch Environ Contam Toxicol 25:422–427

Taniguchi S, Montone RC, Bícego MC, Colabuono FI, Weber RR, Sericano JL (2009) Chlorinated pesticides, polychlorinated biphenyls and polycyclic aromatic hydrocarbons in the fat tissue of seabirds from King George Island, Antarctica. Mar Pollut Bull 58:129–133

Tao L, Kannan K, Kajiwara N, Costa MM, Fillmann G, Takahashi S, Tanabe S (2006) Perfluorooctanesulfonate and related fluoro-chemicals in albatrosses, elephant seals, penguins, and polar skuas from the Southern Ocean. Environ Sci Technol 40:7642–7648

Tartu S, Angelier F, Wingfield JC, Bustamante P, Labadie P, Budzinski H, Chastel O (2015) Corticosterone, prolactin and egg neglect behavior in relation to mercury and legacy POPs in a long-lived Antarctic bird. Sci Tot Environ 505:180–188

Thamban M, Thakur RC (2013) Trace metal concentrations of surface snow from Ingrid Christensen Coast, East Antarctica--spatial variability and possible anthropogenic contributions. Environ Monit Assess 185:2961–2975

Townsend T, Snape I (2008) Multiple Pb sources in marine sediments near the Australian Antarctic Station, Casey. Sci Tot Environ 389:466–474

Trumble SJ, Robinson EM, Noren SR, Usenko S, Davis J, Kanatous SB (2012) Assessment of legacy and emerging persistent organic pollutants in Weddell seal tissue (Leptonychotes weddellii) near McMurdo Sound, Antarctica. Sci Tot Environ 439:275–283

Upreti DK, Pandev V (1994) Heavy metals of Antarctic lichens. 1. Umbilicaria. Feddes Rep 105:197–199

Vallelonga P, Gabrielli P, Balliana E, Wegner A, Delmonte B, Turetta C, Burton G, Vanhaecke F, Rosman KJR, Hongh S, Boutron CF, Cescon P, Barbante C (2010) Lead isotopic compositions in the EPICA Dome C ice core and Southern Hemisphere Potential Source Areas. Quaternary Sci Rev 29:247–255

Vallelonga P, Velde K, Candelone J, Morgan VI, Boutron CF, Rosman KJR (2002) The lead pollution history of Law Dome, Antarctica, from isotopic measurements on ice cores: 1500 AD to 1989 AD. Earth Planet Sci Lett 204:291–306

Van den Brink NW, Riddle MJ, Heuvel-Greve M, Franeker JA (2011) Contrasting time trends of organic contaminants in Antarctic pelagic and benthic food webs. Mar Pollut Bull 62:128–132

Vandal GM, Mason RP, McKnight D, Fitzgerald W (1998) Mercury speciation and distribution in a polar desert lake (Lake Hoare, Antarctica) and two glacial meltwater streams. Sci Total Environ 213:229–237

Vandal GM, Fitzgerald WF, Boutronl CF, Candelone JP (1995) Mercury in ancient ice and recent snow from the Antarctic. In: Ice core studies of global biogeochemical cycle, vol 130. Springer, New York, NY, pp 401–415

Vecchiato M, Argiriadis E, Zambon S, Barbante C, Toscano G, Gambaro A, Piazza R (2015) Persistent Organic Pollutants (POPs) in Antarctica: occurrence in continental and coastal surface snow. Microchem J 119:75–82

Velde K, Vallelonga P, Gaspari V, Cozzi G, Barbante C, Udisti R, Cescon P, Boutron CF (2005) Pb isotope record over one century in snow from Victoria Land, Antarctica. Earth Planet Sci Lett 232:95–108

Venkatesan MI (1988) Organic geochemistry of marine sediments in Antarctic region: marine lipids in McMurdo Sound. Org Geochem 12:13–27

Vodopivez C, Curtosi A, Villaamil E, Smichowski P, Pelletier E, Mac WP (2015) Metals in sediments and soft tissues of the Antarctic clam Laternula elliptica: more evidence as a? possible biomonitor of coastal marine pollution at high latitudes. Sci Tot Environ 502:375–384

Völkening J, Baumann H, Heumann KG (1988) Atmospheric distribution of particulate lead over the Atlantic Ocean from Europe to Antarctica. Atmos Environ (1967) 22:1169–1174
Völkening J, Heumann KG (1988) Determination of heavy metals at the pg/g level in Antarctic snow with DPASV and IDMS. Fresenius' Z Anal Chem 331:174–181
Waheed S, Ahmad S, Rahman A, Qureshi IH (2001) Antarctic marine sediments as fingerprints of pollution migration. J Rad Nucl Chem 250:97–107
Walton DWH, Scarponi G, Cescon P (2001) A scientific framework for environmental monitoring in Antarctica. In: Caroli S, Cescon P, Walton DWH (eds) Environmental contamination in Antarctica. The challenge to analytical chemistry. Elsevier, Amsterdam, pp 33–53
Wania F (1997) Modelling the fate of non-polar organic chemicals in an ageing snow pack. Chemosphere 35:2345–2363
Wania F, Hoff JT, Jia CQ, Mackay D (1998) The effects of snow and ice on the environmental behavior of hydrophobic organic chemicals. Environ Pollut 102:25–41
Wania F, Semkin R, Hoff JT, Mackay D (1999) Modelling the fate of non-polar organic chemicals during the melting of an Arctic snowpack. Hydrol Process 13:2245–2256
Weber K, Goerke H (2003) Persistent organic pollutants (POPs) in antarctic fish: levels, patterns, changes. Chemosphere 53:667–678
Webster J, Webster K, Nelson P, Waterhouse E (2003) The behaviour of residual contaminants at a former station site, Antarctica. Environ Pollut 123:163–179
Witherow RA, Lyons WB (2008) Mercury deposition in a polar desert ecosystem. Environ Sci Technol 42:4710–4716
Wolff EW, Suttie ED, Prrl DA (1999) Antarctic snow record of cadmium, copper, and zinc content during the twentieth century. Atmos Environ 33:1535–1541
Wu Q, Wang X, Zhou Q (2014) Biomonitoring persistent organic pollutants in the atmosphere with mosses: performance and application. Environ Int 66:28–37
Xie Z, Sun L (2008) A 1,800-year record of arsenic concentration in the penguin dropping sediment, Antarctic. Environ Geol 55:1055–1059
Yamamoto Y, Honda K, Hidaka H, Tatsukawa R (1987) Tissue distribution of heavy metals in Weddell seals (Leptonychotes weddellii). Mar Pollut Bull 18:164–169
Yin X, Liu X, Sun L, Zhu R, Xie Z, Wang Y (2006) A 1500-year record of lead, copper, arsenic, cadmium, zinc level in Antarctic seal hairs and sediments. Sci Total Environ 371:252–257
Yogui GT, Sericano JL, Montone RC (2011) Accumulation of semivolatile organic compounds in Antarctic vegetation: a case study of polybrominated diphenyl ethers. Sci Total Environ 409:3902–3908
Yogui GT, Sericano JL (2009) Levels and pattern of polybrominated diphenyl ethers in eggs of Antarctic seabirds: endemic versus migratory species. Environ Pollut 157:975–980
Yogui GT, Sericano JL (2008) Polybrominated diphenyl ether flame retardants in lichens and mosses from King George Island, maritime Antarctica. Chemosphere 73:1589–1593
Yuguang W, Junlin Z (1991) Determination of rare earths and other trace elements in samples of Antarctica by neutron activation analysis. J Rad Nucl Chem 151:345–355
Zhang L, Dickhut R, DeMaster D, Pohl K, Lohmann R (2013) Organochlorine pollutants in Western Antarctic Peninsula sediments and benthic deposit feeders. Environ Sci Technol 47:5643–5651
Zoccolillo L, Amendola L, Cafaro C, Insogna S (2007) Volatile chlorinated hydrocarbons in Antarctic superficial snow sampled during Italian ITASE expeditions. Chemosphere 67:1897–1903

# Important Issues in Ecotoxicological Investigations Using Earthworms

**Mirna Velki and Sandra Ečimović**

## Contents



M. Velki, Ph.D. (✉) • S. Ečimović, Ph.D.
Department of Biology, Josip Juraj Strossmayer University of Osijek,
Cara Hadrijana 8/A, Osijek 31000, Croatia
e-mail: mirna.velki@gmail.com; sandra@biologija.unios.hr



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**Abstract** The importance and beneficial effects of earthworms on soil structure and quality is well-established. In addition, earthworms have proved to be important model organisms for investigation of pollutant effects on soil ecosystems. In ecotoxicological investigations effects of various pollutants on earthworms were assessed. But some important issues regarding the effects of pollutants on earthworms still need to be comprehensively addressed. In this review several issues relevant to soil ecotoxicological investigations using earthworms are emphasized and guidelines that should be adopted in ecotoxicological investigations using earthworms are given. The inclusion of these guidelines in ecotoxicological studies will contribute to the better quantification of impacts of pollutants and will allow more accurate prediction of the real field effects of pollutants to earthworms.

**Keywords** Ecotoxicology • Earthworms • Soil ecosystems • Risk assessment • Biomarker responses • Toxic effects • Pollutants • Pollutant mixtures • Hormesis • Microcosmic systems • Experimental conditions • Temperature change

## 1 Introduction

Earthworms beneficially affect the soil structure and quality and consequently play a significant role in the functioning of the soil ecosystems. Also, earthworms are important model organisms in soil ecotoxicological investigations. They have been used as model organisms for assessment of adverse effects of various pollutants. However, some important issues regarding the effects of pollutants on earthworms require attention and further in-depth investigation. This review gives emphasize on several issues in earthworm ecotoxicology that are of essential importance for soil ecotoxicological investigations and risk assessment but are poorly explored and understood to date. Precisely, the importance of assessment of following issues in earthworm ecotoxicology is discussed—the linkage of responses at different levels of biological complexity, the assessment of the effects of pollutant mixtures, the occurrence and detection of the hormetic effect, the necessity of inclusion of microcosmic systems in ecotoxicological investigations and the possible effects of exposure temperature on the strength of toxic effects of pollutants. By addressing these issues it will be possible to gain a more in-depth understanding of the effects of pollutants on earthworms and soil ecosystem, as well as to improve the assessment of environmental risks of soil pollutants.

## 2 Role of Earthworms in Soil Ecosystems

The role and the importance of earthworms in the functioning of soil ecosystems is well-established. Earthworms can represent a major fraction of the soil invertebrate biomass (>80 %) and are considered as ecosystem engineers in many terrestrial ecosystems (Lee 1985; Edwards and Bohlen 1996). Earthworms play an important role in numerous soil processes and are regarded as useful indicators of soil health and quality (Edwards 2004). Many studies investigated the interactions of earthworms with soil physical conditions, with plants, with soil microorganisms and with other soil invertebrates. These studies demonstrated that earthworms impact the soil physical properties and structure, cause changes in nutrient availability and soil respiration, affect the biomass and composition of soil microorganisms, density of other soil invertebrates, composition of plant communities and aboveground food webs mainly due to their activities (Abbott and Parker 1981; Martin 1982; Doube et al. 1994; Bohlen and Edwards 1995; Fraser et al. 2003; Wurst et al. 2003; Eisenhauer et al. 2007, 2009, 2010; Boyer et al. 2013; Doan et al. 2013; etc.). The burrowing activities of earthworms cause changes in the soil structure and earthworms have important function in soil formation—they consume organic matter, fragment it, mix it with soil mineral particles and form water-stable aggregates (Edwards 2004). In addition, they play a role in decomposition, mineralization processes and in carbon storage or protection from decomposition in stable aggregates (Brown et al. 2000). The stability of aggregates is used as an indicator of soil structure (Six et al. 2000) and is a key factor for physical soil fertility (Abiven et al. 2009).

Besides their immense role in soil functioning, earthworms are important for the investigation of pollutant effects on soil ecosystems. Earthworms are continuously exposed to pollutants present in the soil (via ingestion and passive absorption through their skin) and are suitable species for ecotoxicological assessment of soil pollution (e.g. Reinecke and Reinecke 2004; Sanchez-Hernandez 2006; Zhou et al. 2007; Schreck et al. 2008; Hirano and Tamae 2011; Lionetto et al. 2012). In addition to the beneficial effects on soil functioning and common usage as model organisms in ecotoxicological investigations, it has been shown that earthworms act as promoters of soil enzyme activities (Tao et al. 2009; Jusselme et al. 2013; Sanchez-Hernandez et al. 2014). Since it was demonstrated that earthworms also increase activities of pesticide-detoxifying esterases in soil, the presence of earthworms could have direct benefit for pesticide bioremediation (Sanchez-Hernandez et al. 2014). This indicates that the presence of earthworms can affect the concentration of pollutants, i.e. earthworms can contribute to the reduction of pollutant concentrations in soil and thus may play a role in decreasing the negative effects of pollutants on soil ecosystems. Although more research is needed on this subject, this study shows that earthworms have potential to act as pesticide scavengers and reduce the concentration of pesticides in soil so their presence in agro-ecosystems is highly desirable.

Earthworms also have important roles in maintaining soil quality and in promoting the ecological functioning of the agro-ecosystems, so the reduction in earthworm populations might in different ways negatively affect the soil functioning. Taking this into account, and considering that soil and crop management practices can influence many soil properties that affect earthworms, such as effects of tillage practices to earthworms (e.g. Chan 2001; Birkás et al. 2004; Riley et al. 2008; Ernst and Emmerling 2009; Crittenden et al. 2014; Pelosi et al. 2014), wider adoption of methods that have less negative influence on earthworm biomass and biodiversity should be taken into consideration. Generally, it is advisable to strive towards preservation of earthworm populations in agricultural areas and to implement appropriate soil ecosystem management practices favoring earthworms.

## 3 Advances in Earthworm Ecotoxicology

The most important topics of ecotoxicological studies include investigation of the exposure routes, distribution, transport and accumulation of pollutants in the ecosystem and its compartments; uptake, transformation and elimination of pollutants in the environment and the evaluation of the qualitative and quantitative effects of pollutants on living organisms at all levels of ecosystem organization. Conduction of ecotoxicological studies is of great importance since it provides data useful for the risk assessment. Assessment of environmental risks of soil pollutants is particularly important as an integral part of the overall protection of the soil ecosystems, and is a necessary part of the legislation and all forms of regulations whose ultimate purpose is environmental safety.

Developments in soil ecotoxicology started with observations of pesticide effects on soil invertebrates in the 1960s (van Gestel 2012). Due to their characteristics and lifestyle, earthworms are being commonly used in standardized toxicity tests, as well as model organisms in ecotoxicological studies. The field of ecotoxicological investigations with usage of earthworms as model organisms has undergone a significant progress. From the first standardized test with earthworms (OECD 1984) to the present, there has been a significant shift—from measurement of mortality as only end-point, to measurement of a battery of biomarkers, i.e. monitoring changes at molecular and biochemical level, detection of histological changes, observation of behavioral changes and monitoring changes at the levels of populations and communities. Also, along with the usage of standardized toxicity tests, the application of model microcosmic systems, which enable more realistic conditions of earthworm exposure to pollutants, is gradually increasing (Reinecke and Reinecke 2007; Santos et al. 2011a, b; Wu et al. 2012; Velki et al. 2014; etc.). In addition, besides the usage of *Eisenia fetida* and *Eisenia andrei*, commonly used species in laboratory experiments that are usually ecologically not relevant in the environment, the importance and necessity of usage of other earthworm species has been recognized and effects of pollutants to earthworm

species from all ecological categories (epigeic, endogeic and anecic) are being investigated (LaCourse et al. 2009; van Gestel et al. 2009; Ellis et al. 2010; Tripathi et al. 2010a, b; Vejares et al. 2010; Calisi et al. 2011; Dittbrenner et al. 2011; Kılıç 2011; Klobučar et al. 2011; Velki and Hackenberger 2012, 2013a; Calisi et al. 2013; Leveque et al. 2013; Giska et al. 2014; Velki et al. 2014; etc.).

The effects of various chemical pollutants on earthworms were often the subject of research. Effects of pesticides (e.g. Venkateswara Rao and Kavitha 2004; Capowiez et al. 2010), polyaromatic hydrocarbons (e.g. Brown et al. 2004), metals (e.g. Morgan et al. 2004; Calisi et al. 2013), etc. were assessed, but there is still a large number of uninvestigated substances. Also, some very important aspects of the effects of pollutants on earthworms require further investigation. For example, in case of investigation of the effects of pesticides on earthworms, there are knowledge gaps linked to the lack of representativeness in terms of investigated pesticides and earthworm species (studies on effects of pesticides that are currently being used on earthworm species actually present in the environment are needed), and lack of studies conducted under realistic conditions in terms of soil, pesticide dose and experimental duration (Pelosi et al. 2013). Velki et al. (2014) addressed all of the current knowledge gaps. In addition, most studies are conducted only under laboratory conditions so it is essential to develop and apply tests which will more resemble the conditions in the environment (addressed in detail in Chap. 6). More recently, the usage of omics methods (e.g. Jones et al. 2008) for the toxicity assessment and measuring the effects of emerging pollutants in earthworms, especially nanoparticles and nanomaterials (Hu et al. 2010, 2014; Heckmann et al. 2011; Hooper et al. 2011; Shoults-Wilson et al. 2011a, b; El-Temsah and Joner 2012; Tsyusko et al. 2012; Hayashi et al. 2013), provided new aspects of toxicant effects on earthworms. The assessment of the effects of these pollutants on soil ecosystems is mainly in the initial stage. Ultimately it will be necessary to assess their long-term effects on earthworms at all levels of biological organization. In this context, the further application of omics approach and development of adequate protocols will certainly be a compulsory part of the risk assessment of these pollutants.

## 4 Biomarker Responses and Issue of Linkage to Higher Level Responses

### *4.1 Biomarkers*

The risk assessment of soil pollution cannot be based solely on the chemical analysis of pollutants present in the soil (Sanchez-Hernandez 2006). The monitoring of the type and quantity of pollutants that enter into the soil is extremely consuming due to the complexity and costs resulting from the identification of such chemical substances. Since pollutants can be present in soil at concentrations below the detection limit of the analytical techniques, it is sometimes not possible

to determine their exact concentration. In addition, various factors (such as bioavailability and biomagnification) affect the overall toxicity of pollutant. Consequently, only from the data about the pollutant concentration it is not possible to accurately assess whether the pollutant will have measurable effects on soil ecosystems. So in order to assess the impact of pollutants, it is necessary to determine the direct effects of pollutants (i.e. its bioavailable fraction) on organisms and this is possible by measuring biomarkers. The term biomarker represents a measurable biological response of an organism to pollutant exposure and/or the effects of pollutants on the organism (Kurelec 1998). Biomarkers can be classified as markers of exposure, effects, and susceptibility (WHO 2001) and can be measured at molecular, biochemical, cellular, or physiological levels of biological organization (Ricketts et al. 2003). The utilization of biomarkers is of great importance for the risk assessment because changes detected at lower levels of biological organization can serve as a sensitive and early indicators of possible effects at higher levels of biological organization (Spurgeon et al. 2005), and can provide information about the mode of action of pollutants (Kammenga et al. 2000). The application of biomarkers as tools for evaluation of the effects of pollution is becoming more common and some biomarkers are already included in environmental monitoring programs.

## *4.2 Changes at Different Levels of Biological Organization*

For effective protection of ecological systems it is necessary to promptly detect the occurrence of changes. Since the probability of the repair of the ecosystem decreases with time after the entrance of a pollutant into the system, early detection of biological effects at lower levels of biological organization (molecules, cells, tissues) allows identification of changes and effective action in terms of reparation of higher biological levels (population, ecosystem). Changes at molecular level represent the earliest response of an organism to pollutant exposure and measurement of molecular biomarkers enables the assessment of impact of bioavailable fractions of pollutants, determination of the direct effects of pollutants and identification of interactions between pollutants and organisms (Sarkar et al. 2006). On the other hand, changes at the population level have much higher ecological relevance compared to changes at lower levels, but may be detected only a long period after the exposure when the probability of system repair is very small. So it is clearly evident that there is a need for establishment of links between responses at lower and higher levels in order to enable early detection of changes and at the same time to predict changes that will occur later at higher levels of biological organization. Currently, there is a lack of knowledge on the interconnection of the early biological responses with chemical exposure to ecological responses at the population and community level (Ankley et al. 2010).

### 4.3 *Establishing the Link Between Responses at Different Levels of Biological Complexity*

Studies conducted on effects of different pollutants showed that earthworms are impacted by pollutants at all organizational levels. For earthworms, a wide range of biomarkers have been developed such as monitoring of reproductive output, histopathological alterations, behavioral changes, changes in enzyme activities, gene expression, etc. And although there are numerous studies assessing effects of various pollutants on earthworms by measuring end-points at different levels, only few attempted to establish a link between these responses. Rodríguez-Castellanos and Sanchez-Hernandez (2007) proposed the inhibition of acetylcholinesterase (AChE) activity and carboxylesterase (CES) activity as potential biomarkers of pesticide toxicity at behavioral and reproductive levels. The inhibition of AChE activity was proposed as a biomarker directly implicated in behavior perturbation and the relationship between AChE inhibition and behavior perturbation has been investigated in invertebrates and vertebrates. Earthworm body wall muscles represent vertebrate-like cholinergic neuromuscular junctions (Rosenbluth 1972) which contain the enzyme AChE for regulating the synaptic transmission, and the correlation between inhibition of muscle AChE activity by anti-ChE pesticides and perturbation in locomotor activity has been demonstrated in the study of Gupta and Sundararaman (1991). The activity of CES was proposed as a biomarker that could be related to reproductive fitness. CES over-expression is a common feature in the male reproductive system of organisms as dissimilar as rodents, bivalve molluscs and insects, so Mikhailov and Torrado (1999) suggested that CES activity levels in the male reproductive system could be a determinant in the local protective mechanism for sperm differentiation and maturation against pesticides. Many studies showed that pesticides currently used in agriculture are able to cause reproductive toxicity in earthworms, and the toxic effects on the reproductive system could be correlated to CES activity levels in this tissue. More investigations are needed to enable establishment of link between changes at molecular or biochemical level and changes at higher levels.

In most studies the issue of establishing a direct link between sub-individual biomarkers and adverse effects at individual or population level was a secondary objective of research. Future studies should focus particularly on this issue and endeavor to design the experiment with the main aim of establishing these links. For instance, one of the aims could include the determination of the linkage of AChE inhibition not only to changes in behavior, but also to changes in population parameters through changes in feeding activity or predation susceptibility (e.g. inhibition of AChE activity in earthworms can cause perturbations in locomotor activity which could lead to altered feeding and increased predation) (Fig. 1). Establishing the link between low and high levels responses in earthworms is of great importance for soil risk assessment since it will enable to predict effects of pollutants on earthworm populations based on measurements of early earthworm responses, i.e. molecular or biochemical biomarkers.

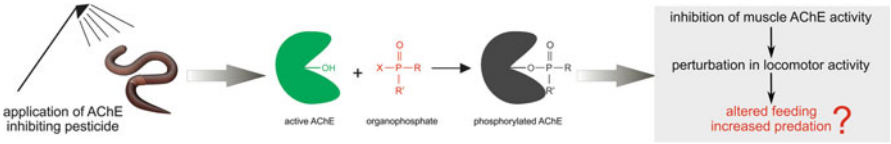


**Fig. 1** Inhibition of acetylcholinesterase (AChE) activity leads to perturbation in locomotor activity and possibly to changes in population parameters through changes in feeding activity or predation susceptibility

## 5 Effects of Mixtures

### *5.1 Environmental Pollutants as Mixtures*

It is generally acknowledged that environmental pollutants exist as mixtures. Of course, the investigation of effects of mixtures is more demanding and challenging compared to effects of single compounds, especially in soil systems that are very complex. Due to occurrence of pollutant mixtures in the soil, the interactions between compounds of the mixtures and the effects of mixtures on soil components, it is of immense importance to assess the pollutant mixture effects. Spurgeon et al. (2010) provided a framework for investigation of mixture effects which highlights the importance of processes involved in determining external exposure, toxicokinetics and toxicodynamics.

The effects of mixtures and the responses of the organisms are consequences of biological activity, bioavailability, characteristics of biochemical processes in organisms and possible interactions of the components in the mixture. Interactions between pollutants in a mixture can occur at different levels and finally lead to higher or lower toxicity compared to the individual compounds. In the soil, a pollutant may affect the level of binding of another pollutant and change its availability to organisms. In organisms, a pollutant may change the detoxification process of another pollutant and therefore affect its toxicity. Consequently, the results obtained from assessment of single compound effects may lead to inaccurate estimation of the effects of pollutant mixtures present in the environment.

### *5.2 Effects of Mixtures on Earthworms*

Effects of pollutant mixtures on earthworms have been investigated (Lydy and Linck 2003; Schreck et al. 2008; Gomez-Eyles et al. 2009; Zhou et al. 2011; Belmeskine et al. 2012; Stepić et al. 2013a, b; Wang et al. 2015; etc.) and different interactions between mixture compounds—e.g. additivity, synergism, antagonism—have been identified (Fig. 2). However, these studies were performed only under laboratory conditions and there is a lack of studies investigating the effects of mixtures of earthworms in terms of realistic environment.

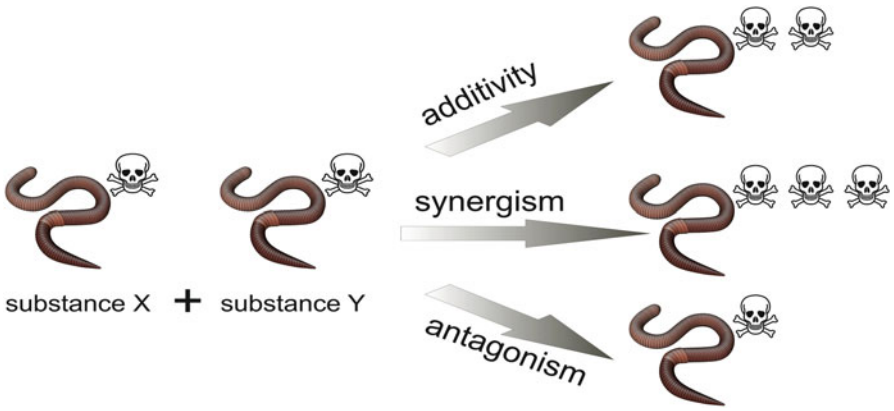


**Fig. 2** Interactions between mixture compounds and changes in toxicity

Recently Schnug et al. (2014, 2015) investigated effects of three biocides using a soil multi-species test system and applying biocides individually and as a mixture on an earthworm community in the field. The results of these studies emphasize the importance of combining structural and functional responses, as well as different life-stages of multiple species, and imply that simple laboratory studies and more complex field and/or semi-field studies may complement one another in the risk assessment process.

## *5.3 Assessment of Effects of Mixtures*

Current practices consider only the effects of single compounds (and mostly under controlled conditions), but for the soil risk assessment it is required to also address the mixture effects. Since it has been already demonstrated that due to synergistic interactions or potentiation effects mixtures can have increased toxicity to earthworms, there is an urgent need for assessment of mixture effects to earthworms. The number of studies investigating effects of mixtures on earthworms is low and a first prerequisite is to increase the number of studies dealing with issue. Secondly, it is necessary to increase the investigations of effects of pollutant mixtures to earthworms under environmentally relevant conditions (in terms of exposure methods, selection of mixture compounds, concentration, duration of exposure) and integrate the obtained data with data obtained using laboratory toxicity tests.

Besides the application of environmentally relevant tests, the aforementioned framework should be also implemented since insight on toxicokinetics and toxicodynamics will provide a better understanding of the mechanisms of interactions. Gaining knowledge on the mechanisms of interactions between compounds in the mixture would enable better prediction of its effects. This is particularly

important in the case of mixtures with different types of pollutants (e.g. mixture of pesticide and metal), as well as in the case of more complex mixtures where several compounds are present, e.g. ternary and quaternary mixtures. For example, Schnug et al. (2013) investigated the toxicity of a ternary biocide mixture to the reproduction and adult survival of two consecutive generations of earthworms and emphasized the need for more advanced mixture toxicity prediction models that consider degradation kinetics and changes in toxic effects over time.

When risk assessment of mixtures is required, testing every possible mixture combination to determine interaction and derive actual joint effects is impossible, and the prediction of the effects of mixtures is a challenging task for researchers. From the data obtained in the studies conducted so far it is not possible to make a general prediction on the effects of new untested mixtures. One of the possibilities to reduce the number of combinations to be tested is to determine the "realistic mixtures" i.e. to focus on the pollutants that actually pose a risk and determine the combinations and concentrations of pollutants that can realistically be found in the environment. After selecting and testing the mixtures of interest, different strategies can be used for analyzing of obtained data, as well as for prediction of cases with interactions between compounds. One possibility is to use mechanistic approaches, such as physiological-based pharmacokinetic modeling, to predict cases where interaction may be expected (Cahill et al. 2003). Also, Jonker et al. (2005) described a framework for analyzing patterns in the data and significance testing of statistical interactions (i.e. deviations from some standard model). This approach may be useful as a first step, but the descriptive nature precludes a mechanistic interpretation of the results, and therefore does not provide a better understanding of mixture toxicity (Jager et al. 2010). We share the opinion that understanding the effects of mixtures cannot be achieved by descriptive methods, but requires a biology-based approach for sublethal endpoints. Biology-based models are effective tools in estimating and managing ecological risks (e.g. Pastorok et al. 2003) and Jager et al. (2010) proposed biology-based mixture analysis for sublethal effects which considers toxicokinetics (going from external concentration to target site) and toxicodynamics (going from target site to effects on specific endpoints). Although more data has to analyzed, this approach seems to be promising in mixture ecotoxicity.

Assessment of mixture effects is extremely complex and demands additional experimental investigations and development of tools that will be able, based on the mechanism of action and identification and structure elucidation, to give insight into the possible interactions between mixture compounds. By knowing the interactions between mixture compounds, as well as toxicokinetics and toxicodynamics of particular compounds, the use of compounds that are known to cause (or are anticipated to cause) a substantial increase in overall toxicity could be avoided. Also, improvement of existing and development of new assessment tools (e.g. prediction models) will contribute to quantifying pollutant mixture effects and reducing the uncertainties in current soil risk assessment arising from considering only the single compound effects.

# 6 Occurrence of Hormetic Effect

## *6.1 Hormesis*

Pollutants in the environment are most commonly present at very low concentrations. However, effects of pollutants are usually investigated only at effect levels, whereas effects of concentrations below the predicted no-effect-concentrations often remain unknown. Although for long time it was considered that these sub-effective concentrations of toxic substances have no effect on organisms, today it is well-known that such concentrations of toxic substances can lead to the opposite effect than effect caused by the higher concentrations, i.e. to the appearance of hormetic effect (Calabrese and Baldwin 2002; Calabrese 2008) (Fig. 3). The hormetic dose response is often described as either an inverted U- or J-shaped dose response, depending on the end-point measured, but it is best described as a dose-time-response, in which there is an initial disruption of homeostasis (i.e. toxicity) followed by a modest overcompensation response which eventually leads to a re-establishment of homeostasis (Calabrese 2003). Previous studies have shown that this effect, i.e. hormetic dose-response model, in toxicology is much more common than the threshold model (Calabrese and Baldwin 2003). Therefore, when investigating effects of pollutants, it is particularly important to also test the sub-effective concentrations (i.e. hormetic concentrations) and to determine the possibility of occurrence of hormesis.

## *6.2 Hormetic Effect in Earthworms*

Regarding the investigations on earthworms, a hormetic effect was recorded in several studies after exposure to different pollutants. Using standardized toxicity tests organophosphate pesticides caused a hormetic effect on AChE and CES

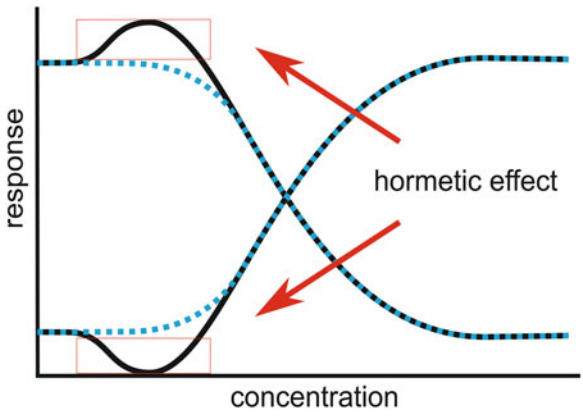


**Fig. 3** Hormetic effect—opposite effect of low and high concentrations

activity (Hackenberger et al. 2008; Velki and Hackenberger 2012, 2013b); formalin caused a hormetic effect on AChE activity (Hackenberger et al. 2012); cadmium caused a hormetic effect on superoxide dismutase (SOD) and catalase (CAT) activity (Zhang et al. 2009) and on CYP3A4 activity (Cao et al. 2012); phenylpryazole and neonicotinoid insecticide caused a hormetic effect on reduction of biomass (Alves et al. 2013). Regarding the hormetic response detection under environmentally relevant conditions, in the study of Łaszczyca et al. (2004) earthworms were sampled in the environment and biphasic (but statistically insignificant) responses of AChE, CES and CAT activities in earthworms from zinc, lead and cadmium polluted areas were recorded, whereas Velki et al. (2014) recorded a hormetic effect of organophosphate pesticides on AChE (and CES) activity using soil microcosmic system. The occurrence of hormesis demonstrates an overcompensation response of the organism elicited by exposure to low concentrations of pollutants (Calabrese and Baldwin 2003). Detection of a hormetic effect in microcosmic systems is of great importance for future ecotoxicological research and biomonitoring studies since in realistic soil environments pollutants are found in low concentrations that could potentially cause occurrence of hormetic effect. Also, in environmental biomonitoring, the hormetic effect can theoretically be anticipated as a marker of exposure to sub-effective concentrations (for example, in case of detection of effect opposite to the expected an exposure to sub-effective concentrations of pollutants and occurrence of hormetic effect may be suspected).

## *6.3 Hormetic Effect in Ecotoxicological Investigations*

Considering that the possibility of occurrence of hormesis in earthworms has been established, when earthworms are used for ecotoxicological parameters research, models that include hormetic effect should be taken into account. Although hormetic effects in earthworms after exposure to different pollutants has been recorded, the occurrence of hormesis in earthworms is generally poorly studied. Due to the potential significance of the hormetic effect in ecological risk assessment, the occurrence and the role of this phenomenon in earthworms should be thoroughly investigated. As pointed out by Calabrese (2003) the concept of hormesis changes the way of thinking about risk assessment. Namely, hormesis argues that there are meaningful biological effects below the toxicological no observed adverse effect level (NOAEL). So there is a challenge to use appropriate experimental designs and endpoints measured that will be able to detect and appropriately interpret the responses below NOAEL.

Although sometimes hormesis is characterized as positive or beneficial effect of low concentrations of some substances, however, this is not correct—hormetic effect is a response characterized by opposite effects of low and high concentrations. As reviewed by Calabrese and Baldwin (2003), in the context of dose-response studies it is difficult to determine the concept of a beneficial effect. Biological systems have a high complexity and beneficial effects are often seen with reference

to a specific and relative setting. So what may be beneficial at the individual level due to low-dose exposures may be harmful at population level, e.g. longevity may be enhanced at low doses but at the expense of fecundity. In case of earthworms, it was determined that different organophosphate pesticides cause a hormetic effect on AChE activity, i.e. exposure to low concentrations cause an increase in AChE activity, whereas exposure to high concentrations cause inhibition of AChE activity (Hackenberger et al. 2008; Velki and Hackenberger 2012, 2013b; Velki et al. 2014). Although it is clear that inhibition of AChE activity negatively affects earthworms due to consequent impairment in synaptic transmission, it is not known whether the increase in AChE activity caused by low doses in the long-term will be positive for earthworms. For example, it is possible that the increase in AChE activity will lead to consumption of more energy and in long-term sense it could adversely affect earthworm growth. So in order to determine the overall effect of pollutants it is essential to assess effects of sub-effective concentrations of pollutants on earthworms. This includes the determination of the mechanism of action and changes at molecular, biochemical and physiological level, as well as determination of changes occurring at higher levels up to the level of earthworm populations.

Therefore, for the proper risk assessment it is necessary to include the investigation of the effects of sub-effective concentrations of pollutants at different levels of biological organization, as well as the chronic exposure to these concentrations in order to determine the long-term effects of such concentrations on earthworms. This means that in ecotoxicological testing it is not sufficient to assess only the effects of predicted or measured effective concentrations (which has so far been the most common case), yet it is required to include the assessment of sub-effective concentrations. Taking hormesis into account will certainly lead to reconsideration of testing results of some pollutants that were regarded as non-harmful due to presence in low concentrations in the environment. Also, as previously mentioned, pollutants in the environment exist as mixtures and it is crucial to investigate the possibility of hormetic effects of mixtures on responses of earthworms in the environment in order to adequately assess the risk posed to earthworms, as well as to other soil organisms.

# 7 Inclusion of Microcosmic Systems in Ecotoxicological Investigations

## *7.1 Characteristics of Soil Microcosm*

A soil microcosm (Fig. 4) is a system that consists of a certain amount of soil with several species of organisms which make up a significant component of soil biocenosis and are characteristic for the area from which the soil originates. A soil microcosm serves for the assessment of pollutant effects at different levels of the biological organization (Burrows and Edwards 2002). The soil for the microcosm can be prepared by various methods (sieving, sterilization, mixing,

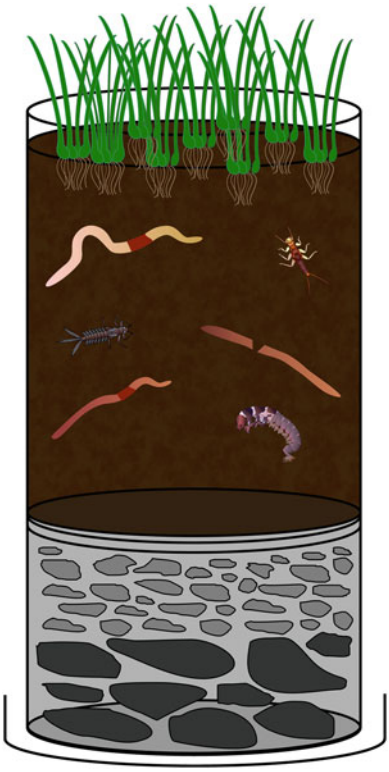

**Fig. 4** Schematic representation of soil microcosmic system

etc.) or can be transferred intact from the environment into the laboratory. The main advantage of applying microcosmic systems in ecotoxicological studies, compared to the classic toxicological tests, is the assessment of pollutant effects under conditions close to environmental conditions and consequently the reduction of the possibility of an inaccurate estimation of the pollutant's adverse effects.

In ecotoxicological studies using earthworms as model organisms, the advantage of application of microcosms is the possibility of usage of earthworm species belonging to all ecological categories (epigeic, endogeic and anecic). Because soil microcosms provide conditions necessary for normal activities and behavior of all earthworm species (e.g. vertical depth of soil column necessary for anecic species), it is possible to simultaneously expose earthworm species from different ecological categories and assess their susceptibility to pollutant exposure. This is of immense importance since it was determined that species belonging to different ecological category may have significantly different sensitivities to particular pollutants (e.g. Ma and Bodt 1993; Langdon et al. 2005; Robidoux et al. 2004; Lukkari et al. 2005; Velki and Hackenberger 2012; Velki et al. 2014). Also, it is known that pollutants in the environment are not homogeneously distributed in the soil, so the exposure of an organism depends on its position in the soil. Unlike in standardized toxicity tests where test substances are homogeneously distributed

at/in the exposure medium, in the microcosm the test substance is applied at a surface. The concentration of test substance in the microcosm differs in different layers of soil and depends on its physical and chemical properties. Consequently, in the microcosmic system, just as in the environment, exposure of earthworms will depend on their location in the soil, i.e. the ecological category they belong to. But although soil microcosms provide advantages compared to standardized laboratory tests, it is important to emphasize that soil microcosmic systems are still artificial systems and not real ecosystems. Although they give a more realistic data about pollutant effects on earthworms in the environment compared to standardized toxicity tests, it must be taken into account that the generalization of the results obtained in soil microcosmic systems to real soil ecosystems is limited.

## *7.2 Soil Microcosm in Ecotoxicological Studies*

Soil microcosms have been applied for the assessment of adverse effects of different pollutants on earthworms. Santos et al. (2011a, b) investigated the effects of insecticides, herbicides and acaricides on the growth reduction and biomass of earthworms, whereas Burrows and Edwards (2002) investigated effects of fungicides on earthworm biomass. Adverse effects of organophosphate insecticides on biomarker responses of earthworms were determined in studies of Reinecke and Reinecke (2007) and Velki et al. (2014). Microcosmic systems were also used for investigation of the effects of metals (Wu et al. 2012), volatile organic compounds (An 2005) and polycyclic aromatic hydrocarbons (Bogomolov et al. 1996) on earthworms. Looking at the total number of studies focusing on the effects pollutants on earthworms, the application of the soil microcosm is just in its initial stage. Due to the above mentioned characteristics of soil microcosms and their advantages compared to standardized laboratory tests, it is necessary to include the usage of soil microcosms in the assessment of the adverse effects of known pollutants, and especially in the assessment of adverse effects of emerging pollutants.

Application of microcosmic systems in soil ecotoxicological research provides significant advantages compared to standardized toxicity tests, such as realistic distribution of pollutants in the soil, simultaneous monitoring of changes at the different levels of biological organization (e.g. measurement of biomarker responses and monitoring of behavior), etc., thus enabling the implementation of experiments under environmentally more relevant conditions. It is certainly important to stress out that soil microcosmic systems are laboratory model systems, rather than ecosystems, and therefore the conditions in the microcosm are by no means identical to environmental conditions. The biological complexity of soil microcosms is lower compared to that in the real environment, but the usage of soil microcosm is still recommended since it shares some common features with real ecosystems and provides rapid testing under conditions close to the conditions of

the realistic environment. Future ecotoxicological studies should aim to improve and optimize the usage of soil microcosms in terms of increasing its biological complexity and aiming at developing systems with greater capabilities of generalization and extrapolation of the results to the situation in the environment. This could be done, for example, by including several trophic levels in a soil microcosm and assessing the effects of pollutants not only to earthworms, but also to other components of the soil ecosystem (e.g. microorganisms, other invertebrates, plants) in order to obtain broader insight into the overall impact of pollutants. Therefore, the application of such microcosmics system should be an integral part of the soil ecotoxicological studies since the obtained results can contribute to the quantification of the impact of pollutants on the environment and increase the predictive power of such studies for the soil risk assessment.

# 8 Effects of Temperature Change on Toxic Effects of Pollutants and Biomarker Responses in Earthworms

## *8.1 Effects of Temperature Change*

Organisms in the environment have to cope with environmental fluctuations of different abiotic factors. Many of them have developed a number of adaptations (biochemical and molecular mechanisms, behavioral changes, etc.) that enable continuous adjustment to fluctuating environmental conditions. Regarding the abiotic factors, temperature is one of the most important regulatory factors in ecotoxicology. In ectotherms, the environmental temperature affects the physiological and biochemical processes, and changes in temperature can act as a stressor and lead to changes in the physiological status of the organism. Previous studies have shown that changes in temperature can affect the behavior of earthworms, lead to changes in survival, growth, development and cause changes in metabolic enzymes (e.g. Presley et al. 1996; Fayolle et al. 1997; Wever et al. 2001; Perreault and Whalen 2006; Tripathi et al. 2011). So it is very likely that changes in temperatures will affect the enzymatic processes that determine the metabolism and detoxification of pollutants. In addition to the biotic component, temperature changes can affect the fate and transport of pollutants in the environment. For example, degradation of pesticides is slow at lower temperatures and faster at higher temperatures (e.g. Pal et al. 2006), leading to different stability and retention in the environment which can affect the pesticide toxicity. It is obvious that changes in temperatures at which earthworms are exposed to pollutants in the environment can ultimately lead to changes in the strength of the toxic effect (Fig. 5).

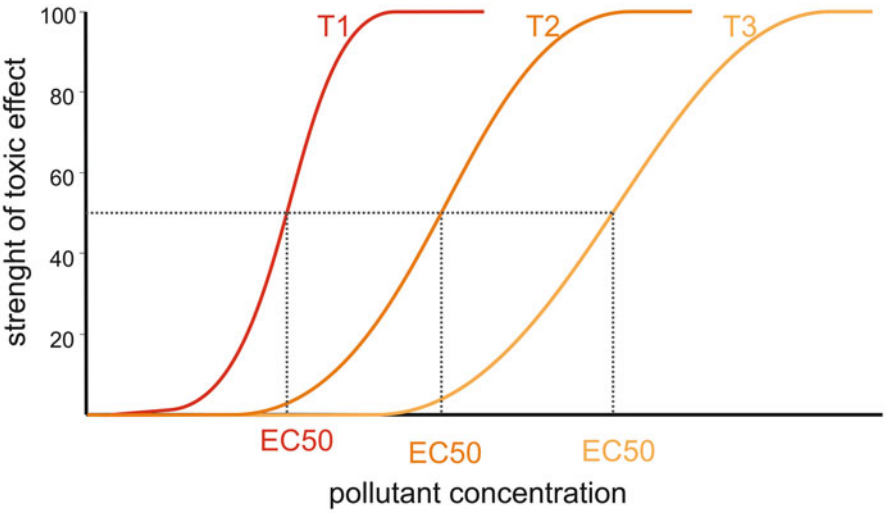


**Fig. 5** Changes in temperature may lead to changes in the strength of the toxic effects of pollutants

## *8.2 Interactions Between Temperature Change and Pollutant Toxicity to Earthworms*

Holmstrup et al. (2010) provided a comprehensive review on the interactions between effects of environmental chemicals and natural stressors, including the interactions between effects of temperature stress and chemicals in different organisms. Regarding the earthworms, in many studies effects of various pollutants on earthworms have been assessed (see Sect. 3); however, there is a smaller number of studies investigating the effects of pollutants under different (stressful) temperatures and the data on the impact of exposure temperature on the final effects of pollutants and biomarker responses of earthworms are scarce. In case of the effects of temperature on metal toxicity to earthworms, Khan et al. (2007) found that an increase in temperature caused an increase in the toxicity of metals Pb, Cu and Zn to *Lumbricus terrestris*. They hypothesized that the increase in toxicity at higher temperatures may be due to limiting the scope of aerobic metabolism (oxygen extraction, transport, and utilization) via quantitative and qualitative effects on hemoglobin. Svendsen et al. (2007) investigated the short-term survival, reproduction and physiological responses of *Lumbricus rubellus* exposed to metal contaminated field soils under different laboratory temperatures and physiological responses of earthworms collected from the field in three different seasons, however no effect of temperature on metal toxicity was determined. Synergistic interaction between freezing temperatures and Cu has been observed in *Dendrobaena octaedra* and *Aporrectodea caliginosa*, and between freezing temperatures and Hg in *D. octaedra* (Holmstrup et al. 1998; Bindesbøl et al. 2005, 2009a, b). Bindesbøl et al. (2009a) hypothesized

that reduced tolerance to freezing temperatures in Cu-exposed earthworms may be due to changes in membrane phospholipids and consequently membrane damage. Wieczorek-Olchawa et al. (2002) investigated effects of temperature and metal polluted soil on *D. veneta*. Better survival in polluted soil at 10 °C compared to 22 °C can was explained by the reduced tissue metal accumulation and mesophilic bacteria proliferation at the lower temperature. Regarding the pesticides, effects of freezing temperatures on toxicities of abamectin and carbendazim were investigated, but no interactions were determined (Bindesbøl et al. 2009b). De Silva et al. (2009) investigated influence of temperature and soil type on the toxicity of pesticides to *E. andrei*. They determined that effects of chlorpyrifos and carbofuran on earthworm survival, growth and reproduction in artificial soil may be higher at higher temperature, whereas carbendazim toxicity was lower at high temperatures. However, there was no clear trend of increased toxicity for sub-lethal endpoints with temperature and toxicity varied with the pesticide, endpoint, soil type and temperature. Using also *E. andrei*, Lima et al. (2015) showed a tendency to synergism when exposed to combined carbaryl and high temperatures, and antagonism when exposed to carbaryl and low temperatures. Another study performed by Garcia et al. (2008) assessed effects of three pesticides on the avoidance behavior of earthworms in laboratory tests performed under temperate and tropical conditions and the results of the avoidance tests did not give a clear answer whether data from tests performed under temperate conditions can be used for pesticide risk assessment in tropical regions. In our recent study (Velki and Ečimović 2015) the toxicity of several insecticides, fungicides and herbicides on the mortality of earthworms at low and high temperature was assessed and an increase in exposure temperature generally led to an increase in toxicity, whereas a decrease in exposure temperature led to a decrease in toxicity. However, there were also some discrepancies (e.g. in case of herbicides fluazifop-p-butyl and glyphosate) in changes in toxicity. Besides metals and pesticides, the effect of temperature was investigated also on the toxicity of surfactant 4-nonylphenol and polycyclic aromatic hydrocarbons pyrene and phenanthrene (Bindesbøl et al. 2009b; Jensen et al. 2009).

## 8.3 *The Need for Further Assessment of the Effect of Temperature on Pollutant Toxicity to Earthworms*

It must be emphasized that there is an urgent need for determination of effects of temperature on the strength of toxic effects of pollutants present in the environment. As evident from the above mentioned studies, some of the results obtained in the conducted investigations are not consistent and validation studies performed under environmental conditions are necessary. Due to climate changes, which include an increase in soil temperature and increased exposure to extreme weather conditions, organisms in the environment are more frequently exposed to temperature stress which can result in greater susceptibility to pollutants. So it is

important to explore effects of temperature stress on physiological status of earthworms, propensity to intoxication and strength of the toxic effects of pollutants. Forthcoming toxicity testing of pollutants should be conducted at adequate temperatures, taking into account possible changes in temperature by utilizing the predictions of climate change. Given that climate change projections indicate that the frequency, intensity and duration of extreme climate events will increase in the future, besides determination of pollutant effects under different exposure temperatures, it is also necessary to assess the effects of preexposure to the extreme temperatures. Finally, there is a need for determination of the response of different tissues to temperature stress. Because of the different functions and characteristics, different tissues may have different sensitivity and may be more or less exposed to temperature stress. In this context, they can manifest different stress responses to temperature change. Determination of the sensitivity of certain tissues will provide an insight into the mechanisms of the effects of temperature stress on the toxicity of pollutants.

## 9 Conclusions

In the field of soil ecotoxicological research there has been an apparent shift—from measurement of only mortality and usage of laboratory toxicity tests for assessment of pollutant effects to the application of model systems that enable obtaining environmentally more relevant data and assessment of effects at different levels of biological organization. However, some important issues in ecotoxicological investigations require more in-depth research. In order to make ecotoxicological testing more effective and the data obtained more applicable for environmental risk assessment, the following guidelines should be adopted in ecotoxicological investigations using earthworms:

1. Establish the link between responses of low levels of biological organization and changes observed at higher levels.
   The success of utilization of biomarker responses in the environmental risk assessment depends on the identification of valid biomarkers and the establishment of process-level linkages between biomarkers and higher-level responses (Adams 2003). Understanding this link will enable the prediction of long-term pollutant effects based on measurements of early responses.
2. Assess the effects of pollutant mixtures.
   Since pollutants in the environment are most commonly present as mixtures, their effects have to be assessed. Prerequisite of such investigations is to assess the effects of realistic mixtures (combinations and concentrations of pollutants that can realistically be found in the environment) in order to reduce the needless testing. The changes in toxicity that can arise from interaction between compounds present in the pollutant mixture must be taken into account in the risk assessment.

3. Consider the possibility of occurrence of hormetic effects under environmental conditions.
   Pollutants in the environment are most commonly present at very low concentrations, but are usually assessed only at the effect levels. Effects of such low (sub-effective) concentrations often remain uninvestigated although it is known that they can cause effects opposite to the effects caused by the higher concentrations, i.e. the hormetic effect. Due to the incidence of hormesis and its potential significance in ecological risk assessment, in order to adequately assess the risk posed to earthworms, it is crucial to consider and investigate the occurrence of hormetic effects.
4. Use of soil microcosmic systems in ecotoxicological investigations.
   Soil microcosmic systems provide significant advantages compared to usage of standardized toxicity tests. Although these are artificial systems, they share some common features with real ecosystems and therefore provide more realistic data compared to laboratory toxicity tests. Since application of soil microcosms can contribute to the quantification of the impact of pollutants, its utilization should be an integral part of the soil ecotoxicological studies.
5. Explore how temperature affects the toxicity of pollutants and earthworm responses in order to determine possible changes in pollutant toxicity.
   Temperature is an important factor in ecotoxicological investigations since it affects physiological and biochemical processes in organisms. Due to climate changes, organisms in the environment are more frequently affected by temperature stress and can therefore be more susceptible to pollutants. Having regard to the prediction of climate change and exploring the effects of pollutants on earthworms under temperature stress, a better insight and prediction of the effects of pollutants in the environment can be obtained.

The inclusion of these guidelines in ecotoxicological studies will contribute to the better quantification of impacts of pollutants in the sense that it will support a more realistic approach in monitoring the adverse effects of pollutants on earthworms. Addressing these issues and promoting the assessment of pollutant effects under conditions mimicking those that occur in the environment will provide insight in the pollutant adverse effects on the soil ecosystem as a whole and will allow more accurate prediction of the real field effects of pollutants.

## 10 Summary

The role and importance of earthworms in the functioning of soil ecosystems is well-established. Due to their feeding and burrowing activities, earthworms beneficially affect the soil structure and quality. Also, earthworms have proved to be important model organisms for investigation of pollutant effects on soil ecosystems. Assessment of effects of various pollutants on earthworms was often a subject of research and valuable data was obtained. However, in future soil ecotoxicological studies it is necessary to address some important issues regarding the effects of

pollutants on earthworms which require further in-depth investigation. The aim of this review is to emphasize and discuss several issues in soil ecotoxicological investigations using earthworms that are of essential importance for risk assessment but are poorly explored and understood to date.

In order to enable an early detection of pollutant effects and prediction of subsequent adverse effects at population and ecosystem levels, it is necessary to establish links between biomarker responses at different levels of biological complexity. Gaining such information will help in developing protocols for predicting effects of pollutants on earthworm populations based on measurements of early earthworm responses.

Pollutants in the environment are commonly present as mixtures and the results of previous studies have provided clear evidence that the interactions between compounds of the mixtures could lead to changes in the intensity of the toxic effect. Therefore it is crucial to assess mixture effects to earthworms under environmentally relevant conditions and to develop methods for assessing the risks of pollutant mixtures. Also, since pollutants in the environment are often present at low concentrations, the possibility of occurrence of hormesis has to be considered and the understanding of hormesis mechanisms has to be addressed in detail.

One of the major future research goals should be to improve the understanding of how experimental conditions affect the responses of earthworms to pollutants. In this sense, the application of environmentally more relevant experimental conditions and inclusion of microcosmic systems in the assessment of pollutant effects is discussed. Also, consideration of effects of climate change to the strength of toxic effects of pollutants and biomarker responses of earthworms is taken into account.

Inclusion of these issues in future investigations will enable obtaining comprehensive data which will facilitate development of new assessment protocols and improved guidelines for better quantification of impacts of pollutants on earthworms and soil ecosystems.

## References

Abbott I, Parker CA (1981) Interactions between earthworms and their soil environment. Soil Biol Biochem 13:191–197

Abiven S, Menasseri S, Chenu C (2009) The effects of organic inputs over time on soil aggregate stability—a literature analysis. Soil Biol Biochem 41:1–12

Adams SM (2003) Establishing causality between environmental stressors and effects on aquatic ecosystems. Hum Ecol Risk Assess 9:17–35

Alves PR, Cardoso EJ, Martines AM, Sousa JP, Pasini A (2013) Earthworm ecotoxicological assessments of pesticides used to treat seeds under tropical conditions. Chemosphere 90:2674–2682

An YJ (2005) Assessing soil ecotoxicity of methyl tert-butyl ether using earthworm bioassay; closed soil microcosm test for volatile organic compounds. Environ Pollut 134:181–186

Ankley GT, Bennett RS, Erickson RJ, Hoff DJ, Hornung MW, Johnson RD, Mount DR, Nichols JW, Russom CL, Schmieder PK, Serrrano JA, Tietge JE, Villeneuve DL (2010) Adverse

outcome pathways: a conceptual framework to support ecotoxicology research and risk assessment. Environ Toxicol Chem 29:730–741
Belmeskine H, Haddad S, Vandelac L, Sauvé S, Fournier M (2012) Toxic effects of PCDD/Fs mixtures on *Eisenia andrei* earthworms. Ecotoxicol Environ Saf 80:54–59
Bindesbøl A, Holmstrup M, Damgaard C, Bayley M (2005) Stress synergy between environmentally realistic levels of copper and frost in the earthworm *Dendrobaena octaedra*. Environ Toxicol Chem 24:1462–1467
Bindesbøl A-M, Bayley M, Damgaard C, Hedlund K, Holmstrup M (2009a) Changes in membrane phospholipids as a mechanistic explanation for decreased freeze tolerance in earthworms exposed to sub-lethal copper concentrations. Environ Sci Tech 43:5495–5500
Bindesbøl A-M, Bayley M, Damgaard C, Holmstrup M (2009b) Impacts of heavy metals, PAHs and pesticides on freeze tolerance of the earthworm *Dendrobaena octaedra*. Environ Toxicol Chem 28:2341–2347
Birkás M, Jolánkai M, Gyuricza C, Percze A (2004) Tillage effects on compaction, earthworms and other soil quality indicators in Hungary. Soil Tillage Res 78:185–196
Bogomolov DM, Chen S-K, Parmelee RW, Subler S, Edwards CA (1996) An ecosystem approach to soil toxicity testing: a study of copper contamination in laboratory soil microcosms. Appl Soil Ecol 4:95–105
Bohlen PJ, Edwards CA (1995) Earthworm effects on N dynamics and soil respiration in microcosms receiving organic and inorganic nutrients. Soil Biol Biochem 27:341–348
Boyer J, Reversat G, Lavelle P, Chabanne A (2013) Interactions between earthworms and plant-parasitic nematodes. Eur J Soil Biol 59:43–47
Brown GG, Barois I, Lavelle P (2000) Regulation of soil organic matter dynamics and microbial activity in the drilosphere and the role of interactions with other edaphic functional domains. Eur J Soil Biol 36:177–198
Brown PJ, Long SM, Spurgeon DJ, Svendsen C, Hankard PK (2004) Toxicological and biochemical responses of the earthworm *Lumbricus rubellus* to pyrene, a noncarcinogenic polycyclic aromatic hydrocarbon. Chemosphere 57:1675–1681
Burrows LA, Edwards CA (2002) The use of integrated soil microcosms to predict effects of pesticides on soil ecosystems. Eur J Soil Biol 38:245–249
Cahill TM, Cousins I, Mackay D (2003) Development and application of a generalized physiologically based pharmacokinetic model for multiple environmental contaminants. Environ Toxicol Chem 22:26–34
Calabrese EJ (2003) The maturing of hormesis as a credible dose-response model. Nonlinearity Biol Toxicol Med 1:319–343
Calabrese EJ (2008) Hormesis: why it is important to toxicology and toxicologists. Environ Toxicol Chem 27:1451–1474
Calabrese EJ, Baldwin LA (2002) Defining hormesis. Hum Exp Toxicol 21:91–97
Calabrese EJ, Baldwin LA (2003) The hormetic dose-response model is more common that the threshold model in toxicology. Toxicol Sci 71:246–250
Calisi A, Lionetto MG, Schettino T (2011) Biomarker response in the earthworm *Lumbricus terrestris* exposed to chemical pollutants. Sci Total Environ 409:4456–4464
Calisi A, Zaccarelli N, Lionetto MG, Schettino T (2013) Integrated biomarker analysis in the earthworm *Lumbricus terrestris*: application to the monitoring of soil heavy metal pollution. Chemosphere 90:2637–2644
Cao X, Song Y, Kai J, Yang X, Ji P (2012) Evaluation of EROD and CYP3A4 activities in earthworm *Eisenia fetida* as biomarkers for soil heavy metal contamination. J Hazard Mater 243:146–151
Capowiez Y, Dittbrenner N, Rault M, Triebskorn R, Hedde M, Mazzia C (2010) Earthworm cast production as a new behavioural biomarker for toxicity testing. Environ Pollut 158:388–393
Chan KY (2001) An overview of some tillage impacts on earthworm population abundance and diversity—implications for functioning in soils. Soil Tillage Res 57:179–191

Crittenden SJ, Eswaramurthy T, de Goede RGM, Brussaard L, Pulleman MM (2014) Effect of tillage on earthworms over short- and medium-term in conventional and organic farming. Appl Soil Ecol 83:140–148

De Silva PM, Pathiratne A, van Gestel CA (2009) Influence of temperature and soil type on the toxicity of three pesticides to *Eisenia andrei*. Chemosphere 76:1410–1415

Dittbrenner N, Moser I, Triebskorn R, Capowiez Y (2011) Assessment of short and long-term effects of imidacloprid on the burrowing behaviour of two earthworm species (*Aporrectodea caliginosa* and *Lumbricus terrestris*) by using 2D and 3D post-exposure techniques. Chemosphere 84:1349–1355

Doan TT, Ngo PT, Rumpel C, Nguyen BV (2013) Interactions between compost, vermicompost and earthworms influence plant growth and yield: a one-year greenhouse experiment. Sci Hortic 160:148–154

Doube BM, Stephens PM, Davoren CW, Ryder MH (1994) Interactions between earthworms, beneficial soil microorganisms and root pathogens. Appl Soil Ecol 1:3–10

Edwards CA (2004) The importance of earthworms as key representatives of the soil fauna. In: Edwards CA (ed) Earthworm ecology. CRC Press, Boca Raton, FL, pp 3–11

Edwards CA, Bohlen PJ (1996) Biology and ecology of earthworms, 3rd edn. Chapman and Hall, London

Eisenhauer N, Hörsch V, Moeser J, Scheu S (2010) Synergistic effects of microbial and animal decomposers on plant and herbivore performance. Basic Appl Ecol 11:23–34

Eisenhauer N, Milcu A, Sabais ACW, Scheu S (2009) Earthworm and belowground competition effects on plant productivity. Oecologia 161:291–301

Eisenhauer N, Partsch S, Parkinson D, Scheu S (2007) Invasion of a deciduous forest by earthworms: changes in soil chemistry, microflora, microarthropods and vegetation. Soil Biol Biochem 39:1099–1110

Ellis SR, Hodson ME, Wege P (2010) The soil-dwelling earthworm *Allolobophora chlorotica* modifies its burrowing behaviour in response to carbendazim applications. Ecotoxicol Environ Saf 73:1424–1428

El-Temsah YS, Joner EJ (2012) Ecotoxicological effects on earthworms of fresh and aged nano-sized zero-valent iron (nZVI) in soil. Chemosphere 89:76–82

Ernst G, Emmerling C (2009) Impact of five different tillage systems on soil organic carbon content and the density, biomass, and community composition of earthworms after a ten year period. Eur J Soil Biol 45:247–251

Fayolle L, Michaud H, Cluzeau D, Stawiecki J (1997) Influence of temperature and food source on the life cycle of the earthworm *Dendrobaena veneta (Oligochaeta)*. Soil Biol Biochem 29:747–750

Fraser PM, Beare MH, Butler RC, Harrison-Kirk T, Piercy JE (2003) Interactions between earthworms (*Aporrectodea caliginosa*), plants and crop residues for restoring properties of a degraded arable soil. Pedobiologia 47:870–876

Garcia M, Römbke J, de Brito MT, Scheffczyk A (2008) Effects of three pesticides on the avoidance behavior of earthworms in laboratory tests performed under temperate and tropical conditions. Environ Pollut 153:450–456

Giska I, van Gestel CA, Skip B, Laskowski R (2014) Toxicokinetics of metals in the earthworm *Lumbricus rubellus* exposed to natural polluted soils—relevance of laboratory tests to the field situation. Environ Pollut 190:123–132

Gomez-Eyles JL, Svendsen C, Lister L, Martin H, Hodson ME, Spurgeon DJ (2009) Measuring and modelling mixture toxicity of imidacloprid and thiacloprid on *Caenorhabditis elegans* and *Eisenia fetida*. Ecotoxicol Environ Saf 72:71–79

Gupta SK, Sundararaman V (1991) Correlation between burrowing capability and AChE activity in the earthworm, *Pheretima posthuma*, on exposure to carbaryl. Bull Environ Contam Toxicol 46:859–865

Hackenberger BK, Jarić-Perkušić D, Stepić S (2008) Effect of temephos on cholinesterase activity in the earthworm *Eisenia fetida* (Oligochaeta, Lumbricidae). Ecotoxicol Environ Saf 71:583–589

Hackenberger BK, Velki M, Stepić S, Hackenberger DK (2012) The effect of formalin on acetylcholinesterase and catalase activities, and on the concentration of oximes, in the earthworm species *Eisenia andrei*. Eur J Soil Biol 50:137–143

Hayashi Y, Heckmann LH, Simonsen V, Scott-Fordsmand JJ (2013) Time-course profiling of molecular stress responses to silver nanoparticles in the earthworm *Eisenia fetida*. Ecotoxicol Environ Saf 98:219–226

Heckmann L-H, Hovgaard M, Sutherland D, Autrup H, Besenbacher F, Scott-Fordsmand J (2011) Limit-test toxicity screening of selected inorganic nanoparticles to the earthworm *Eisenia fetida*. Ecotoxicology 20:226–233

Hirano T, Tamae K (2011) Earthworms and soil pollutants. Sensors 11:11157–11167

Holmstrup M, Bindesbøl AM, Oostingh GJ, Duschl A, Scheil V, Köhler HR, Loureiro S, Soares AM, Ferreira AL, Kienle C, Gerhardt A, Laskowski R, Kramarz PE, Bayley M, Svendsen C, Spurgeon DJ (2010) Interactions between effects of environmental chemicals and natural stressors: a review. Sci Total Environ 408:3746–3762

Holmstrup M, Petersen BF, Larsen MM (1998) Combined effects of copper, desiccation, and frost on the viability of earthworm cocoons. Environ Toxicol Chem 17:897–901

Hooper HL, Jurkschat K, Morgan AJ, Bailey J, Lawlor AJ, Spurgeon DJ, Svendsen C (2011) Comparative chronic toxicity of nanoparticulate and ionic zinc to the earthworm *Eisenia veneta* in a soil matrix. Environ Int 37:1111–1117

Hu CW, Zhang LJ, Wang WL, Cui YB, Li M (2014) Evaluation of the combined toxicity of multi-walled carbon nanotubes and sodium pentachlorophenate on the earthworm *Eisenia fetida* using avoidance bioassay and comet assay. Soil Biol Biochem 70:123–130

Hu CW, Li M, Cui YB, Li DS, Chen J, Yang LY (2010) Toxicological effects of $TiO_2$ and ZnO nanoparticles in soil on earthworm *Eisenia fetida*. Soil Biol Biochem 42:586–591

Jager T, Vandenbrouck T, Baas J, De Coen WM, Kooijman SA (2010) A biology-based approach for mixture toxicity of multiple endpoints over the life cycle. Ecotoxicology 19:351–361

Jensen D, Bayley M, Holmstrup M (2009) Synergistic interaction between 4-nonylphenol and high but not low temperatures in *Dendrobaena octaedra*. Ecotoxicol Environ Saf 72:10–16

Jones OA, Spurgeon DJ, Svendsen C, Griffin JL (2008) A metabolomics based approach to assessing the toxicity of the polyaromatic hydrocarbon pyrene to the earthworm *Lumbricus rubellus*. Chemosphere 71:601–609

Jonker MJ, Svendsen C, Bedaux JJM, Bongers M, Kammenga JE (2005) Significance testing of synergistic/antagonistic, dose level-dependent, or dose ratio-dependent effects in mixture dose-response analysis. Environ Toxicol Chem 24:2701–2713

Jusselme MD, Miambi E, Mora P, Diouf M, Rouland-Lefèvre C (2013) Increased lead availability and enzyme activities in root-adhering soil of *Lantana camara* during phytoextraction in the presence of earthworms. Sci Total Environ 445–446:101–109

Kammenga JE, Dallinger R, Donker MH, Köhler H-R, Simonsen V, Triebskorn R, Weeks JM (2000) Biomarkers in terrestrial invertebrates for ecotoxicological soil risk assessment. Rev Environ Contam Toxicol 164:93–147

Khan MA, Ahmed SA, Salazar A, Gurumendi J, Khan A, Vargas M, von Catalin B (2007) Effect of temperature on heavy metal toxicity to earthworm *Lumbricus terrestris* (Annelida: Oligochaeta). Environ Toxicol 22:487–494

Kılıç GA (2011) Histopathological and biochemical alterations of the earthworm (*Lumbricus Terrestris*) as biomarker of soil pollution along Porsuk River Basin (Turkey). Chemosphere 83:1175–1180

Klobučar GI, Štambuk A, Šrut M, Husnjak I, Merkaš M, Traven L, Cvetković Z (2011) *Aporrectodea caliginosa*, a suitable earthworm species for field based genotoxicity assessment? Environ Pollut 159:841–849

Kurelec B (1998) Biomarkers and the ecological risk assesment paradigm. In: Werner E, Muller G (eds) Modern aspects in monitoring of environmental pollution in the sea. Akademie gemeinnutziger Wissenschaften zu Erfurt, Erfurt

LaCourse EJ, Hernandez-Viadel M, Jefferies JR, Svendsen C, Spurgeon DJ, Barrett J, Morgan AJ, Kille P, Brophy PM (2009) Glutathione transferase (GST) as a candidate molecular-based biomarker for soil toxin exposure in the earthworm *Lumbricus rubellus*. Environ Pollut 157:2459–2469

Langdon CJ, Hodson ME, Arnold RE, Black S (2005) Survival, Pb-uptake and behaviour of three species of earthworm in Pb treated soils determined using an OECD-style toxicity test and a soil avoidance test. Environ Pollut 138:368–375

Łaszczyca P, Augustyniak M, Babczyńska A, Bednarska K, Kafel A, Migula P, Wilczek G, Witas I (2004) Profiles of enzymatic activity in earthworms from zinc, lead and cadmium polluted areas near Olkusz (Poland). Environ Int 30:901–910

Lee KE (1985) Earthworms. Their ecology and relationships with soils and land use. Academic, Sydney

Leveque T, Capowiez Y, Schreck E, Mazzia C, Auffan M, Foucault Y, Austruy A, Dumat C (2013) Assessing ecotoxicity and uptake of metals and metalloids in relation to two different earthworm species (Eiseina hortensis and Lumbricus terrestris). Environ Pollut 179:232–241

Lima MP, Cardoso DN, Soares AM, Loureiro S (2015) Carbaryl toxicity prediction to soil organisms under high and low temperature regimes. Ecotoxicol Environ Saf 114:263–272

Lionetto MG, Calisi A, Schettino T (2012) Earthworm biomarkers as tools for soil pollution assessment. In: Hernandez-Soriano MC (ed) Soil heath and soil use management. InTech—Open Access Publisher, Rijeka (Croatia), pp 305–332

Lukkari T, Marjo Aatsinki M, Väisänen A, Haimi J (2005) Toxicity of copper and zinc assessed with three different earthworm tests. Appl Soil Ecol 30:133–146

Lydy MJ, Linck SL (2003) Assessing the impact of triazine herbicides on organophosphate insecticide toxicity to the earthworm *Eisenia fetida*. Arch Environ Contam Toxicol 45:343–349

Ma WC, Bodt J (1993) Differences in toxicity of the insecticide Chlorpyrifos to six species of earthworms (Oligochaeta, Lumbricidae) in standardized soil tests. Bull Environ Contam Toxicol 50:864–870

Martin NA (1982) The interaction between organic matter in soil and the burrowing activity of three species of earthworms (Oligochaeta: Lumbricidae). Pedobiologia 24:185–190

Mikhailov AT, Torrado M (1999) Carboxylesterase overexpression in the male reproductive tract: a universal safeguarding mechanism? Reprod Fertil Dev 11:133–145

Morgan AJ, Stürzenbaum SR, Winters C, Grime GW, Aziz NAA, Kille P (2004) Differential metallothionein expression in earthworm (*Lumbricus rubellus*) tissues. Ecotoxicol Environ Saf 57:11–19

OECD (1984) Guidelines for testing of chemicals, earthworm, acute toxicity tests. Filter paper test and artificial soil test, vol 207. Organization for Economic Cooperation and Development, Paris

Pal R, Chakrabarti K, Chakraborty A, Chowdhury A (2006) Degradation and effects of pesticides on soil microbiological parameters-a review. Int J Agric Res 1:240–258

Pastorok RA, Akçakaya R, Regan H, Ferson S, Bartell SM (2003) Role of ecological models in risk assessment. Hum Ecol Risk Assess 9:939–972

Pelosi C, Barot S, Capowiez Y, Hedde M, Vandenbulcke F (2013) Pesticides and earthworms. A review. Agron Sustain Dev 34:199–228

Pelosi C, Pey B, Hedde M, Caro G, Capowiez Y, Guernion M, Peigné J, Piron D, Bertrand M, Cluzeau D (2014) Reducing tillage in cultivated fields increases earthworm functional diversity. Appl Soil Ecol 83:79–87

Perreault JM, Whalen JK (2006) Earthworm burrowing in laboratory microcosms as influenced by soil temperature and moisture. Pedobiologia 50:397–403

Presley ML, McElroy TC, Dieh WI (1996) Soil moisture and temperature interact to affect growth, survivorship, fecundity, and fitness in the earthworm *Eisenia fetida*. Comp Biochem Physiol 114A:319–326

Reinecke AJ, Reinecke SA (2004) Earthworm as test organisms in ecotoxicological assessment of toxicant impacts on ecosystems. In: Edwards CA (ed) Earthworm ecology. CRC Press LLC, Boca Raton, FL, USA, pp 299–320

Reinecke SA, Reinecke AJ (2007) Biomarker response and biomass change of earthworms exposed to chlorpyrifos in microcosms. Ecotoxicol Environ Saf 66:92–101

Ricketts HJ, Morgan AJ, Spurgeon DJ, Kille P (2003) Measurement of annetocin gene expression: anew reproductive biomarker in earthworm toxicology. Ecotoxicol Environ Saf 57:4–10

Riley H, Pommeresche R, Eltun R, Hansen S, Korsaeth A (2008) Soil structure, organic matter and earthworm activity in a comparison of cropping systems with contrasting tillage, rotations, fertilizer levels and manure use. Agr Ecosyst Environ 124:275–284

Robidoux PY, Svendsen C, Sarrazin M, Thiboutot S, Ampleman G, Hawari J et al (2004) Assessment of a 2,4,6-trinitrotoluene contaminated site using *Aporrectodea rosea* and *Eisenia andrei* in mesocosms. Arch Environ Contam Toxicol 48:56–67

Rodríguez-Castellanos L, Sanchez-Hernandez JC (2007) Earthworm biomarkers of pesticide contamination: current status and perspectives. J Pest Sci 32:360–371

Rosenbluth J (1972) Myoneural junctions of two ultrastructurally distinct types in earthworm body wall muscle. J Cell Biol 54:566–579

Sanchez-Hernandez JC (2006) Earthworm biomarkers in ecological risk assessment. Rev Environ Contam Toxicol 188:85–126

Sanchez-Hernandez JC, Martinez Morcillo S, Notario del Pino J, Ruiz P (2014) Earthworm activity increases pesticide-sensitive esterases in soil. Soil Biol Biochem 75:186–196

Santos MJG, Ferreira V, Soares AMVM, Loureiro S (2011a) Evaluation of the combined effects of dimethoate and spirodiclofen on plants and earthworms in a designed microcosm experiment. Appl Soil Ecol 48:294–300

Santos MJG, Morgado R, Ferreira NGC, Soares AMVM, Loureiro S (2011b) Evaluation of the joint effect of glyphosate and dimethoate using a small-scale terrestrial ecosystem. Ecotoxicol Environ Saf 74:1994–2001

Sarkar A, Ray D, Amulya NS, Subhodeep S (2006) Molecular biomarkers; their significant and application in marine pollution monitoring. Ecotoxicology 15:333–340

Schnug L, Ergon T, Jakob L, Scott-Fordsmand JJ, Joner EJ, Leinaas HP (2015) Responses of earthworms to repeated exposure to three biocides applied singly and as a mixture in an agricultural field. Sci Total Environ 505:223–235

Schnug L, Jakob L, Hartnik T (2013) The toxicity of a ternary biocide mixture to two consecutive earthworm (*Eisenia fetida*) generations. Environ Toxicol Chem 32:937–947

Schnug L, Jensen J, Scott-Fordsmand JJ, Leinaas HP (2014) Toxicity of three biocides to springtails and earthworms in a soil multi-species (SMS) test system. Soil Biol Biochem 74:115–126

Schreck E, Geret F, Gontier L, Trilhou M (2008) Neurotoxic effect and metabolic responses induced by a mixture of six pesticides on the earthworm *Aporrectodea caliginosa nocturna*. Chemosphere 71:1832–1839

Shoults-Wilson WA, Reinsch BC, Tsyusko OV, Bertsch PM, Lowry GV, Unrine JM (2011a) Effect of silver nanoparticle surface coating on bioaccumulation and reproductive toxicity in earthworms (*Eisenia fetida*). Nanotoxicology 5:432–444

Shoults-Wilson WA, Zhurbich O, McNear D, Tsyusko O, Bertsch P, Unrine J (2011b) Evidence for avoidance of Ag nanoparticles by earthworms (*Eisenia fetida*). Ecotoxicology 20:385–396

Six J, Elliott E, Paustian K (2000) Soil macroaggregate turnover and microaggregate formation: a mechanism for C sequestration under no-tillage agriculture. Soil Biol Biochem 32:2099–2103

Spurgeon DJ, Jones OA, Dorne JL, Svendsen C, Swain S, Stürzenbaum SR (2010) Systems toxicology approaches for understanding the joint effects of environmental chemical mixtures. Sci Total Environ 408:3725–3734

Spurgeon DJ, Ricketts H, Svendsen C, Morgan AJ, Kille P (2005) Hierarchical responses of soil invertebrates (earthworms) to toxic metals stress. Environ Sci Tech 39:5327–5334

Stepić S, Hackenberger BK, Velki M, Hackenberger DK, Lončarić Ž (2013a) Potentiation effect of metolachlor on toxicity of organochlorine and organophosphate insecticides in earthworm *Eisenia andrei*. Bull Environ Contam Toxicol 91:55–61

Stepić S, Hackenberger BK, Velki M, Lončarić Ž, Hackenberger DK (2013b) Effects of individual and binary-combined commercial insecticides endosulfan, temephos, malathion and pirimiphos-methyl on biomarker responses in earthworm *Eisenia andrei*. Environ Toxicol Pharmacol 36:715–723

Svendsen C, Hankard PK, Lister LJ, Fishwick SK, Jonker MJ, Spurgeon DJ (2007) Effect of temperature and season on reproduction, neutral red retention and metallothionein responses of earthworms exposed to metals in field soils. Environ Pollut 147:83–93

Tao J, Griffiths B, Zhang S, Chen X, Liu M, Hu F, Li H (2009) Effects of earthworms on soil enzyme activities in an organic residue amended rice-wheat rotation agro-ecosystem. Appl Soil Ecol 42:221–226

Tripathi G, Kachhwaha I, Dabi I (2010a) Ecophysiological category based toxicological responses in metabolism of earthworms: Impact of a pyrethroidal insecticide. Pestic Biochem Physiol 98:333–341

Tripathi G, Kachhwaha N, Dabi I (2010b) Comparative studies on carbofuran-induced changes in some cytoplasmic and mitochondrial enzymes and proteins of epigeic, anecic and endogeic earthworms. Pestic Biochem Physiol 96:30–35

Tripathi GKN, Dabi I, Bandooni N (2011) Temperature-dependent alterations in metabolic enzymes and proteins of three ecophysiologically different species of earthworms. Braz Arch Biol Tech 54:769–776

Tsyusko OV, Hardas SS, Shoults-Wilson WA, Starnes CP, Joice G, Butterfield DA, Unrine JM (2012) Short-term molecular-level effects of silver nanoparticle exposure on the earthworm, *Eisenia fetida*. Environ Pollut 171:249–255

van Gestel CA (2012) Soil ecotoxicology: state of the art and future directions. Zookeys 176:275–296

van Gestel CA, Koolhaas JE, Hamers T, van Hoppe M, van Roovert M, Korsman C, Reinecke SA (2009) Effects of metal pollution on earthworm communities in a contaminated floodplain area: linking biomarker, community and functional responses. Environ Pollut 157:895–903

Vejares SG, Sabat P, Sanchez-Hernandez JC (2010) Tissue-specific inhibition and recovery of esterase activities in *Lumbricus terrestris* experimentally exposed to chlorpyrifos. Comp Biochem Physiol C Toxicol Pharmacol 151:351–359

Velki M, Ečimović S (2015) Changes in exposure temperature lead to changes in pesticide toxicity to earthworms: a preliminary study. Environ Toxicol Pharmacol 10.1016/j.etap.2015.09.009. Accepted for Publication

Velki M, Hackenberger BK (2012) Species-specific differences in biomarker responses in two ecologically different earthworms exposed to the insecticide dimethoate. Comp Biochem Physiol C Toxicol Pharmacol 156:104–112

Velki M, Hackenberger BK (2013a) Different sensitivities of biomarker responses in two epigeic earthworm species after exposure to pyrethroid and organophosphate insecticides. Arch Environ Contam Toxicol 65:498–509

Velki M, Hackenberger BK (2013b) Biomarker responses in earthworm *Eisenia andrei* exposed to pirimiphos-methyl and deltamethrin using different toxicity tests. Chemosphere 90:1216–1226

Velki M, Hackenberger BK, Lončarić Ž, Hackenberger DK (2014) Application of microcosmic system for assessment of insecticide effects on biomarker responses in ecologically different earthworm species. Ecotoxicol Environ Saf 104:110–119

Venkateswara Rao J, Kavitha P (2004) Toxicity of azodrin on the morphology and acetylcholinesterase activity of the earthworm *Eisenia foetida*. Environ Res 96:323–327

Wang Y, Chen C, Qian Y, Zhao X, Wang Q, Kong X (2015) Toxicity of mixtures of λ-cyhalothrin, imidacloprid and cadmium on the earthworm *Eisenia fetida* by combination index (CI)-isobologram method. Ecotoxicol Environ Saf 111:242–247

Wever LA, Lysyk TJ, Clapperton MJ (2001) The influence of soil moisture and temperature on the survival, aestivation, growth and development of juvenile *Aporrectodea tuberculata* (Eisen) (Lumbricidae). Pedobiologia 45:121–133

Wieczorek-Olchawa E, Niklinska M, Miedzobrodzki J, Plytycz B (2002) Effects of temperature and soil pollution on the presence of bacteria, coelomocytes and brown bodies in coelomic fluid of *Dendrobaena veneta*. Pedobiologia 47:702–709

World Health Organization (WHO) (2001) Environmental Health Criteria 222. Biomarkers in risk assessment: validity and validation. World Health Organization, Geneva, Switzerland

Wu S, Zhang H, Zhao S, Wang J, Li H, Chen J (2012) Biomarker responses of earthworms (*Eisenia fetida*) exposured to phenanthrene and pyrene both singly and combined in microcosms. Chemosphere 87:285–293

Wurst S, Langel R, Reineking A, Bonkowski M, Scheu S (2003) Effects of earthworms and organic litter distribution on plant performance and aphid reproduction. Oecologia 137:90–96

Zhang Y, Shen G, Yu Y, Zhu H (2009) The hormetic effect of cadmium on the activity of antioxidant enzymes in the earthworm *Eisenia fetida*. Environ Pollut 157:3064–3068

Zhou S, Duan C, Michelle WH (2011) Individual and combined toxic effects of cypermethrin and chlorpyrifos on earthworm. J Environ Sci 23:676–680

Zhou SP, Duan CQ, Fu H, Chen YH, Wang XH, Yu ZF (2007) Toxicity assessment for chlorpyrifos-contaminated soil with three different earthworm test methods. J Environ Sci (China) 19:854–858

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