General Principles of Ecological Risk Assessment

General Principles of Ecological Risk Assessment:

Protecting Ecosystems in the Third Millennium

Edited by

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Cambridge Scholars
Publishing

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This book first published 2024

Cambridge Scholars Publishing

Lady Stephenson Library, Newcastle upon Tyne, NE6 2PA, UK

British Library Cataloguing in Publication Data
A catalogue record for this book is available from the British Library

ISBN (10): 1-0364-0421-8
ISBN (13): 978-1-0364-0421-5

In memory of Don Mackay, one of the pioneers of our science

(30 October 1936 - 20 October 2023)

CONTENTS

CHAPTER 1

INTRODUCTION: A SHORT HISTORY OF ECOTOXICOLOGY, THE SCIENCE OF ECOLOGICAL RISK ASSESSMENT

MARCO VIGHI

Although the impact of human activities on the environment started at the beginning of cultural development, several thousands of years ago, public awareness of environmental damage is relatively recent, starting in the middle of the 20th century. In particular, the serious impacts of exposure to potentially dangerous chemicals on the natural environment were recognized by public opinion only after the famous book *Silent Spring* by Rachel Carson (Carson 1962). At that time, it was already evident that the environmental emission of chemicals produced by human activities, especially in surface water ecosystems, were likely to produce effects at the lethal and sub-lethal levels in natural populations and communities.

Therefore, ecotoxicology emerged in the second half of the last century to respond to the growing concern about the potential ecosystem effects of chemical emissions. The term “ecotoxicology” was introduced by Jean-Michel Jouany and René Truhaut in the 1960s (Vasseur *et al.* 2021). However, the first complete definition of ecotoxicology was proposed by Butler (1978): “Ecotoxicology is concerned with the toxic effects of chemical and physical agents on living organisms, especially on populations and communities within defined ecosystems; it includes the transfer pathways of those agents and their interactions with environment.”

This is a very modern definition of ecotoxicology. Indeed, it considers the effects at the highest levels of ecological hierarchy (populations, communities, and ecosystems). Moreover, it recognizes that ecotoxicology is exposure-driven, unlike human toxicology that is mainly hazard-driven.

However, it was difficult to apply these concepts with the level of scientific knowledge available at that time.

Given the recognition that mankind produces vast numbers of different chemicals, the challenge for this new science was producing tools capable of providing solutions for the management of chemical pollution using the relatively scarce information available.

The strategy followed in the decades from 1960 to 1990 was based on the development of relatively simplified approaches for Ecological Risk Assessment (ERA), capable of estimating exposure to dangerous chemicals, of evaluating their effects on living organisms, and of characterizing the risk for ecosystems, based on experimental data sets suitable to be produced in relatively short time and at low costs. It was logical not to treat all chemicals similarly (simply due to the sheer numbers), but to try prioritizing applied sciences efforts to those chemicals likely posing most harm, either derived from "warnings" from field data, or from ranking potential harm of the different chemicals.

The first major obstacle to overcome was the need for improving knowledge on the quantitative presence of potentially dangerous chemicals in the environment. This held especially for prospective risk assessment, to answer the question "shall we produce this chemical and allow it on the market – and can it eventually pose harm?" that was posed, because it is evident that a prospective assessment can assist in preventing novel problems from emerging after some years of use of a (novel) chemical. Thus, mathematical models have been developed for the prediction of the environmental concentration (PEC) after emission into air, water or soil, which can be used as a measure of exposure to organisms and populations in aquatic and terrestrial ecosystems (Trapp & Matthies 1998).

A fundamental step for the estimation of environmental exposure to pollutants was the development of the multimedia fugacity approach proposed by Don Mackay in the late 1970s (Mackay 1979). Like all brilliant discoveries, the fugacity approach is based on simple concepts: the fate of a chemical substance in the main environmental compartments (air, water, soil, biota) is regulated by the simple physical-chemical properties of the substance.

In the first formulation of the fugacity approach, Mackay introduced the concept of a "Unit of Word", an ideal parallelepiped with a base of 1 km^2 and a height of 6 km, where all major environmental compartments were present in a quantitative amount comparable to the ratios existing in the real world (Figure 1.1). Using simple equations to quantify the partitioning and degradation of a chemical substance in the different compartments and the transfer between them, it is possible to estimate the concentrations in the environmental media after the emission of a given amount of the chemical into the system.

The versatility of the approach is enormous. It may be adapted to many types of environmental scenarios, from the global to the local scale. Therefore, it represents the basis of approaches for the prediction of exposure to organic pollutants that have been developed to date (Mackay & Parnis 2021). At present, predictive models capable of estimating environmental concentrations of chemicals, even before their commercialization, represent a fundamental tool for prospective risk assessment.

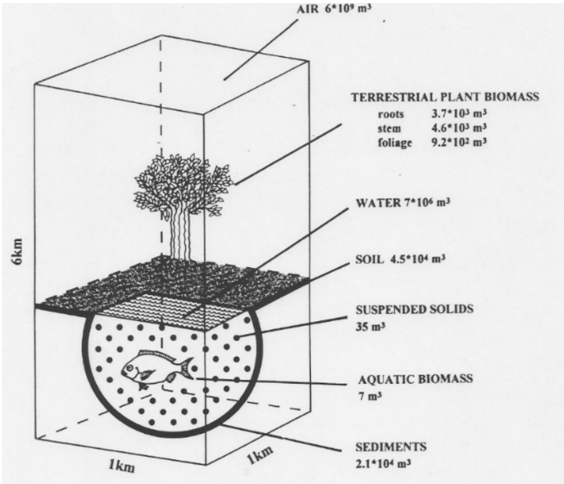

Figure 1.1. A schematic picture of the "Unit of World" introduced by Mackay for describing the distribution and fate of organic contaminants in the environment. The unit represents a system where all major environmental compartments (air water, soil, sediments, biota) are present in a volumetric ratio comparable to those present in the real world. The original Unit of World has been modified for the inclusion of the terrestrial plant biomass (modified after Calamari *et al*. 1987).

On the side of assessing the effects of pollutants on ecosystems, the early and later steps developed swiftly. Initially, the focus was on searching "the most sensitive species" because the chemical safety assessment could proceed in a simple and universal way once this species was identified and tested for all chemicals being considered. If the predicted environmental concentration would be lower than the critical no-effect concentration for the most sensitive species, then the chemical would fall in the outcome class of likely safe use. Soon, it was however recognized that the most sensitive species was a “mythical beast” (Cairns 1986), as it was understood that the sensitivities of species to chemicals rather followed a bell-shaped distribution. Thereupon it was assumed that a battery of a few selected organisms can be considered representative of the entire biological community. For example, for the aquatic environment, ecotoxicological tests performed on a planktonic unicellular alga, a planktonic crustacean (usually *Daphnia spp.*) and a fish were assumed as sufficient for extrapolating effects from these tested species to freshwater ecosystems. Indeed, the selected organisms cover the main trophic levels of the food chain (primary producers, primary consumers, secondary consumers) and the main types of metabolic and physiologic organization (photosynthetic organisms, invertebrates, and vertebrates). In this frame, one important group of organisms, with different ecological and physiological characteristics, is missing: bacteria, as prokaryote decomposers. To cover this gap, a test on bacteria (respiration inhibition test) is generally included in the base set.

The pragmatic principle of representing the enormous complexity of natural ecosystems with a limited battery of selected organisms suffers from a lack of ecological realism. However, considering the impossibility of performing experimental tests on the variety of natural biodiversity, the approach represents a realistic possibility for obtaining at least indicative values to quantify the potential hazard of pollutants, at least in a relative way (to rank chemicals in their potency to cause harm to the three species).

Moreover, the selected organisms are relatively simple to culture in laboratory conditions and the test procedures are relatively inexpensive, making it possible to perform several tests with a moderate investment of resources.

Nevertheless, the number of potentially dangerous chemicals emitted into the environment is enormous (more than 300,000 registered for production and use worldwide (Wang *et al.* 2020)) and performing experimental tests on all of them is realistically impossible.

Therefore, the need for in *silico* approaches able to predict the biological effect of toxic chemicals was recognized and, in the late 1970s, the Quantitative Structure Activity Relationship (QSAR) approach, proposed one decade before by the pioneering work of Corvin Hansch (Hansch & Fujita 1964), has proved applicable in aquatic toxicology (Könemann 1981). Despite the further development of QSARs, based on modern chemometric approaches, predictive models for toxicological effects are not yet used as extensively as the models for predicting exposure.

Given the development of both exposure and effect assessment methods, there are ample opportunities to use these data for different purposes. One of the key ones is prospective ecological risk assessment, where each novel chemical is subjected in a transparent, reproducible way to the process of chemical safety assessment. The further step that is made here is the extrapolation of experimental or theoretical data on the toxicity of chemicals to a few selected individual species to derive concentration values that represent the level at and below which an exposure concentration is considered sufficiently safe, and beyond which this may not be so. The traditional procedure for the calculation of a PNEC (Predicted No Effect Concentration), intended as a concentration that must not produce adverse effects on the ecosystem, is based on the use of ecotoxicity test data combined with an application factor (AF) accounting for the uncertainties of the data available (see, for example, the European Technical Guidance Document (TGD) on Risk Assessment of Chemical Substances (EC 2003)).

The final objective of these simplified approaches was the characterization of lower-tier risk that may be simply performed trough a comparison between the PNEC and a predicted environmental concentration (PEC), where a value of one of the ratio PEC/PNEC represents the threshold below which adverse effects are deemed negligible or acceptable (Figure 1.2).

The methods, tools and procedures described above and developed in the first decades of ecotoxicology history, do not consider the enormous complexity of the structure and functioning of natural ecosystems and may appear extremely simplified and coarse. Nevertheless, they were the most feasible way to deal with the problem of assessing environmental risks with the scarce knowledge available and the vast number of chemicals that were listed to be judged in this way. Indeed, these approaches represented the basis for the development of international regulations in the context of chemical safety assessments that were likely to yield concentration thresholds that would serve in the key prospective approach of safeguarding the environment against overexposure to hazardous chemicals. Some of these regulations are directed to protect specific environmental systems, such as freshwater (e.g., the European Water Framework Directive (WFD: EC 2000) and the US Clean Water Act (US 1972)), the marine coastal environment and the oceans (e.g., the European Marine Strategy (EC 2008) and the OSPAR Convention (OSPAR 2006)), the soil ecosystem (e.g., The European Soil Thematic Strategy (EC 2006)). Others were focused on the control of chemical in general (e.g., the US TSCA, Toxic Substances Control Act (US 2021)) and the European REACH, *Registration, Evaluation, Authorisation, and restriction of Chemicals* (EC 2006)) or of specific classes of chemicals considered particularly dangerous (e.g., the

Stockholm Convention for the ban of persistent organic pollutants (POPs) (UNEP 2001)).

These regulatory tools led to an increased level of chemical control and to an improvement of environmental quality. Indeed, severe effects of environmental damage, such as extensive fish mortalities, frequent in the past, are now occurring only in extreme events (e.g., accidental spills).

Despite these important achievements, the problem of environmental exposures, risks and impacts of chemicals is far from being solved. The effects of anthropogenic stress factors may still lead to serious damage to the structure and functions of ecosystems, although not so evident as acute mortality events have been in the early days of ecotoxicology. The assessment and quantification of these types of damages require more sensitive and sophisticated approaches than what essentially are sets of single species dose-response assays combined with some simple extrapolation method and a threshold idea.

The increase in our knowledge and the evolution of regulatory tools also produced a substantial change in the concept of what must be protected. This change appears evident considering the evolution of environmental quality criteria (EQC) and objectives (EQO) (Vighi *et al.* 2006). The first definition of water quality criteria (WQC) was proposed in 1974 by the U.S. Environmental Protection Agency (US EPA, 1974), to protect water bodies allowing for major uses of water resources (drinking, bathing, fisheries, agricultural and industrial uses) for humans. A substantially different and more ecologically based approach was proposed many years later in Europe (CSTE/EEC, 1994), stating that a water quality objective indicate the level of a chemical or physical factor that: "*should not produce conditions capable of altering the structure and functions of the aquatic ecosystem*".

A further important step has been addressed with the European WFD, which overcomes the traditional chemical-based concept of water quality assuming ecological effects as a basis of control. Therefore, the assessment of environmental quality must be defined in terms of the structure and functioning of ecological systems, rather than be only based on chemical contamination. Thus, the assessment of the community structure can indicate effects by pollutants not included in the chemical monitoring programs yet.

The new challenges

A milestone for highlighting the conceptual evolution of ecotoxicology in the third millennium is represented by a fundamental paper by Nico van Straalen (2003). According to van Straalen the goal of modern ecotoxicology is providing answers to more complex problems than the simple dose-response relationships. The predictive power of ecotoxicology for describing effects of stress factors at the highest hierarchical levels of ecological organization (i.e., biological communities and ecosystems), and the ecological realism of ERA, must be improved to better describe the actual consequences for ecosystems.

From a practical point of view, the extreme simplification of the single species ecotoxicological approach adopted in the lower tier ERA procedures for chemical safety assessment makes it difficult to extrapolate the results for predicting the actual consequences on the structure and functions of ecosystems. A ratio between PEC and PNEC higher than one is just a rough indication of the chance of an adverse effect on ecosystem to occur and cannot allow a quantification of the actual damages to ecosystem health. Some of the major drawbacks to achieve this objective are:

- the standard conditions of laboratory tests may not reproduce the time and space variability of physical, chemical, and biological parameters of aquatic and terrestrial ecosystems;
- the sensitivity of a few selected test species may not be representative of the distribution of sensitivity among the species of complex biological communities;
- the possible interactions among stress factors of different origin that may affect the ecosystem are not accounted for;
- single species tests cannot account for the ecological interactions and indirect effects that regulate the functioning of biological communities; and
- the standard endpoint measured in laboratory text (i.e., mortality, immobility, growth, etc.) may not capture more subtle effects (e.g., behavioral) which can produce significant effects at a higher level of ecological organization.

The ecological realism of the effect assessment must be substantially improved using more complex approaches accounting for the complexity of ecosystems. This improvement is made possible by the knowledge achieved during decades of development of the ecotoxicological science.

A first step in the direction of a more advanced approach may be based on the use of data referring to larger assemblages of species instead of a few selected species assumed as representative of worldwide ecosystems. The species sensitivity distribution (SSD) approach, originally developed in the late 1980s (Kooijman 1987; Van Straalen & Denneman 1989) and substantially improved for its use in ERA in the early 2000s (Posthuma *et* *al*. 2002), allows moving from the deterministic approach to a probabilistic one capable of evaluating the probability of a species being affected by a given concentration of a toxic substance.

Moreover, higher tier testing methods, such as model ecosystems (e.g., micro- or mesocosms), semi—field and field studies were developed and proposed as a possible alternative to traditional laboratory tests in ERA procedures (Van den Brink *et al*. 2005) and their use in ERA has rapidly grown. Indeed, they represent a powerful tool for improving the understanding of the responses to stress factors at a higher hierarchical level accounting for the indirect effects due to ecological interactions among the different species of a biological community that may strongly affect the actual consequences of stress factors at the ecosystem level.

Higher tier tests also allow accounting for the recovery capability of populations and communities that may occur if the stress factors are not continuous, an issue that is extremely important for understanding the consequences of the impact of pollution on ecosystems and that cannot be accounted for in the traditional laboratory single species testing.

In the field of exposure assessment, the need for an increased realism is also recognized. The concept of continuous and constant exposure, applied to the traditional ERA approaches, must be substituted by more realistic scenarios accounting for the time and space variability of contaminant concentrations determined by discontinuous and intermittent emission patterns, as well as by the complex environmental fate patterns of chemicals. Therefore, the need for the development of increasingly effective and reliable modeling approaches for the prediction of the distribution and fate of chemicals, applicable to specific and realistic pollution scenarios, is recognized. In addition, the long lifetime of many chemicals in the environment and their potential for long-range transport (LRTP) called for the development of methods for estimating their global fate and behavior (Wania & Mackay 1998).

Moreover, realistic exposure scenarios must also consider the combination of multiple stressors acting simultaneously on the exposed targets (populations, communities, ecosystems). Indeed, natural ecosystems are never exposed to individual chemicals. Complex mixtures, with variable composition in space and time, are always present in the environment and the responses of living organisms to their effects must be considered (Backhaus & Faust 2012). In addition, the interactions of chemical contaminants with other types of stressors such as physical or climatic factors (temperature, drought, etc.) may affect either the environmental behavior of chemicals or the biological response of living organisms.

The increased complexity of ecosystem characteristics and of exposure patterns considered in the ecologically realistic approaches, creates a practically infinite variability of environmental scenarios that cannot be described through experimental testing alone. Therefore, there is the need for the development of new theoretical concepts capable of representing this complexity. For assessing the effects of variable exposures and describing the processes that link exposure to effects in an organism, toxicokinetic/toxicodynamic (TK/TD) models have been developed (Ashauer *et al*. 2006), while ecological modeling may allow describing indirect ecological effects produced by the complex interactions occurring among different populations in a biological community (Thorbek *et al.* 2010).

All these improvements led to a new conceptual approach for risk characterization in modern ERA. The simplified PEC/PNEC ratio must be improved considering the ecotoxicological achievements of the last few decades. An example of the improved risk characterization approach is shown in Figure 1.2. In this scheme, ecological risk is not quantified through a simple number (i.e., a PEC/PNEC ratio) that represents a threshold that must not be exceeded to avoid adverse effects to ecosystems.

An "ecologically" based ERA, performed using more extensive information on ecologically relevant endpoints and ecologically realistic exposure assessment, should be based on a probabilistic assessment of the likelihood of a given adverse effect to occur, developing sound statistical approaches to quantify variability and uncertainty.

The scope of this book

This book presents an overview of the most modern concepts and procedures for ERA developed in the last decades.

Experimental and theoretical approaches for assessing and predicting exposure at different scale levels, from local to global, will be presented and discussed.

The effects of individual contaminants and mixtures will be described, starting from the responses at the sub-individual level up to the impacts on the structure and functions of complex communities, also accounting for the interactions with additional stress factors, particularly those depending on climate change (temperature, drought, etc.).

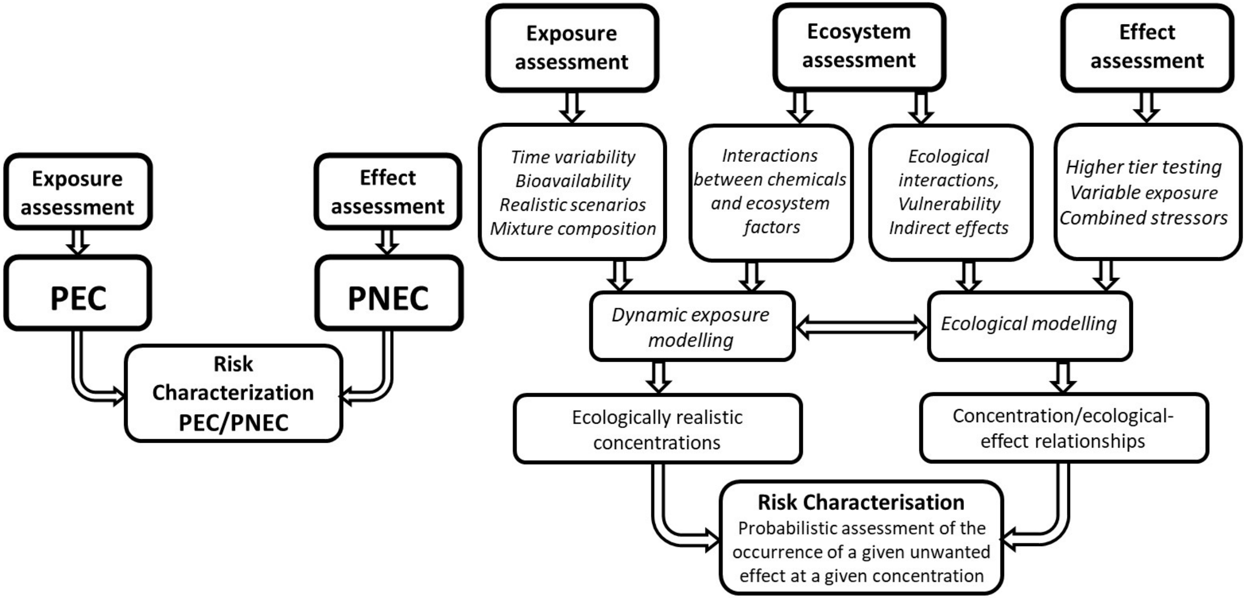

Figure 1.2. The first-tier traditional approach for ecological risk characterization (left) is based on the calculation of the ratio between a PEC (Predicted Environmental Concentration) and a PNEC (Predicted No Effect Concentration). A ratio higher than one represents the threshold above which adverse effects on ecosystems may occur. The advanced approach (right) accounts for the complexity of ecosystems, of exposure scenarios and of direct and indirect ecological responses of the biological community. The result is not a simple threshold number but an evaluation of the probability that given unwanted effects may occur (modified after EC 2013a).

The possibilities for predicting the effects and for extrapolating experimental data obtained in specific conditions to wider environmental scenarios, using different modeling approaches (QSARs, TD/TK, ecological modeling) will be explored.

The advanced procedures for risk characterization, capable of providing not only a deterministic threshold for the possible occurrence of adverse effects but also a more complete and probabilistic description of the possible changes on structure and functions of ecological systems, will be presented.

A series of chapters will be dedicated to the description of the environmental impact of specific groups of stressors, including the risks of substances of emerging concern, such as nanomaterials and plastics, and the impact of physical stressors on terrestrial and aquatic organisms.

Finally, the social issues related with the communication of risk and the most important international regulatory tools for controlling and mitigating ecosystem damages will be described.

Considering the variety of the topics treated, the book cannot be a detailed cookbook of methods and procedures. The focus will be on the conceptual basis for the understanding of the modern approaches for assessing the risk for ecosystems and for protecting the environment from anthropogenic stressors. However, advanced references for a more detailed and in-depth exploration of all topics will be provided.

CHAPTER 2

EXPOSURE ASSESSMENT

2.1 Measuring exposure

2.1.1. Sampling procedures

Rainer Lohmann

2.1.1.1. Active sampling

a. Water

Sampling contaminants in water is made difficult, particularly for organic chemicals, by their wide range of aqueous solubilities. Some chemicals, such as PFOS, hexachlorocyclohexane isomers or endosulfan, are highly soluble, and collecting a few liters of water has been sufficient for their detection (Muir & Lohmann 2013). Other compounds, including most PCBs, PCDD/Fs and OCPs, are only present in trace (often pg/L) amounts, and often require the collection of large volumes of water through a combination of (for particles) filter-sorbent sampling trains. Water samples can be collected near the surface through hand-held sampling containers, or by relying on Niskin bottles that can be triggered to collect water at a specific depth. Pump-based sampling operations are used to collect and filter larger water volumes, for which the depth can often be specified. A commercial battery-operated unit (e.g., Inflitrex) can be lowered to depth to pump water through a filter-sorbent sampling train for a specific period. In extreme circumstances, a stainless-steel pump has been lowered overboard from ships to filter water at different depths in the North Atlantic and Arctic Oceans.

No matter how aqueous samples are collected, organic chemicals partition between colloidal material, particles and the freely dissolved phase (Schwarzenbach *et al.* 2016). The separation of being particle-bound or dissolved is operationally defined by the filter's cutoff size and retention on the filter, while there is no easy way to distinguish chemicals bound to the colloidal fraction from the “dissolved phase.” Instead, the routine measure of the concentration of dissolved organic carbon (DOC) can be used, in combination of the chemicals' DOC-water partitioning, to estimate (and potentially correct) for the "third" phase effect on measured dissolved concentrations.

b. Air

Low- or high-volume sampling of Persistent Organic Pollutants (POPs) is now routinely achieved through a sampling train consisting of a filter for collecting particles, combined with a gas-phase adsorbent. For filters, either a glass fiber filter (GFF), or a quartz fiber filter (QFF) are typically used, while either polyurethane foam (PUF) plugs or PUF with resin adsorbents (e.g., XAD) are most typically used (Bidleman & Melynuk 2019). Numerous studies have highlighted the potential sampling artifacts associated with this sampling approach, though field results do not suggest a major problem with the filter-sorbent method. As an alternative that minimizes sampling artifacts, denuders (that remove the gas-phase compounds first) have been developed (Kaupp and Umlauf, 1992). Overall, though, the high-volume filter-sorbent sampling method remains the basis for most active air sampling operations, such as in the Arctic Monitoring and Assessment (AMAP) Program (Hung *et al.* 2010).

Figure 2.1. A high-volume active air sampler (with opened lid) on a roof in Providence. Rhode Island. On the left, an inverted stainless steel bowl housing a passive air sampling can be seen (Photographed by Rainer Lohmann).

c. Biota

The collection of biological specimens or samples relies on well-established methods of gathering and hunting. For fish and aquatic species, samples are often collected via nets of different sizes. Plankton nets (which are incidentally also used for microplastics), depending on the cut-off size, capture phyto- and zooplankton; larger nets are used for bigger species (fish), while seines, trawls, reels, and hook lines are also relied upon. Electrofishing is also used to gather larger yields quickly. Often, amateur or professional fisher(wo)men are relied upon to gather representative samples. Benthic species can be collected through manual collection and sieving to capture clams and worms, while crabs and lobsters can be captured in cages and traps. In the Arctic regions, hunting of marine mammals often relies on indigenous and local communities. Similar sampling strategies (hunting and trapping for larger animals, digging and sieving) are relied upon in the terrestrial environment, too.

2.1.1.2. Passive sampling

Passive sampling typically involves a receiving phase, typically a polymer, sometimes a sorbent-filled membrane, which collects HOCs, and results can be converted into dissolved/porewater concentrations. Passive samplers typically operate either in the kinetic (linear sampling uptake) or equilibrium sampling regime (Figure 2.2). Samplers operating in the linear uptake phase approximate time-weighted average conditions during the deployment period, while equilibrium samplers represent the chemical activity (fugacity) of the dissolved phase. The most common passive sampling materials consist of simple polymers, such as low-density polyethylene (LDPE) (Adams *et al.* 2007; Lohmann 2012) or silicone rubber sheets (Smedes 2019), or silicone-coated solid-phase micro extraction (SPME) fibers (Muijs & Jonker 2012).

To ensure quality control, sometimes performance reference compounds (PRCs) are used as a means to gauge how far compounds have moved towards equilibrium (Figure 2.3). Ideally, several PRCs with a wide range of physico-chemical properties are chosen that cover the range of the target analytes. To ensure that there is no competition with target HOCs, PRCs are chosen that are either isotopically labeled (e.g., 13C-HOCs, D-PAHs), or compounds are used that were not intentionally produced (e.g., PCB congeners that were not part of commercial Aroclor mixtures). Booij *et al.* (2002) provided a method of adding PRCs to single-phase polymers, and in subsequent work detailed how to best interpret the data obtained from the loss rates of PRCs (Booij & Smedes 2010).