Monitors of Organic Chemicals in the Environment

Monitors of Organic Chemicals in the Environment

Semipermeable Membrane Devices

James N. Huckins
Columbia Environmental Research Center
Center, Missouri, USA

Jimmie D. Petty
Columbia Environmental Research Center
Center, Missouri, USA

Kees Booij
Royal Netherlands Institute for Sea Research
Den Burg, The Netherlands

Springer

James N. Huckins
USGS Columbia Environmental
Research Center
4200 New Haven Road
Columbia, Missouri 65201
jhuckins@usgs.govc

Jimmie D. Petty, Ph.D.
USGS Columbia Environmental
Research Center
4200 New Haven Road
Columbia, Missouri 65201
jdpetty@usgs.gov

Kees Booij, Ph.D.
Royal Netherlands Institute for Sea
Research
P.O. Box 59
1790 AB Den Burg
The Netherlands
booij@nioz.nl

Cover photos: *(Left)* Deployment of SPMDs under Antarctica ice, courtesy of Carl Orazio, USGS. *(Right)* Exposure chambers with passive samplers deployed in Australian grasslands, courtesy of Don Butler, Australian Environmental Protection Agency. The photo above the title is a standard lipid-containing SPMD, courtesy of Randal Clark, USGS (see Figure 1-1, p. 18, for a complete description).

Library of Congress Control Number: 2005933715

ISBN-10: 0-387-29077-X
ISBN-13: 978-0387-29077-5

Printed on acid-free paper.

© 2006 Springer Science+Business Media, LLC
All rights reserved. This work may not be translated or copied in whole or in part without the written permission of the publisher (Springer Science+Business Media, LLC, 233 Spring Street, New York, NY 10013, USA), except for brief excerpts in connection with reviews or scholarly analysis. Use in connection with any form of information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed is forbidden.
The use in this publication of trade names, trademarks, service marks, and similar terms, even if they are not identified as such, is not to be taken as an expression of opinion as to whether or not they are subject to proprietary rights.

Printed in the United States of America. (TB/MVP)

9 8 7 6 5 4 3 2 1

springer.com

This book is dedicated to the memory of Jon Lebo. Jon was integrally involved in many aspects of the development and especially in the field deployment of SPMD technology. His untimely death cut short a very productive research career. Jon was a good friend and an excellent colleague, and we will all miss his insight and research contributions.

Foreword

Modern, industrialized societies depend on a wide range of chemical substances such as fuels, plastics, biocides, pharmaceuticals and detergents for maintaining the high quality lifestyle to which we aspire. The challenge is to ensure that while we enjoy the benefits of these substances, their inevitable release into our biosphere does not result in unwanted human and ecosystem exposures, and the risk of adverse effects. One response to this challenge has been the extensive effort to detect and analyze or monitor a multitude of chemicals in a variety of environmental media, especially toxic organic compounds in air, water, soils and biota. The conventional monitoring strategy of sampling liters or kilograms of the environmental medium followed by analytical determination of the quantity of chemical in the sample extract has been the successful cornerstone of investigative environmental chemistry. No doubt, it will continue to be so. An extensive literature on these traditional techniques has evolved over the years.

In parallel with conventional techniques, and I believe entirely complementary to them, a variety of *in situ* sensing systems have been developed which operate on the principle of the preferential partitioning of contaminants into a device, often at concentrations which are large multiples of environmental levels. Advocates point out that these partitioning devices have the advantage of integrating chemical concentrations over a prolonged period, thus "averaging" ambient levels. Their high partition coefficients can yield significant quantities of analyte and reduce problems arising from short-term pulses of concentration and from sample contamination. They can be less expensive, require less sample work-up and can be deployed more widely. They may or may not approach thermodynamic equilibrium or equi-fugacity with the media they sense, thus interpretation of the

partitioned quantities can be challenging but possible when appropriate methods are applied. Proponents have demonstrated ingenuity in designing, modifying and exploiting the valuable features of these partitioning devices, not only to sense our environment by absorbing chemical from it, but also by using them to deliver chemical in controlled quantities in laboratory settings such as bioassays.

Accordingly, as this technology has matured and the literature has expanded, the need has arisen for a comprehensive and authoritative review of these devices, the principles on which they operate and the practice of using them. Fortunately and appropriately, Huckins, Petty and Booij have taken on this task and share with the reader their long experience in designing, using, and interpreting the performance of these devices. In this volume, all relevant aspects of these devices are addressed, thus the reader will find it an invaluable source of information and insight. It therefore adds significantly to the environmental literature by supplementing the many texts concerning traditional chemical analysis.

In closing, it is satisfying to note two themes that permeate this work. The authors have been notable for their willingness to share their expertise and enthusiasms with the wider community of environmental scientists and managers. The result has been a continuing evolution of a variety of partitioning devices in an innovative, open and constructive atmosphere in which the over-riding goal has been to improve and maintain environmental quality. Finally, it is satisfying and perhaps ironic to see acknowledgment that these ingenious artificial devices have their ancestry in observations of natural bioconcentration of contaminants in plants and animals. The thermodynamic or partitioning mechanisms that have resulted in the regrettable contamination of plants and animals, and often in their demise, are now being exploited to protect them and us. We owe a debt of gratitude to the authors for the rigor with which they present the science and technology of these devices and their sensitivity to the need for environmental protection to which this book contributes.

DON MACKAY
Peterborough, Canada

Preface

The complexity of the modern world is often beyond the explicit understanding of any individual. Much of this complexity stems from the technology inherent in our lifestyle, resulting in a standard of living undreamed of by some futurists. The standard of living, in terms of comfort, convenience, health and safety is however, not without its cost.

The quality of life mankind has come to expect often comes with a cost to the environment, which includes the adverse effects of chemical contaminants. These contaminants are global in nature and are of increasing concern. The sources of anthropogenic pollution are legion and all too often the release of contaminants into environmental systems is considered an unavoidable cost of development. As a result, many areas of the global environment are under stress from a broad array of chemicals, both waterborne and airborne.

Because of the potential of these chemicals to adversely affect organisms in diverse ecosystems and ultimately humans, numerous resource management and regulatory agencies globally require high quality data defining the presence, identities and potential biological consequences of exposure to environmental contaminants. During the past 50 years, successful control measures have been implemented for many well known contaminants. Substitutes are now being used for many toxic contaminants, e.g., organochlorines pesticides such as DDT, but the overall number and variety of chemicals used by modern societies has increased, while measures to stem their inadvertent release into environmental systems have not been fully successful. Thus, the need continues for new technologies and techniques to provide reliable data for assessing the potential threats associated with low levels of increasingly complex mixtures of environmental contaminants.

The authors have been intimately involved in conducting research to address many aspects of environmental contaminants for about three decades. Historically, samples of environmental matrices, particularly water and air have been collected at narrow windows of time (i.e., minutes or several hours) which are not representative of the exposure experienced by organisms. Consequently, we initiated the development of what would ultimately be the semipermeable membrane device (SPMD). The SPMD has subsequently proven to be an effective passive sampler for a wide range of hydrophobic contaminants in multiple media. To date, there are more than 180 peer reviewed publications in the open scientific literature, where SPMDs are used for a variety of applications. Some of these publications are critical of the use of passive samplers for certain applications. However, constructive criticism has greatly aided in defining information gaps and limitations of the passive sampling approach.

Clearly, SPMDs are becoming a mature technology, with increasing global acceptance as an effective and reproducible passive sampling system for individual contaminants or complex mixtures. However, new applications continue to be described and analytical methodology continues to be refined. The growing interest in the passive sampling approach and its many potential applications ensures that SPMDs and other passive samplers represent a fertile research area for scientists involved in studies targeting the presence or effects of environmental contaminants.

It is the intent of the authors to provide a general introduction to passive samplers and a detailed description of SPMD technology. In short, this work is intended as a guide or handbook for users and managers faced with contaminant issues. We address the topical areas of study design, field deployment, sample processing and residue enrichment, analysis of accumulated chemicals, models for determining ambient environmental concentrations of target compounds, bioassay of SPMD extracts, quality control/quality assurance approaches, and selected case studies describing the results of field deployments of SPMDs. Furthermore, the reader will find that a number of aspects of the technology await additional research and development to fully utilize the potential of SPMDs to address contaminant issues.

It is our sincere hope that this book will provide not only details and explanations for those scientists interested in applying SPMDs and other passive samplers, but that it also serves as a springboard for new research to expand and enhance the field of passive sampling. Also, it is important that the reader realize that many of the techniques and mathematical models presented herein apply to other passive samplers as well. We are confident that in the future, managers and regulators will increasingly realize the utility of SPMDs and other passive samplers for addressing site specific and global contaminant issues.

Acknowledgments

> "*What a person thinks on his own without being stimulated by the thoughts and experiences of other people is even in the best case rather paltry and monotonous.*"
>
> ALBERT EINSTEIN

The authors gratefully acknowledge the many people that have contributed to the development and application of the SPMD technology. These include environmental chemists, biologists, engineers and technical specialists who have contributed their ideas and efforts. We also acknowledge the numerous agencies and scientific organizations worldwide who have demonstrated their faith in our work by granting funds for the research and development of SPMD technology.

The authors acknowledge the support of the U.S. Geological Survey and the Royal Netherlands Institute for Sea Research during the research and development of SPMDs and during the writing of this book. Also, the research in this book represents the combined efforts of many other colleagues and we are very much in their debt. In particular, we thank Randal Clark and Lynne Johnson for their efforts to meet format requirements of this manuscript and Don Mackay for the Foreword. Last but not least, the authors recognize the patience of their families for enduring the diversion of their attention during the writing of this book.

Contents

1. Introduction to Passive Sampling **1**

1.1 The Need for Passive In Situ Samplers 1
1.2 Passive Sampler Development 7
1.3 Topics Covered in Subsequent Chapters 23
1.4 References 24

2. Fundamentals of SPMDs **29**

2.1 SPMD Description and Rationale 29
2.2 Applicability of SPMDs 32
2.3 Accumulation of Chemicals by SPMDs 36
2.4 Passive Sampler Fundamentals and Terminology 38
2.5 References 41

3. Theory and Modeling **45**

3.1 Uptake Models 45
3.2 Kinetic and Equilibrium Sampling 49
3.3 Dissipation of Performance Reference Compounds (PRCs) 50
3.4 Potential Effects of Dissolved Organic Carbon (DOC)
on SPMD Calibration Data 51
3.5 SPMD-Water Partition Coefficients 53
3.6 Water Sampling Rates 55
3.7 Pore Water Sampling 72

3.8 Groundwater Samplng 74
3.9 Air Sampling 75
3.10 References 81

4. Study Considerations 87

4.1 Overview 87
4.2 Sources of SPMDs 87
4.3 Evaluation of Components and Preparation of SPMDs 88
4.4 Specifications of the Standard SPMD 89
4.5 Pre-Exposure Considerations 89
4.6 Storage, Transport and Retrieval 93
4.7 Deployment Devices 94
4.8 References 98

5. Analytical Chemistry Related to SPMDs 101

5.1 Analytical Speed, Selectivity and Quantitation Limits 101
5.2 Quality Control 103
5.3 Sample Preparation 107
5.4 Potential Interferences 111
5.5 Instrumental Analysis 113
5.6 Data Format and Comparability 113
5.7 References 117

6. Bioassay of SPMD Extracts or Diluents 121

6.1 Overview and Rationale of the SPMD-Toxicity Screening Approach 121
6.2 Microtox and Mutatox 124
6.3 Mixed Function Oxidase-7-Ethoxyresorufin-*O*-Deethylase (MFO-EROD) 127
6.4 Neurotoxicity Endpoints 128
6.5 Endocrine Effects 131
6.6 Exposure of Laboratory Animals to SPMD Extracts 132
6.7 Overview of Additional Assays 134
6.8 Potential Interferences 134
6.9 References 136

7. Comparisons to Biomonitoring Organisms 139

7.1 Background 139
7.2 Implications of Selected Models Used for SPMDs and BMOs 142
7.3 Comparison of SPMDs and BMOs 144

7.4 Relative Amounts Accumulated 150
7.5 Independence of Concentration Factors Relative to Exposure Concentration 153
7.6 Similarity of Elimination or Equilibration Rate Constants 155
7.7 Comparability of Estimated and Measured *BCF*s or *BAF*s 158
7.8 Dietary Uptake and Biomagnification 160
7.9 Do SPMDs Qualify as Biomimetic Samplers? 160
7.10 References 162

8. Selected Case Studies 169

8.1 Review of SPMD Applications 169
8.2 Air-Water-Microlayer Equilibrium 169
8.3 Sampling Indoor Air 171
8.4 Further Comparisons of Bivalves and SPMDs 173
8.5 Estimation of Exposure to Dioxin-Like Compounds Using Sediments, Caged Fish, and SPMDs 175
8.6 Using SPMDs in Conjunction with Bioassays and Chemical Analysis to Characterize Toxic Pollutants 177
8.7 References 180

Appendix A: SPMD Calibration Data 183

A.1 SPMD-Water Partition Coefficients 183
A.2 Water Sampling Rates 185
A.3 Air Sampling Rates 198
A.4 References 200

Appendix B: SPMD Bibliography 203

Glossary 215

Index 219

Chapter 1

Introduction to Passive Sampling

1.1. THE NEED FOR PASSIVE IN SITU SAMPLERS

Tens of thousands of chemicals are in commercial production throughout the world and the total number increases each year (Mackay et al., 1992a). Unfortunately, significant amounts of many of these anthropogenic chemicals are released into terrestrial and aquatic ecosystems. Organic compounds represent the largest portion, in terms of numbers of these chemicals. The distribution and fate of contaminants in environmental systems is controlled by three factors: 1) physicochemical properties of the chemical; 2) environmental conditions (e.g., hydrodynamics, pH, and solar radiation) and physicochemical properties of abiotic components (e.g., organic content of soil and sediment), and 3) the composition, mass, and physiological, anatomical and behavioral characteristics of the species inhabiting exposed ecosystems. Many studies and programs worldwide are designed to monitor for the presence of environmental contaminants and to determine trends in their distribution and concentrations. In some cases, data from these studies and programs are used for guidance on chemicals which are of sufficient concern to warrant further study.

To aid in assessing the risks associated with large numbers of environmental contaminants, quantitative-structure-activity relationships (QSARs) have been developed covering nearly all biological effects or other endpoints in both aquatic and terrestrial species (Connell, 1990). QSARs relate chemical structural

characteristics or measured physiochemical properties to endpoints such as bioconcentration factors (*BCF*s; i.e., the ratios obtained by dividing the equilibrium concentrations of chemicals in an organism by the concentrations of the same chemicals in the surrounding medium, where residue uptake is due to water or air alone) or toxicity. Mackay et al. (1992a) have defined a subset of QSARs as quantitative-structure-property relationships (QSPRs). QSPRs use chemical structure alone to predict contaminant physicochemical properties, partitioning behavior, fate, and the tendency to be accumulated in organism tissues. QSPRs can also be used to reveal likely errors in data representing measured values of physicochemical properties, which enhances the quality of data used for QSAR estimates. Both QSARs and QSPRs are widely accepted as screening tools for prioritizing research efforts on environmental contaminants. Some QSPRs can be used to estimate the most likely routes of chemical exposure. For example, the dissolved phase is the most likely route of aquatic organism exposure for compounds with log octanol-water partition coefficients (K_{ow}s) ≤ 6 (Connell, 1990). Similarly, the vapor phase is the most likely route of exposure for many terrestrial organisms, when log octanol-air partition coefficients (K_{oa}s) of organic compounds are ≤ 8.5 (McLachlan, 1999). In general, these predictions have been borne out by laboratory and field studies (Connell, 1990; McLachlan, 1999), but there are exceptions (Mueller, 2004).

The development of multi-media mathematical models (MMMs) by Neely (1980), Mackay and Paterson (1981), Mackay et al. (1992a, 1992b, 1997) and others (Klein and Schmidt-Bleek, 1982; Schnoor et al., 1982; Rand and Petrocelli, 1985) has provided a more holistic means to model chemicals released into the environment. MMM models permit simultaneous estimation of the transport, distribution, fate and bioconcentration (uptake from water alone) or bioaccumulation (uptake from water and diet) of contaminants in multiple environmental compartments. Furthermore, the development of the "fugacity" (i.e., escaping tendency) approach by Mackay and Paterson (1981) provides a realistic mechanism by which diverse environmental data can be modeled. In general, QSPRs (Mackay et al., 1992a) provide adequate data for screening chemicals with these models. The media modeled may include air and associated particulates, water, soil, suspended and benthic sediments, and biota. Use of MMM models beyond chemical screening requires knowledge of the characteristics of relevant components in the compartments, and the magnitude of contaminant inputs or residue concentrations in one or more compartments. Frequently, the quantities of chemicals entering an environmental system are unknown. Thus, validation of mathematical models generally requires direct measurements of the concentrations of target compounds in one or more environmental medium. In cases where concentrations vary temporally or equilibration times are long, multiple sampling through time is necessary.

Although QSARs, QSPRs, and MMMs generate screening data, which provide a much-improved focus on the risks associated with environmental contaminants, organism exposure must be confirmed by direct determination of contaminant identities and measurement of concentrations in water or air or estimated

by indirect measurements (e.g., via sorbents). At this juncture, a definition of exposure and related terms is instructive. In the broadest sense, exposure is defined as the concentration of a chemical in the media processed by organisms of concern (Rand and Petrocelli, 1985), where chemical contact is largely controlled by factors external to the species of concern. More specifically, exposure is defined as the amount of chemical residues directly contacting an organism's membranes capable of residue exchange, i.e., skin, gills or lungs and gut. Landrum et al. (1994) describe this level of exposure as the chemical "encounter-volume rate", which can be given as L g^{-1} d^{-1} of the exposure medium. The "bioavailability" of a chemical is also a key determinant in chemical exposure. In an environmental context, bioavailability can be viewed as the ratio of a chemical's uptake rate (L g^{-1} d^{-1}) divided by the encounter-volume rate (Landrum et al., 1994). Using this definition, environmental bioavailability is equivalent to the combined inputs from skin absorption, gill or lung extraction and gut assimilation. Finally, dose is defined as the molar concentration of a chemical at a specific site of toxicological action. Because the dose of a chemical to an organism is often difficult to determine (an exception may be the use of critical body residues for narcotic acting chemicals), most risk assessments rely on measurements or measurement-based estimates of chemical exposure.

Clearly, the choice of analytical methods used for measuring environmental contaminant concentrations potentially affects mathematical model validation, the quality and relevance of environmental monitoring data, and the outcomes of environmental risk assessments. Although method accuracy and precision are important, other factors should be considered as well. Based on the example QSPRs given earlier, the method selected should be capable of discriminating between the relevant (bioavailable) fractions of chemicals from the total amounts of chemicals present in environmental compartments. Furthermore, in cases where chemicals bioconcentrate and their environmental concentrations vary temporally, determination of time-weighted average residue concentrations provides a more complete picture of organism exposure than those concentrations measured in single or a few grab samples. In light of the importance of environmentally relevant concentration data for the assessment of chemical exposure, a brief review of commonly used sampling or monitoring methods is appropriate.

1.1.1. Active Sampling Methods for Water and Air

Active sampling techniques represent the most widely used approach for the collection and extraction or trapping of contaminant residues in water. "Active sampling" refers to those methods that require physical intervention or external energy input for sample collection and/or residue extraction or trapping. Often, samples are excised or removed (i.e., grab sampling) from the exposure medium before residues are extracted. Traditionally, grab samples of water were nearly always extracted with organic solvents (i.e., liquid-liquid extraction, LLE). Using the LLE approach, the data generated are limited to the total chemical concentration

in all waterborne phases, which includes microorganisms and algae, particulate organic carbon (*POC*), dissolved organic carbon (*DOC*), inorganic particulates, and the dissolved phase. Thus, the fraction of the total waterborne residues represented by the dissolved phase (i.e., the most readily bioavailable phase) is not distinguished from generally less bioavailable residues in other waterborne phases. To reduce the use of organic solvents and to discriminate between aqueous residues associated with *POC-DOC* and the more bioavailable dissolved phase, solid-phase extraction (SPE) systems were developed. This method is based on the percolation or pumping of water or air samples through columns, tubes or cartridges of sorbents consisting of polymeric phases bound to silica cores or various types of polymeric beads or foam. The SPE approach also includes Empore extraction disks (Kraut-Vass and Thoma, 1991). These disks or membranes consist of a Teflon fibril network loaded with SPE sorbents, but the particle size of these sorbents is smaller than those described for standard SPE columns. Although methods using SPE cartridges or columns and Empore disks are categorized as active sampling, the sample extraction involves diffusional and partitioning-sorptive steps. Thus, at some fundamental level active sampling involves passive (defined later) processes.

In cases where water is turbid, samples are generally filtered through glass fiber filters (GFF) prior to percolation through sorbents. This step recovers waterborne particulates and microorganisms with average diameters >0.7 μm, which are analyzed separately. However, chemicals associated with colloid-sized particulates and *DOC* are not removed by GFFs.

More recently, solid-phase micro extraction (SPME) fibers have gained widespread acceptance as equilibrium samplers for the extraction of water samples (Arthur and Pawliszyn, 1990). The SPME fiber consists of a small-diameter fused silica fiber coated with one of several polymeric phases for the sorption of analytes. The polymeric-film thickness for commercially available SPMEs generally ranges from 7 to 100 μm with the total phase volume of a 1 cm segment being 0.028 to 0.612 μL. Traditionally, SPME methods are only applied to excised samples and stirring is used to expedite analyte extraction or times to equilibrium. Also, analyte concentrations in SPMEs generally represent the total residues in a water sample (Mayer, 2003). The approach has a number of advantages over active sampling methods, which include the elimination of pre-filtration and organic solvent extraction steps, typically required for sample preparation, and the direct injection of the total sample into a gas chromatograph (GC) for analysis.

Nearly all grab sampling methods suffer from potential problems with sample preservation such as losses due to volatilization, sorption to container walls, and chemical degradation. For water samples, some of these problems can be avoided by the addition of an appropriate "keeper" solvent immediately after sample collection. However, the use of SPEs and SPMEs is thereby precluded and the ability to discriminate residue distribution among water-borne phases is lost. Data from grab samples and other active sampling methods represent only a single point or small window in time, which does not account for temporal variations in contaminant concentrations at study sites. Thus, adequate assessment of organism exposure

requires labor-intensive multiple sample collections. Generally, the volume of collected samples is limited to ≤5 L, due to the difficulty in the handling, transport, processing, and extraction of large amounts of water. Consequently, method quantitation limits (MQL) may not be adequate for the analysis of trace (≤ 1 μg L^{-1} or mg m^{-3}) or ultra-trace (≤1 ng L^{-1} or μg m^{-3}) levels of hydrophobic organic chemicals (HOCs). These relatively low quantitation limits are especially needed for assessing the environmental significance of HOCs that bioconcentrate (uptake from water by respiration or skin absorption) or bioaccumulate (uptake via skin absorption, respiration, and diet), and for some highly toxic organic compounds, which may or may not bioaccumulate.

To overcome the limitations of grab sample preservation and method sensitivity, *in situ* large-volume SPE systems, equipped with submersible pumps, have been developed (e.g., the Infiltrix Column System by AXYS Environmental Systems, Sidney, BC, Canada) for sampling aquatic environments. An alternative method for ultra-trace analyses of HOCs in water is the Goulden large sample extractor developed at the Canada Centre for Inland Waters (Forbes and Afghan, 1987). Detection limits are much lower for these types of systems (Rantalainen et al., 1998), but significant concerns still exist about sample contamination, analyte losses to exposed surfaces, filter plugging in turbid waters, the use of toxic chlorinated solvent, and procedurally mediated changes in the distribution of contaminants among phases constituting environmental waters. For many studies or programs involving multiple sites, *in situ* large-volume samplers are often too labor intensive and costly to use at all sites. Thus, simultaneous replication of sampling for statistical purposes is seldom performed.

Methods used for the active sampling and extraction or concentration of organic vapors in air are generally related to those described for water. For example, samples of volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs) are often collected and concentrated by *in situ* pumping of air through SPE tubes or cartridges. Even when grab sampling is the method of choice (e.g., VOC sample collection in Summa-polished canisters and Tedlar bags), SPEs are often used for sample preconcentration or trapping prior to instrumental analysis. In all cases, GFFs are used when discrimination between the vapor and particulate phases is needed to estimate the relative contributions of the two-exposure pathways (e.g., SVOCs with log K_{oa}s > 8.5). The SPE sorbents used to concentrate vapors of trace to ultra-trace levels of SVOCs in large volumes of air include polyurethane foam plugs, Tenax and XAD-2 resin (Ockenden et al., 1998). These sorbents are also used for the extraction of ultra-trace levels of dissolved-phase waterborne residues (Rantalainen et al., 1998).

Many of the shortcomings listed for active sampling of waterborne residues apply to the analysis of VOC and SVOC vapors in air. Also, sampling analytes in an equivalent mass of air and water requires about a 10^3 larger volume of air, thereby practically limiting the applicability of grab sampling for the analysis of trace and ultra-trace SVOCs in air. Furthermore, because sampling sites for assessing global-atmospheric transport of contaminants are often in rugged terrain in remote

locations, the choice of sampling methods may be limited by the size, weight and portability of the sampling apparatus and the need for electrical power.

In summary, active sampling and extraction or trapping methods provide reasonably reliable information on the total waterborne and airborne concentrations of HOCs, but only during one point in time or a relatively brief interval of time, which is in marked contrast to the exposure duration of most organisms. Most of these methods permit some discrimination between analyte concentrations in material trapped by the filter, representing the total residues associated with *POC*, inorganic particulates, and microorganisms (e.g., algae and spores), and dissolved and vapor phase residue concentrations in filtrates. Unfortunately, the potential effects of sampling, transport and filtration on the environmental distribution of contaminant residues among the various phases in water and air are difficult to predict *a priori*. For example, solutes and vapors can adsorb on GFFs and be misidentified as part of the particulate phase, while residues associated with fine particulates can desorb and be incorrectly identified as part of the dissolved phase (Mackay, 1994). Thus, residue concentrations in filtrates are not necessarily representative of the dissolved or vapor phases in the undisturbed sample media. With the exception of programmable *in situ* active sampling systems (e.g., the Infiltrix water sampling system and high volume [HiVol] air samplers) sample size may not be adequate for the analysis of trace and ultra-trace levels of contaminants. Also, active sampling methods (excludes the Infiltrix system) are generally relevant only to a few points in time and do not provide time-weighted average (TWA) concentrations. Strictly speaking, measurement of TWA concentrations during a specified time period requires continuous, additive extraction (i.e., integrative sampling, where the extraction medium acts as an infinite sink) of an exposure medium. TWA concentration data are useful indicators of organism exposure to HOCs.

1.1.2. Biomonitoring Organisms for Water and Air

Biomonitoring organisms (BMOs) are often used for chemical risk assessments because they address many of the limitations related to the biological relevance of data from point in time analytical-based sampling methods. In particular, residues accumulated in BMO tissues were, by definition, bioavailable. Also, many HOCs are highly concentrated in fatty tissues of organisms by the process of bioconcentration or bioaccumulation. Unfortunately, certain physiological, anatomical and behavioral characteristics specific to the BMO species used and site-exposure conditions can affect the magnitude and variability of HOC concentrations accumulated in tissues (Livingstone et al., 1985; Barron, 1990; Huebner and Pynnönen, 1992; Gobas et al., 1993; Goudreau et al., 1993; Gilek et al., 1996; Björk and Gilek, 1997; Moring and Rose, 1997; Baumard et al., 1998a, 1998b; Axelman et al., 1999; Wang and Fisher, 1999; Baussant et al., 2001, Gray, 2002). For example, investigators have found that bioaccumulation factors (*BAF*s; i.e., the ratios obtained by dividing the equilibrium concentrations of chemicals in an organism by the concentrations of the same chemicals in the surrounding

medium, where residue accumulation is based on water or air and the diet) of HOCs in many organisms are affected by residue metabolism (Livingstone et al., 1985; Moring and Rose, 1997), food ration (Björk and Gilek, 1997), size of the organism (Gilek et al., 1996), and toxic stress (Huebner and Pynnönen, 1992; Goudreau et al., 1993). This data suggests that *BCF*s and *BAF*s may be site- and species-specific, and do not necessarily represent thermodynamic equilibrium, where residues in tissues are proportional to environmental exposure concentrations (Huckins et al., 2004). Thus, steady state is often a more appropriate descriptor of constant tissue concentrations than equilibrium. Furthermore, the concentrations of HOC residues in tissues of BMO species may not be representative of tissue concentrations in species of concern (Gray, 2002). Altogether, these complications limit the applicability of aquatic BMOs for the extrapolation of exposure concentrations, and for determining HOC sources and concentration gradients.

Terrestrial BMOs have also been widely used for monitoring environmental contaminants. In particular, the lipid-like waxy cuticle layer of various types of plant leaves has been used to monitor residues of HOCs in the atmosphere. However, some of the problems associated with aquatic BMOs apply to terrestrial BMOs as well. For example, Böhme et al. (1999) found that the concentrations of HOCs with log K_{oa}s < 9 (i.e., those compounds that should have attained equilibrium) varied by as much as 37-fold in plant species, after normalization of residue concentrations to levels in ryegrass (*Lolium* spp.). These authors suggested that differences in cuticular wax composition (quality) were responsible for this deviation from equilibrium partition theory. Other characteristics of plant leaves may affect the amount of kinetically-limited and particle-bound HOCs sampled by plant leaves but to a lesser extent (i.e., $<$4-fold), these include age, surface area, topography of the surface, and leaf orientation.

1.2. PASSIVE SAMPLER DEVELOPMENT

In this work, we define “passive” samplers as human-made devices where sample collection and residue extraction occur simultaneously in a completely passive manner. The sampling or concentration process is mediated by the diffusion of chemicals from a matrix where chemical fugacity or potential is high to a matrix (receiving medium or sorbent) where chemical fugacity or potential is low. Three requirements must be met to derive reasonable estimates of ambient concentrations of analytes from their concentrations in a passive sampler: 1) concentrations in the device must be proportional to environmental concentrations and the associated rate constants for chemical exchange and partition coefficients must be independent of ambient analyte concentrations; 2) calibration data (rate constants and partition coefficients) applicable to site conditions must be available for target compounds; and 3) the sampling process should not significantly reduce analyte concentrations in the medium sampled. Also, if samplers are calibrated in the laboratory or by the use of mathematical models, the potential effects of

site-specific exposure conditions must be taken into account. Unfortunately, efforts to validate the accuracy of estimates of environmental concentrations based on passive samplers are often impeded by the lack of an accurate independent method for measuring trace or ultra-trace residues of analytes in environmental media. Furthermore, the discrimination of dissolved and vapor phase residues from those associated with particulates, aerosols, micelles or macromolecules can be problematic for both active and passive sampling methods.

In the following sections we highlight only selected works that have contributed toward the further development of passive samplers for SVOCs and/or HOCs. The literature related to the development and use of passive samplers for monitoring gases or VOCs in occupational environments is large. However, these publications are discussed only briefly, because lipid-containing semipermeable membrane devices (SPMDs) are primarily designed for SVOCs.

1.2.1. Air

The first passive samplers were small personal diffusional monitors (PDMs). These devices were developed in the early seventies and were designed to determine occupational exposure to VOCs in air using linear uptake kinetics. PDMs contain a sorbent or reactive material separated from the sampled medium by a rate limiting air filled diffusional zone or a rate limiting semipermeable membrane (Fowler, 1982). The sorbent or reactive material acts as an infinite sink during an exposure. Analytes are accumulated in an integrative manner because no significant losses of accumulated residues occur during an exposure, regardless of any decreases in ambient concentrations. This performance characteristic permits the determination of TWA analyte concentrations. The American Conference of Governmental Industrial Hygienists (ACGIH) has accepted PDMs as the best available technology to gauge human exposure to most VOCs in occupational environments (ACGIH, 1990). In particular, PDM-derived TWAs provide the most satisfactory way of determining the compliance of the work atmosphere to threshold limit values of VOCs (ACGIH, 1990).

More recently, Harner et al. (2003) coated ethylene vinyl acetate (EVA) onto glass (polymer coated glass [POG]) for use as fugacity sensors or equilibrium samplers of SVOCs in indoor and outdoor air. The EVA film thickness was 1.1 and 2.4 μm depending on the application and as expected, SVOC sorption capacity and times to equilibrium were shown to be directly proportional to film thickness. The clearance capacity (E_v; volume of sample medium cleared of chemical) of a sorbent for an analyte is given by

$$E_v = K_{pa} A \delta_p = K_{pa} V_p \quad (1.1)$$

where K_{pa} is the polymer-air partition coefficient, A is the surface area, δ_p is film thickness and V_p is the volume of the polymeric phase. Equation 1.1 indicates that sorption capacity for vapor-phase samplers is the volume of air cleared of

vapor-phase chemical for a specified volume of sorbent or partitioning phase, and that for a fixed A, E_v is directly proportional to both film thickness and K_{pa}.

For a 1 μm film thickness, the surface-area (A; cm^2)-to-sorbent-volume (V; cm^3)-ratio (AV^{-1}) of the Harner et al. (2003) device is 1×10^4 cm^{-1} with a total sorbent volume of 2.9 μL. Earlier, Wilcockson and Gobas (2001) devised a POG with a 0.05 μm EVA film thickness, but it was not used for air sampling. Assuming first-order kinetics, times to 95% of equilibrium (t_{95}) are given by

$$t_{95} = -\ln 0.05/(k_a/K_{pa}\delta_p) = 2.99/k_e \quad (1.2)$$

where k_a is the mass transfer coefficient for the air boundary layer (ABL) and k_e is the release or elimination rate constant. The effect of the magnitude of compound K_{pa} on time to equilibrium is underscored by the finding that polychlorinated biphenyl (PCB) congeners 28 and 153 required 7 and 217 days (d), respectively, to reach equilibrium with the 1 μm thick EVA coated POG. The ABL was shown to control the uptake rates of SVOC vapors and thus wind speed and turbulence largely mediates exchange kinetics. To minimize flow-induced variability in exchange kinetics, Harner et al. (2003) designed and applied a deployment device that dampened flow differences. Clearly, the use of these samplers can be extended to outdoor air, assuming adequate analyte mass can be sampled for quantitation of trace to ultra-trace levels of HOC vapors.

Coutant et al. (1985) first extended the application of small PDM-like devices to VOCs in soils. Also, Zabik et al. (1992) first reported the development of passive samplers for SVOCs in soil. Unlike PDMs for VOCs, the device of Zabik et al. (1992) contained XAD-4 resin or C_{18} enclosed in a polymeric Whirlpak Bag made of low-density polyethylene (LDPE). Vapors with moderate- to high-K_{oa}s were sampled in an integrative manner during exposures of 21 d. Also, analytes were recovered by solvent elution of sorbents, as opposed to thermal desorption often used for PDMs. The amount of chemical in the LDPE was not measured. Johnson et al. (1995) further developed this approach utilizing C_{18} alone in Whirlpack bags for sampling SVOC vapors in soils. Again only the residues in the sorbent were measured. They were able to accurately estimate areal distribution of a PCB mixture in soil (concentrations varied by 4-orders of magnitude) at a hazardous waste site from PCB concentrations in deployed samplers. Although Johnson et al. (1995) noted that sampling rate (in this case, μg PCBs g^{-1} C_{18}) was inversely proportional to moisture content; no analysis of the rate-limiting step in vapor sampling was performed. The exchange kinetics of SVOC vapors or solutes with this type of sampler are more complicated than with the POG design, as both the membrane and the sorbent phases are involved and analytes must diffuse through the membrane and desorb as vapors from the inside wall of the bag (i.e., partial pervaporation) to reach the sorbent.

Shoeib and Harner (2002) and Wania et al. (2003) separately developed large capacity passive samplers for integratively monitoring the atmospheric transport of HOCs. The sorbents used in these devices act as an infinite sink for HOC vapors, and have been used earlier to actively sample large volumes of air and

water (i.e., HiVol samplers). The Shoeib and Harner (2002) device is based on the use of a polyurethane foam (PUF) disk, while the Wania et al. (2003) device uses XAD-2 resin in a finely perforated stainless steel column. We are unable to compute the AV^{-1} ratio of the sampler because the area for chemical exchange could not be determined with the available information. The Wania et al. (2003) device showed a steady uptake of HOC vapors in outdoor air over the course of one year and the rate of HOC uptake was controlled by the effective thickness of the boundary layer associated with the sorbent. Similar to Harner et al. (2003), a deployment device was used which dampens air flow-turbulence, minimizing the effects of these variables among sites. However, field calibration of the same set of chemicals at three different sites showed that apparent sampling rates (R_s; m^3 or cm^3 d^{-1} cleared of analyte) varied by two to as much as 5-fold for α-HCH. Wania et al. (2003) suggested that some of the observed variation in R_s values among sites was due to problems associated with the HiVol samplers such as analyte breakthrough of the PUF sorbent at sites with higher temperatures and differences in sampling time scales.

1.2.2. Water

In 1980, Byrne and Aylott (1980) were the first to patent a simple device that passively sampled organic contaminants from water. The device consists of a reservoir of nonpolar organic solvent separated from water by selected "non-porous" polymeric membranes. The word nonporous refers to polymeric films or membranes, where solutes essentially dissolve into rubbery or amorphous regions of the polymer, as there are no fixed holes (other than defects) in the matrix for diffusive transport. The membranes used in the Byrne and Aylott device included cellulose, vinyl chlorides, polyvinylidene fluoride, and polytetrafluoroethylene. No publications other than the patent are known to exist for the use of this device. Södergren (1987) first reported the development and testing of an *in situ* mimetic (mimics key elements of complex biological processes in simple media) passive sampling device for the accumulation of waterborne HOCs. This device consisted of 3 mL of hexane sealed in a hydrophilic regenerated cellulose dialysis bag ($A = 12.6$ cm^2). The AV^{-1} ratio for the device was 4.2 cm^{-1}. The cellulose membrane bag had a molecular-weight cutoff of 1000 Daltons, which allows only dissolved phase HOCs to concentrate in the hexane. Field-testing showed that PCBs were accumulated in the hexane and that the hexane could be directly injected into a gas chromatograph equipped with an electron capture detector (GC-ECD) for sample analysis. Using the Södergren device, the estimated linear uptake rate for several HOCs (i.e., DDTs and PCBs) over a 7-d exposure period was about 0.05 L d^{-1}. Unfortunately, the stability of cellulose membranes is poor in warm (i.e., >20 °C) turbulent aquatic environments, which may be caused by its fragility and/or the presence of microorganisms with cellulase enzymes. Prest et al. (1992) suggested that the very polar hydrophilic nature of cellulose reduces the permeability of HOC solutes relative to nonpolar membranes

such as nonporous LDPE. Sabaliūnas and Södergren (1996) found that identical size ($A \approx 25$ cm^2) cellulose and LDPE membrane tubes, containing a 4-mL mixture of cyclohexane and the lipid triolein (AV^{-1} of both devices is 6.2 cm^{-1}), exhibited marked differences in their uptake rates of HOCs. More specifically, the HOC uptake rates of the solvent-containing LDPE bags were 24 to 84-times higher than the solvent containing cellulose bags (Sabaliūnas and Södergren, 1996), but the loss of cyclohexane was much greater from LDPE bags. This finding confirmed that the cellulose dialysis membranes (thickness not specified) tested had much greater resistance to mass (HOC solutes) transfer when compared to 75 μm thick LDPE membranes.

In an effort to optimize the solvent-containing passive sampler design, Zabik (1988) and Huckins (1988) evaluated the organic contaminant permeability and solvent compatibility of several candidate nonporous polymeric membranes (Huckins et al., 2002a). The membranes included LDPE, polypropylene (PP), polyvinyl chloride, polyacetate, and silicone, specifically medical grade silicone (silastic). Solvents used were hexane, ethyl acetate, dichloromethane, isooctane, etc. With the exception of silastic, membranes were <120-μm thick. Because silicone has the greatest free volume of all the nonporous polymers, thicker membranes were used. Although there are a number of definitions of polymer free volume based on various mathematical treatments of the diffusion process, free volume can be viewed as the free space within the polymer matrix available for solute diffusion.

The criteria used for membrane evaluation in these studies included organic solvent compatibility, durability, HOC uptake rates, and cost. The results of the solvent-polymer compatibility tests ranged from no apparent impact on membrane properties to dissolution. For example, hexane-filled silastic tubing swelled to greater than twice its original volume, but returned to its original volume in a matter of minutes in air (i.e., hexane pervaporated) and in a few hours in water. Of the polymers tested, LDPE and PP demonstrated the best overall compatibility with organic solvents (Huckins et al., 2002a). Subsequent to the above experimental work, Huckins et al. (1990a) suggested the use of Hildebrand and Hansen solubility parameters (i.e., cohesive energy density based numerical values that indicate the relative tendency of a specific solvent to solvate a material such as a polymer) as a screening tool for matching of appropriate combinations of polymer and solvent. An extensive list of solubility parameter values and an in-depth discussion of solubility parameter theory and use are available (Grulke, 1989).

Even when using LDPE and PP, the diffusive losses of most nonpolar solvents may be unacceptably large for AV^{-1} designs that exceeded 1 cm^{-1}. This is especially true at higher exposure temperatures because both solute diffusion and polymer free volume increase with temperature (Comyn, 1985). Even when solvent losses were not excessive, uptake of HOCs by membrane-enclosed solvents appeared to become curvilinear well before thermodynamic equilibrium was approached. This phenomenon is likely due to the outward flux of sampler solvent with elevated HOC levels (relative to water), which appears to facilitate residue

export to the exterior surface of the membrane (Huckins et al., 1990a, 1993; Prest et al., 1992). This process is similar to a known membrane transport process described in the membrane separations literature as facilitated diffusion (Hwang and Kammermeyer, 1984), where analyte transport through a membrane is enhanced by the mass transfer of a carrier substance (solvent in this case).

Independently, Hassett et al. (1989) developed the passive *in situ* concentration and extraction sampler (PISCES), which consists of a chrome-plated brass reservoir containing 200 mL of hexane or isooctane and dual LDPE membranes having a combined A of about 23 cm^2. This design features a low AV^{-1} ($\approx$0.1 cm^{-1}), which reduces excessive solvent losses. Litten et al. (1993) successfully field-tested PISCES for locating the source of PCB inputs into a riverine system, where most conventional active sampling methods were ineffectual. Linear uptake (sampling) rates ranged from 0.5 to 0.9 L d^{-1} for individual devices and did not differ among sampled PCB congeners. Unfortunately, gas or vapor buildup inside the reservoir caused bulging of the membranes and potential leaks, and non-reproducible solvent losses of replicates were noted.

More recently, Kingston et al. (2000) developed a passive sampling system (PSS), which consists of several types of diffusion (rate)-limiting membranes and Empore disks as the analyte sequestration phase. In this study, polysulfone and polyethylene membranes were used as rate-limiting barriers. Both designs used a C_{18} Empore disk as a receiving or sequestration phase. The polysulfone membrane was best suited for target compounds with log K_{ow}s between 2.0 and 4.0, and a polyethylene membrane was best suited for target compounds with log K_{ow}s $>$ 4.0. Using these designs, they successfully concentrated chemicals as polar as atrazine and chemicals as hydrophobic as PCB congener 153. Because the PSS is not limited to the membranes listed above or only one type of Empore disk, sampling of a wide range of chemicals is possible. Alvarez et al. (2004) designed a polar organic chemical integrative sampler (POCIS) for a broad spectrum of hydrophilic organic chemicals. The POCIS is suited for polar pesticides, pharmaceuticals, hormones, or organic compounds with log K_{ow}s $<$ 4.0. The device is commonly used in conjunction with SPMDs to enable a more holistic assessment of the presence of organic contaminants in aquatic systems (Petty et al., 2004). POCIS units are constructed by forming a membrane-sorbent-membrane sandwich, which maximizes the surface area for chemical uptake. The membrane is polyethersulfone and the sorbent used is a triphasic admixture of polymeric resins and a small amount of activated carbon, or Oasis HLB. The choice of sorbent depends on the classes of chemicals targeted but is not necessarily limited to the two types listed. Table 1.1 provides additional details on both the PSS and the POCIS.

Huckins (1989) first evaluated the use of LDPE strips (PESs) alone as passive samplers. The PESs (75 μm thick; $A = 400$ cm^2) were exposed to three concentrations (0.8, 8.2, and 61 ng L^{-1}) of ^{14}C-2,2′,5,5′-tetrachlorobiphenyl (TCB) for 28 d in flow-though, constant concentration exposures. Replicate PESs ($n = 4$) were collected on day 1, 3, 7, 14, 21 and 28. Considerable biofouling was observed on

Table 1.1 Comparison of Passive Sampler Characteristics and Applications for Organic Compounds

	SPMDs	SPMEs	POGs	LDPE strips	PISCES	POCIS	PSSs
Classification	integrative (log K_{ow}s > 4.5)	equilibrium (log K_{ow}s < 6)	equilibrium (log K_{oa}s < 10)	integrative (log K_{ow}s > 5)	integrative	integrative	integrative
Sample media	surface water, groundwater, air sediment, soil	surface water, groundwater, sediment, soil	surface water, air	surface water groundwater, air, sediment	surface water	surface water, groundwater, sediment	surface water groundwater, air, sediment, soil
Chemicals sampled	HOCs (SVOCs)	HOCs (VOCs, SVOCs)	HOCs (SVOCs)	HOCs (SVOCs)	HOCs (SVOCs)	HPOCs[a]	HOCs, HPOCs
Sampling rate control	EBL[b] (log K_{ow}s > 4.5)	EBL (log K_{ow}s >?)	EBL	EBL (log K_{ow}s > ?)	EBL (log K_{ow}s >?)	EBL	diffusive membrane
A/V[c]	90 cm^{-1} (91.4 × 2.5 cm)	1,400 cm^{-1} (7 μm film)	10^4 cm^{-1} (1 μm film)	230 cm^{-1} (85 μm film)	0.1 cm^{-1}	150 cm^{-1}	110 cm^{-1}
A	460 cm^2 (91.4 × 2.5 cm)	0.4 cm^2, 7 μm film × 10 cm	290 cm^2, 6.8 × 7.0 cm	460 cm^2 (91.4 × 2.5cm)	23 cm^2	41 cm^2	16 cm^2
Sorbent-liquid phase volume	5,000 μL	0.28 μL 7 μm film	29 μL 1 μm film	2,000 μL 85 μm film	2.0 × 10^5 μL	240 μL	145 μL C18
Clearance capacity[d]	560 L (w) 360 m^3 (a)	0.027 L (w) 18 L (a)	16 L (w) 10.4 m^3 (a)	79 L (w)	1.3 × 10^5 L (w)	?	75 L (w)

[a] Hydrophilic organic chemical.
[b] EBL is external boundary layer, water or air.
[c] A/V is the surface area (cm^2) of the sampler divided by the volume (cm^3) of the accumulating phase.
[d] Volume of water or air cleared (E_v) by a specific sampler configuration at equilibrium. We use PCB congener 52 in this example.

PESs by the end of the exposure. Differences in exposure concentrations did not affect the sampling rates of PESs, which indicate that these devices obey first-order uptake kinetics. The sampling rate of ^{14}C-2,2',5,5'-TCB by PESs (4.8 L d^{-1}) was similar to that observed for 1 mL triolein SPMDs, with the same surface area.

By using a PES with a different thickness, one can conveniently change the AV^{-1} ratio. This approach permits some control over the time required to reach equilibrium concentrations. Bartkow et al. (2004) has reported an excellent example of the impact of AV^{-1} ratio or thickness on the time to equilibrium. These investigators showed that a 200 μm thick PE sheet took twice as long to reach equilibrium in air as a 100 μm thick PE sheet. In theory, changing membrane thickness will not affect polymer diffusivity and equilibrium membrane-water partition coefficients (K_{mw}s) or solubility coefficients (S_p). However, in practice different values of K_{mw}, K_{ma} (membrane-air partition coefficient) and membrane diffusivity may be obtained from films of different thickness because of changes in polymer chain orientation and crystallinity (Pauly, 1989). For example, Rogers (1985) has shown that S_p, which is given as the K_{mw} when Henry's Law convention applies, is dependent on polymer crystallinity as shown by

$$S_p = S_a \phi_a \tag{1.3}$$

where S_a is the solubility coefficient for a completely amorphous or rubbery polymer with due consideration of surface and void defects and ϕ_a is the amorphous volume fraction of the polymer. In particular, this relationship has been shown to hold true for PE. Also, some variations in these parameters are expected for LDPE films of the same thickness from different manufactures due to a lack of uniformity in fabrication conditions. Recently Booij et al. (2003a) have shown that PES partition coefficients are affected by temperature (2 to 30 °C) while temperature effects on SPMDs are insignificant over the same range of temperatures. Thus, the reliability of environmental concentration estimates from polymeric film-based samplers is contingent on the availability of reproducible polymer, and a means to estimate the effects of biofouling, flow-turbulence, and temperature on the times to equilibrium. Booij et al. (2002) have made progress in this area by developing a method to spike PESs with performance reference compounds (PRCs; see discussion on PRCs in Section 1.2.3.1. and Chapter 3). PRCs are analytically non-interfering compounds with moderate- to relatively high-fugacities, which are added to a passive sampler (e.g., the lipid of SPMDs) prior to deployment. The rate of PRC loss during an exposure can be used to estimate *in situ* sampling rates of analytes of interest.

We also examined the use of medical-grade silicone or silastic tubing (ST) alone as a passive sampler medium (Huckins and Petty, 1994a). The ST had the following dimensions: 30.5 cm long, a wall thickness of 0.24 mm, an outside diameter of 1.9 mm, and an A of 18.7 cm^2. Replicate STs were exposed to 8.4 ng L^{-1} of ^{14}C-2,2',5,5'-TCB for 7 d in a flow-though, constant concentration system. STs ($n = 3$) were collected on day 2, 5, and 7. The STs contained about 82% of the amount of ^{14}C-2,2',5,5'-TCB concentrated in lipid-containing STs of the same dimensions (i.e., silastic SPMDs; see Section 1.2.3.1.).

According to the polymer literature (Flynn and Yalkowsky, 1972; Rogers, 1985), silicone has the greatest free volume of the commonly available nonporous polymers. However, partition coefficients and diffusion coefficients for this type of polymer may not necessarily be independent of chemical concentration, i.e., Henry's law convention may not apply (Rogers, 1985) when ambient environmental HOC concentrations are very high (e.g., oil spills). As HOC solute concentrations in the silicone rise, free volume increases more rapidly than in other polymers, which at some undefined point, results in increases in both polymer diffusivity and partition coefficients. The Flory-Huggins equation likely fits this type of behavior. Under membrane control, one would observe increasing sampling rates with rising solute concentrations, while under water boundary layer (WBL; a thin hydrodynamically complex region separating the SPMD membrane from the bulk water, where molecular diffusion dominates mass transfer and resistance to mass transfer) control, analyte sampling rates would remain constant for extended periods unless extensive biofouling occurs. Fortunately, this type of scenario is unlikely for trace levels of environmental contaminants. Furthermore, unlike sorbents used in some samplers, residues are readily recovered by soaking silicone or silastic in the appropriate solvent.

In regard to the potential effects of silicone membrane or film thickness (e.g., polydimethylsiloxane [PDMS]) on partition coefficients, Paschke and Popp (2003) have shown that that at equilibrium an SPME fiber with a 7 μm thick film of PDMS had about a 6-fold higher K_{pw} than a similar fiber with a 100 μm thick film. However, this could be the result of interactions with the silica core. Recent research (Smedes, 2004) has shown that silicone sheeting with PRCs can be employed for water sampling with good results.

As suggested earlier, SPMEs are essentially equilibrium sampling devices but are typically used in an active sampling mode. However, Górecki and Pawliszyn (1997) and Mayer et al. (2000) have used SPMEs in an *in situ* passive extraction mode in the laboratory, which is described by Mayer et al. (2000) as matrix-SPME. In this case, sediment was collected from the field and sieved prior to SPME exposures. The goal was to estimate the concentrations of a number of HOCs in field-sediment pore water using SPMEs. The approach relies on non-depletive extraction, where the total residues extracted by an SPME at equilibrium do not significantly change the concentrations of the sampled medium (i.e., pore water and sediment particles). Thus, equilibrium concentrations of analytes in the fiber's polymer can be readily related to their pre-exposure concentrations in sediment pore water by a simple equilibrium partition coefficient.

Because SPMEs are equilibrium samplers similar to POGs, the thickness of the fiber's polymeric phase must be kept relatively small to ensure that times to equilibrium are reasonable (e.g., $\leq$1 month) for high K_{ow} analytes (log K_{ow}s > 6), under conditions of minimal turbulence. Also, to ensure non-depletive extraction of analytes from excised sediments, the sorption capacity of the organic carbon in the excised sediment sample should be at least 50-fold greater than the sorption capacity of the SPME polymeric phase (i.e., $m_{oc}K_{oc} \gg K_{pw}V_p$; where m_{oc} represents the mass of the organic carbon, K_{oc} is the equilibrium sediment organic

carbon-water partition coefficient, p represents the SPME polymeric phase, and K_{pw} is the equilibrium polymer-water partition coefficient). The δ_p of the 7 cm PDMS fiber used by Mayer et al. (2000) was 15 μm and the AV^{-1} ratio was 670 cm^{-1}. The total volume of the fiber's PDMS phase was 0.71 μL. For comparison purposes, the δ_p values of commercially available SPMEs generally range from 7 to 100 μm and the sorbent phase volumes of a 1 cm segment are generally <0.7 μL. It is interesting to note that SPMEs with 15 μm film thickness appear to reach steady state with high K_{ow} compounds in sediments in less than 30 d with some agitation, while 1 μm thick POGs failed to reach steady state with high K_{oa} vapors (log $K_{oa} > 9.3$) in 100 d. The findings of Booij et al. (2003b) offer a potential explanation for this difference in times to equilibrium. They found that sampling rates for PESs (70 μm film thickness) were much higher in sediment slurries (≈0.1 cm s^{-1} flow at the polymer surface) than in stagnant sediments. The authors proposed that resistance to solute uptake posed by the WBL is greatly reduced by contaminant desorption from particles (i.e., *POC*) very near or in contact with the polymer. It seems likely that upon close contact or collision of particles with the PESs or the SPME sorbent, both the WBL around the polymeric films and the WBL around the particles are effectively thinned, thus resistance to mass transfer is reduced (Eq. 3.9). Contaminant desorption is induced by the depleted levels of these solutes at the exterior surface of the sorbent phase (i.e., the concentration gradient across the LDPE or SPME boundary layer). Furthermore, computations by Mackay (1994) indicate that chemicals in small particles (≤1 mm) desorb rapidly, reaching equilibrium in milliseconds to minutes for compounds with log particle-water partition coefficient ranging from 1 to 6. Even though this analysis assumed that desorption was dominated by the facile portion of the desorption isotherm, it appears quite likely that particle desorption contributions may greatly reduce times to equilibrium in sediment slurries.

Although SPMEs, and POGs are useful tools for many sampling scenarios, their strengths for one application can be the source of their limitations for another application. This characteristic applies to all sampling devices designed to accumulate compounds with a broad range of physicochemical properties. For example, the low sorbent phase volumes and high surface areas of thin-film SPMEs and POGs enable the attainment of equilibrium in relatively short exposure times, but the volumes of water cleared of chemical are relatively low compared to systems with higher sorbent volumes. Using a 7 cm SPME fiber coated with a 15 μm thick polymeric phase (0.7 μL V) to sample a compound with a log K_{pw} of 6 permits the extraction of only 0.7 L of water at equilibrium. Using a 1 μm thick POG with a total A of 290 cm^2 (2.9 μL V) to sample the same compound with a log K_{pa} of 8, permits the extraction of only 0.3 m^3 of air at equilibrium. These sample volumes may be inadequate for the quantification of ultra-trace analytes. Although the 1 μm POGs, as described by Harner et al. (2003), would be expected to reach equilibrium more rapidly and have a greater capacity, the method detection limits may not be as low as those described for the 15 μm SPMEs. This is because the entire SPME sample is injected into the GC or the instrument used

for analyte quantification. However, the potentially lower method detection limits of SPMEs are contingent on minimal co-extracted interferences and on the ability of the GC column to resolve different classes of chemicals without additional chromatographic separations.

Because high AV^{-1} ratios of SPMEs and POGs also mean rapid desorption of accumulated residues, samplers must be frozen at sub-zero temperatures and transport and storage times must be minimized. Mayer et al. (2000) analyzed SPMEs by GC within 20 s of sample removal in the matrix-SPME study. To enable rapid turn-around times for sample data, and to minimize transport and storage problems, Górecki and Pawliszyn (1997) developed a field-portable SPME/fast GC system for sampling VOCs. However, at more remote sites the need for electrical power is problematic.

An inherent problem for all passive samplers designed to attain equilibrium is the very wide range of K_{ow}s and K_{oa}s of the broad array of organic compounds of interest. However, a significant body of evidence suggests that K_{pw}s and K_{pa}s of large, very nonpolar molecules appear to be less than their respective K_{ow}s and K_{oa}s (Huckins et al., 1990a, 1993; Lefkovitz et al., 1994; Harner et al., 2003; Paschke and Popp, 2003). Chiou (1985) has discussed one potential factor that may account for this phenomenon, which relates to the effect of a decrease in the size difference between a macromolecular phase and solutes with relatively large molar volumes. Even if K_{pw}s and K_{pa}s are less than the corresponding K_{ow}s and K_{oa}s, equilibrium values of target analytes may vary as much as 6-orders-of-magnitude.

Table 1.1 compares key aspects and performance characteristics of selected passive samplers, including the triolein-containing SPMD. Of the eight devices examined, only a few appear to have overlapping functions. Clearly, no one device can provide the desired data for all exposure scenarios.

1.2.3. Lipid-Containing SPMDs and Closely Related Devices

Similar to the previous section, we discuss only selected works to highlight the development of SPMDs. Also, we include some discussion of several unpublished pilot studies (Huckins, 1989) that influenced our early development of SPMDs. These pilot studies were directed solely toward sampling the aqueous phase. The first application of SPMDs for sampling organic vapors did not occur until several years later (Petty et al., 1993). To our knowledge, only SPMDs, PESs and SPMEs are being applied in both air and water, because the use of many passive samplers is limited to a specific medium and exposure scenario.

1.2.3.1. Aqueous Phase Sampling

Based on earlier work (Lieb and Stein, 1969; Chiou, 1985; Södergren, 1987; Zabik, 1988) Huckins et al. (1989, 1990a, 1993) first developed and tested two types of lipid-containing semipermeable membrane devices (SPMDs) for *in situ* passive sampling of bioavailable dissolved aqueous-phase HOCs. The lipid-containing

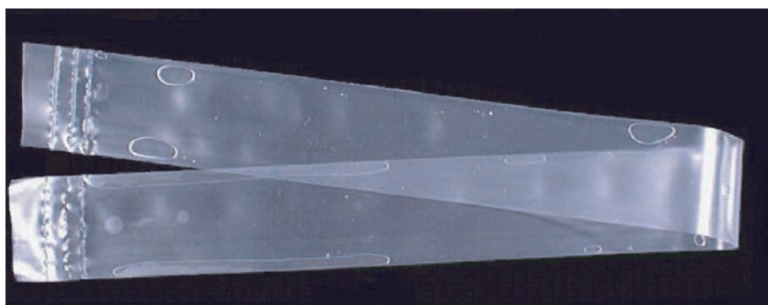

FIGURE 1.1 A standard lipid-containing SPMD with three molecular welds near each end. Note the low interfacial tension causes intimate contact (i.e., the presence of a lipid film on the membrane interior surface) between the triolein and the membrane even where air bubbles exist. Reprinted with permission from the American Petroleum Institute (Huckins et al., 2002a).

SPMDs consisted of 99% triolein in layflat-LDPE tubing (Figure 1.1) and 99% triolein in small-bore ST. The following tests were conducted in these studies: 1) a 28 d flow-though, constant concentration exposure of LDPE triolein-containing SPMDs to three concentrations (0.8, 8.2, and 61 ng L^{-1}) of ^{14}C-2,2′,5,5′-TCB; 2) a 7 d flow-though, constant concentration exposure of silastic triolein-containing SPMDs to 8.4 ng L^{-1} of ^{14}C-2,2′,5,5′-TCB; and 3) a 21 d static exposure of LDPE SPMDs (three types of lipid) to ^{14}C-2,2′,5,5′-TCB (single application). The goals of these tests were to determine the relative uptake rates of LDPE and silastic SPMDs, the independence of LDPE SPMD concentration factors to exposure concentrations, and the steady-state partition coefficients between each of the three types of SPMD lipid used and the water.

The reasons for the selection of high purity triolein as a test lipid in these pilot studies are given in Chapter 2. Two other types of lipid were examined in this pilot study as well. Grass carp (*Ctenopharyngodon idella*) lipids (liquid phase) were obtained by dichloromethane-extraction of whole-body grass carp tissues, and were used as a representative for complex lipid mixtures found in fish and other organisms. The phospholipid lecithin (MW $\approx$ 787 Daltons, $\approx$85% purity, wax at room temperature) was used as a representative of organisms such as algae. Also, lecithin enclosed in an SPMD membrane may provide a reasonable surrogate for estimating partitioning of HOCs between phospholipids in biomembranes and biological fluids. In light of current research (Leslie et al., 2002), this type of data is needed for assessing the potential impacts of narcotic-acting HOCs because toxicity is only elicited when biomembrane concentrations attain or exceed the critical body threshold.

The layflat-LDPE tubing used for making SPMDs was 2.6 cm wide and had a wall thickness of about 75 μm. The A of the 0.5 mL triolein SPMDs used in these flow-through tests was about 200 cm^2 with an AV^{-1} (lipid + membrane) ratio of about 80 cm^{-1}. The A of the 1 mL triolein SPMDs used in the static exposures was about 360 cm^2 (i.e., $AV^{-1} = 72$ cm^{-1}). The surface area of the 1 mL lipid

SPMDs was about 20% less than the currently used 1 mL triolein SPMDs. The silastic SPMDs contained 0.5 mL triolein and the AV^{-1} (membrane + lipid) was 22 cm^{-1}. Replicate SPMDs ($n = 4$) used in the 28 d flow-though tests (well water) were collected at d 1, 3, 7, 14, 21 and 28. Some biofouling was observed on SPMDs near the end of the exposure, but less than that observed on similarly exposed PESs, as discussed earlier. The uptake rates of ^{14}C-2,2′,5,5′-TCB by the SPMDs was about 4.2 L d^{-1} (Huckins, 1989). This uptake rate is 4.7- to 8.8-fold greater than the PISCES, but the difference between SPMDs and PISCES is less than predicted on the basis of the relative surface areas (i.e., SPMDs have about a 10-fold greater surface area). Greater than 50% of the total ^{14}C-2,2′,5,5′-TCB residues accumulated in SPMDs at 28 d were present in the triolein (i.e., triolein-membrane partition coefficient [K_{Lm}] $\approx$ 4) even though triolein represented only about 20% of the sampler mass. Differences in exposure concentrations did not affect the sampling rates of SPMDs, which indicates that these devices obey first-order exchange kinetics. Based on an equivalent weight of SPMD and PES (see earlier discussion), the estimated steady state concentrations of ^{14}C-2,2′,5,5′-TCB in triolein-containing SPMDs would be about two-fold greater than those in the PES.

Lipid-containing silastic SPMDs ($n = 3$) used in 7 d flow-through tests (well water) were collected on days 1, 3, and 7. After normalizing the surface area of the silastic SPMDs to that of the standard design LDPE SPMD used in the 28 d exposures (7 d, 8.2 ng L^{-1} treatment), it was found that the 7-d silastic SPMDs accumulated about 1.4 times as much ^{14}C-2,2′,5,5′-TCB as the corresponding 7-d LDPE SPMDs. Surprisingly, the K_{Lm} for the silastic SPMD configuration at 7 d was 16, which is about 4-fold higher than the LDPE SPMD configuration. Because the same flow-through exposure system was used for both the LDPE and silastic SPMD exposures and test temperatures were identical, this disparity between silastic SPMD and LDPE SPMD uptake rates is likely due to one or both of the following factors: 1) differences in flow-turbulence at the LDPE and silastic membrane surfaces, which affect the effective thickness of the WBL; and 2) analytical error. In light of more recent research indicating that small variations in flow-turbulence at the membrane surface can affect SPMD sampling rates (Vrana and Schüürmann, 2002), the most likely factor causing the observed differences in sampling rates is the effective thickness of the WBL.

Finally, LDPE SPMDs with grass carp lipid were exposed for 21 d to ^{14}C-2,2′,5,5′-TCB, ^{14}C-3,3′,4,4′-TCB, ^{14}C-mirex and ^{14}C-fenvalerate, whereas SPMDs with triolein or lecithin were exposed to only ^{14}C-2,2′,5,5′-TCB. After 21 d, the largest mass fraction of these test chemicals (^{14}C-mirex was an exception) was in the triolein. The ^{14}C-2,2′,5,5′-TCB log triolein-water partition coefficient was 6.01, whereas the ^{14}C-2,2′,5,5′-TCB partition coefficients for the grass carp lipid-water and lecithin-water systems were 30% and 35% lower, respectively. Comparison of these data to literature log K_{ow}s of 2,2′,5,5′-TCB showed that the partition coefficients for the grass-carp lipid and the lecithin were not significantly different from median values reported for the log K_{ow} of ^{14}C-2,2′,5,5′-TCB. However, the partition coefficient of 2,2′,5,5′-TCB in triolein and water in direct

contact (Chiou, 1985) is only 41% of the membrane enclosed triolein-water partition coefficient derived from SPMDs (Huckins et al., 1990b). A possible explanation for the discrepancy in these partition coefficients is that the SPMD membrane maintains true binary integrity of the triolein and water phases during tests due to the low permeation of the relatively high molecular weight triolein and polar hydrogen-bonding water molecules through LDPE. Note that direct mixing of water with triolein during partitioning results in a triolein layer with about 11% water at 25 °C, which likely affects the magnitude of the partition coefficients of very hydrophobic compounds (Chiou, 1985).

Petty and Orazio (1996) developed an interesting variation in SPMD liquid phases. The approach consisted of both LDPE and silastic tubes containing silicone fluid (50 cSt or 3200 MW) with 3% by weight PX-21 activated carbon. The presence of the activated carbon enhanced retention of planar molecules such as PAHs and the silicone fluid remains liquid at temperatures below freezing. However, the partition coefficients of HOCs for this type of silicone fluid are much lower than for triolein.

At about the same time that the lipid-containing SPMD was introduced, Huckins et al. (1990b) first described an organic solvent dialysis (OSD) method for the recovery of HOCs accumulated in intact SPMDs and in the LDPE membrane alone. Essentially, the process involves submersion of an exposed lipid-containing SPMD into a glass container with a suitable solvent such as hexane or cyclopentane for at least 24 hrs. Solvation of the nonporous LDPE-SPMD membrane enhances the outward diffusive flux of analytes (compared to non-solvated membrane) into the bulk solvent of the reservoir, whereas the diffusion of triolein through the swollen polymer is still very slow. By matching the Hildebrand or Hansen solubility parameters (commonly available in the literature) of a solvent to LDPE or other nonporous polymers of interest, the amount of polymer swelling and dissolution can be predicted (Brandrup and Immergut, 1989). The amount of lipid carried over with analytes of interest during OSD is dependent on the amount of low-molecular weight impurities (e.g., oleic acid and methyl oleate) in the triolein used in the SPMD, the solvent used, temperature, and duration of the dialytic procedure. When performing hexane dialysis of standard SPMDs with $\geq$95% triolein for $\leq$48 hr, only 3–4% of the lipid components are co-dialyzed with the analytes. Interestingly, analyte residues contained in PES and many other nonporous polymers are readily recovered by the same method.

OSD also provides an enrichment method for the extraction and separation of HOCs from tissue or egg extracts with large volumes of lipids (Huckins et al., 1990a; Meadows et al., 1993). The OSD method has been further advanced by the work of others (Bergqvist et al., 1998; Strandberg et al., 1998). The bags employed are made of several sizes of LDPE tubing that are heat sealed at one end and subsequently charged with the lipid to be treated by the OSD procedure. Quality control procedures for the LDPE bags are similar to those used for SPMDs. Application of the OSD method to silicone or silastic SPMDs or tubes (wall thickness $\approx$ 500 µm) with lipid extracts was unsuccessful. Solvation of silicone or silastic membranes

with solvents typically employed in OSD greatly expands the polymeric free volume, which results in the co-dialysis of most of the triolein (or other lipid) with the analytes. However, analytes were quantitatively recovered in a matter of minutes instead of hours (i.e., LDPE) thus future examination of much thicker membranes and different solvents deserves additional attention.

Until early 1993, lipid-containing SPMDs were only used to determine the presence and identities of contaminants, relative differences in SPMD concentrations among deployment sites, and to compare HOC residues accumulated in SPMDs to those accumulated in biomonitoring organisms. Extrapolation of SPMD concentrations to HOC concentration in ambient water requires appropriate mathematical models and calibration data relevant to exposure conditions. In 1993, several mathematical models were developed for SPMDs providing the basis for the estimation of water concentrations (Huckins et al., 1993). These models contained most of the variables affecting SPMD uptake and elimination rates, but the rate-limiting step in the residue exchange process was not well defined. Factors potentially affecting overall mass transfer rates of HOCs include the additive resistances of the membrane, the WBL and any biofilm (i.e., periphyton and any imbibed detritus) on the exterior surface of the membrane, and the effects of temperature. Huckins et al. (1993) also provided calibration data for a model PCB and a model polycyclic aromatic hydrocarbon (PAH). However, in this paper the authors incorrectly hypothesized that diffusion of most HOCs through the SPMD membrane is the rate-limiting step in HOC exchange. Subsequently, Booij et al. (1998) demonstrated that resistance in the WBL is the rate-limiting step in the uptake and elimination of most HOCs by SPMDs. This finding has had considerable impact on the direction of SPMD research.

While diffusion of HOCs in water is much less complex and more predictable than diffusion in nonporous polymeric membranes, accounting for the effects of site-specific variations in flow-turbulence on effective thickness of the aqueous boundary layer is not straightforward. In light of the number of variables potentially affecting the sampling rates of this new generation of passive monitoring devices, the acceptability of their use beyond screening level assessments for dissolved phase concentrations of HOCs is dependent on the ability of investigators to predict *in situ* sampling rates. Recent work by Booij et al. (2003a and 2003b) has greatly improved our ability to use mathematical models to predict *in situ* SPMD sampling rates.

The use of PRCs to determine the effects of SPMD membrane biofouling on the uptake rates of HOCs was first proposed in 1991 (Huckins et al., 2002a). The PRC method can also account for the effects of flow-turbulence and temperature differences (Huckins et al., 2002b). Implicit in the PRC approach is that the overall uptake and elimination rates of HOCs in SPMDs are governed by first-order kinetics and that residue exchange with the sampled medium is isotropic. Isotropic exchange can be described by analogy as a two-way door (where the door is the rate limiting step in chemical exchange), with equal resistances to mass transfer in either direction. Huckins et al. (1993) showed that the k_e determined from the

uptake of phenanthrene by replicate SPMDs was within 25% of the k_e determined from the loss of phenanthrene from replicate SPMDs, which is slightly less than the error propagated by the derivation procedure. However, similar k_es derived from the uptake and release of a chemical does not necessarily mean that an exchange process is isotropic (especially in the case of BMOs). Finally, using the strict definition of isotropic exchange, any change in the linear uptake rate constants k_u and k_e should not result in a significant change in the equilibrium partition coefficient of the sampling matrix.

Prest et al. (1992) first used phenanthrene as a PRC in a field exposure of SPMDs. The results of their study appeared to be consistent with PRC theory. However, it was several years later before the validity of the use of PRCs for biofouled SPMDs was further substantiated in controlled laboratory studies (Huckins et al., 1994b).

Because SPMD membranes often biofoul during extended exposures in warm surface waters and because this biofilm may impede the uptake rates of HOCs by unknown amounts, Huckins et al. (1990a) hypothesized that the use of certain antifouling chemicals spiked into SPMD triolein might reduce the severity of this potential problem. This hypothesis was contingent on the availability of an environmentally safe, non-interfering (i.e., analytically) and effective biocide-biostat with appropriate LDPE diffusional characteristics (i.e., controlled release). A pilot experiment (unpublished data) was conducted with a candidate organo-arsenical. Unfortunately, the results of this experiment suggested that very high concentrations (i.e., almost one percent of the SPMD weight) are necessary for controlling biofouling. This effort was discontinued due to the hazards associated with high levels of these chemicals and the potential licensing requirements for this type of application.

1.2.3.2. Atmospheric Sampling

Petty et al. (1993) were the first to use SPMDs as passive samplers of SVOC vapors. Standard (subsequently defined) SPMDs were exposed to laboratory air containing background levels of PCBs. An active sampling method based on pumping air through a GFF and a Florisil column, which is a modification of the National Institute of Occupational Safety and Health (NIOSH) Method 5503, was used to independently monitor air levels during 14- and 28-d SPMD exposures. The mean temperature during the exposure periods was 26 °C and air around the samplers was relatively quiescent. The uptake of total PCB vapors was linear throughout the 28 d exposure period. Based on a 1 mL triolein SPMD configuration, total PCB congeners were sampled at a rate of 4.6 m^3 d^{-1} (i.e., volume of air cleared of chemical per d). After fourteen d exposure, SPMDs concentrated total PCB congeners by about 2×10^4 fold (mass basis) or 2×10^7 (volume basis). Congener-specific analysis of PCBs concentrated in SPMDs exposed to laboratory air for 28 d (Petty et al., 1993), indicated that the uptake rates generally increased with the degree of chlorination. Congeners with fewer *ortho*-Cls within a homolog

group (e.g., tetrachlorobiphenyls) had higher sampling rates than other isomeric positions. Sampling rates or R_ss were determined for fourteen of the congeners, which ranged from 0.9 m^3 d^{-1} for a mono-*ortho* dichlorobiphenyl (congener 007) to 9.6 m^3 d^{-1} for a tri-*ortho* octachlorobiphenyl (congener 201).

These data seem to support resistance to diffusion across the membrane (LDPE) as a significant factor in sampling airborne PCBs. Under membrane control, sampling rates increase with membrane-air partition coefficients (K_{ma}s) or K_{oa}s, whereas under ABL control, sampling rates decrease slightly with increasing molar volume or molecular weight (see Section 3.9.2.). Decreased *ortho*-Cl substitution enhances rotational freedom to assume a more planar configuration, which increases heats of fusion, heats of adsorption (e.g., charcoal) and polymer permeability, and decreases vapor pressure. Also, the K_{oa}s of PCB congeners increase with the degree of PCB chlorination (Harner and Bidleman, 1996). Because some tetra- and pentachlorobiphenyls, most hexachlorobiphenyls and more highly chlorinated congeners have log K_{oa}s > 9, a significant portion of the total residues is associated with airborne particulates (McLachlan, 1999).

A thin film of oil-like material was visible after 28 d on the exterior surfaces of the SPMD membrane. Analysis of this film indicated that the triolein impurities, oleic acid and methyl oleate, were the major constituents. This external lipid film (Petty et al., 1993) appeared to contain imbibed particulates. Although the film was removed from the SPMDs by solvent rinsing and analyzed separately, some lipid-mediated desorption of particle-associated PCBs and subsequent diffusion into the SPMD may have occurred prior to solvent-removal of the film. This observation suggests the potential for SPMD concentrations to reflect both vapor phase concentrations and to a lesser extent, lipid-extracted particulate-associated residues (see Section 3.9.2.). Unfortunately, concentrations of more chlorinated congeners in particulates collected on GFFs from the NIOSH method were often below quantitation limits, because only a small volume of air was sampled (1 m^3) using this active method.

1.3. TOPICS COVERED IN SUBSEQUENT CHAPTERS

In subsequent chapters, we provide an overview of SPMD fundamentals and applications (Chapter 2); the theory and modeling which includes the extrapolation of SPMD concentrations to ambient environmental concentrations (Chapter 3); study considerations such as the necessary precautions and procedures during SPMD transport, deployment, and retrieval (Chapter 4); the analytical chemistry and associated quality control for the analysis of SPMD dialysates or extracts (Chapter 5); a survey and brief description of bioassays-biomarkers used to screen the toxicity of SPMD environmental extracts (Chapter 6); discussions on how HOC concentrations in SPMDs may or may not relate to similarly exposed biomonitoring organisms (Chapter 7); and selected examples of environmental studies using SPMDs (Chapter 8). In addition, two appendices are included which provide

SPMD calibration data for many HOCs (Appendix A) and sources of additional information on SPMDs (Appendix B).

1.4. REFERENCES

Alvarez, D.A.; Petty, J.D.; Huckins, J.N.; Jones-Lepp, T.L.; Getting, D.C.; Goddard, J.P.; Manahan, S.E. 2004, Development of a passive, in situ, integrative sampler for hydrophilic organic contaminants in aquatic environments. *Environ. Toxicol. Chem.* **23**: 1640–1648.

American Conference of Governmental Industrial Hygienists (ACGIH) 1990, *Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices*; Cincinnati, OH.

Arthur, C.L.; and Pawliszyn, J. 1990, Solid phase microextraction with thermal desorption using fused silica optical fibers. *Anal. Chem.* **62**: 2145–2148.

Axelman, J.; Næs, K.; Näf, C.; Broman, D. 1999, Accumulation of polycyclic aromatic hydrocarbons in semipermeable membrane devices and caged mussels (Mytilus edulis) in relation to water column phase distribution. *Environ. Toxicol. Chem.* **18**: 2454–2461.

Barron, M.G. 1990, Bioconcentration: Will water-borne organic chemicals accumulate in aquatic organisms. *Environ. Sci. Technol.* **24**: 1612–1618.

Bartkow, M.E.; Hawker, D.W.; Kennedy, K.E.; Müller, J.K. 2004, Characterizing uptake kinetics of PAHs form the air using polyethylene-based passive air samplers of multiple surface area-to-volume ratios. *Environ. Sci. Technol.* **38**: 2701–2706.

Baumard, P.; Budzindki, H.; Garrigues, P. 1998a, PAHs in Arcachon Bay, France: Origin and biomonitoring with caged organisms. *Mar. Pollut. Bull.* **36**: 577–586.

Baumard, P.; Budzinski, H.; Garrigues, P.; Sorbe, J.C.; Burgeot, T. Bellocq, J. 1998b, Concentrations of PAHs (polycyclic aromatic hydrocarbons) in various marine organisms in relation to those in sediments and to trophic level. *Mar. Pollut. Bull.* **36**: 951–960.

Baussant, T.; Sanni, S.; Jonsson, G.; Skadsheim, A.; Børseth, J.F. 2001, Bioaccumulation of polycyclic aromatic compounds: 1. Bioconcentration in two marine species and in semipermeable membrane devices during chronic exposure to dispersed crude oil.*Environ. Toxicol. Chem.* **20**: 1175–1184.

Bergqvist, P.-A.; Strandberg, B.; Rappe, C. 1998, Lipid removal using semipermeable membranes in PCDD and PCDF analysis of fat-rich environmental samples. *Chemosphere* **38**: 933–943.

Björk, M. and Gilek, M. 1997, Bioaccumulation kinetics of PCB 31, 49, and 153 in the blue mussel, Mytilus edulis L. as a function of algal food concentration. *Aquat. Toxicol.* **38**: 101–123.

Böhme, F.; Welsch-Pausch, K.; Mclachlan, M.S. 1999, Uptake of airborne semivolatile organic compounds in agricultural plants: Field measurements of interspecies variability. *Environ. Sci. Technol.* **33**: 1805–1813.

Booij, K.; Sleiderink, H.M.; Smedes, F. 1998, Calibrating the uptake kinetics of semipermeable membrane devices using exposure standards. *Environ. Toxicol. Chem.* **17**: 1236–1245.

Booij, K.; Smedes, F.; van Weerlee, E.M. 2002, Spiking of performance reference compounds in low density polyethylene and silicone passive water samplers. *Chemosphere* **46**: 1157–1161.

Booij, K.; Hofmans, H.E.; Fischer, C.V.; van Weerlee, E.M. 2003a, Temperature-dependent uptake rates of nonpolar organic compounds by semipermeable membrane devices and low-density polyethylene membranes.*Environ. Sci. Technol.* **37**: 361–366.

Booij, K.; Hoedemaker, J.R.; Bakker, J.F. 2003b, Dissolved PCBs, PAHs, and HCB in pore waters and overlying waters of contaminated harbor sediments. *Environ. Sci. Technol.* **37**: 4213–4220.

Brandrup, J. and Immergut, E.H., Eds. 1989, *Polymer Handbook*; 3rd ed.; Wiley & Sons: New York, NY.

Byrne, B.A. and Aylott, R.I. 1980, Concentrator for Removing Organic Materials from Aqueous Systems. British Patent 1566253.

Chiou, C.T. 1985, Partition coefficients of organic compounds in lipid-water systems and correlations with fish bioconcentration factors. *Environ. Sci. Technol.* **19**: 57–62.

Comyn, J., Ed. 1985, *Polymer Permeability*; Elsevier Applied Science LTD: London, England.

Connell, D.W. 1990, *Bioaccumulation of Xenobiotic Compounds*. CRC Press: Boca Raton, FL.

Coutant, R.W.; Lewis, R.G.; Mulik, J. 1985, Passive sampling devices with reversible adsorption. *Anal. Chem.* **57**: 219–223.

Flynn, G.L. and Yalkowsky, S.H. 1972, Correlation and prediction of mass transport across membranes I: Influence of alkyl chain length on flux-determining properties of barrier and diffusant. *J. Pharm. Sci*. **61**: 838–852.

Forbes, M. and Afghan, B.K. 1987, *Analytical Protocol for Monitoring Ambient Water Quality at the Niagra-On-The-Lake and Fort Erie Stations*. Canada Centre for Inland Waters: Burlington, Ontario, Canada.

Fowler, W.K. 1982, Fundamentals of passive vapor sampling. *Am. Lab*. **14**: 80–87.

Gilek, M.; Björk, M.; NäF, C. 1996, Influence of body size on the uptake, depuration, and bioaccumulation of polychlorinated biphenyl congeners by Baltic Sea blue mussels, Mytilus edulis. *Mar. Biol*. **125**: 499–510.

Gobas, F.A.P.C.; Zhang, X.; Wells, R. 1993, Gastrointestional magnification: the mechanism of biomagnification and food chain accumulation of organic chemicals. *Environ. Sci. Technol*. **27**: 2855–2863.

Goudreau, S.E.; Neves, R.J.; Sheehan, R. 1993, Effects of wastewater treatment plant effluents of freshwater mollusks in the upper Clinch River, Virginia, USA. *Hydrobiologia* **252**: 211–230.

Gray, J.S. 2002, Perceived and real risks: Produced water from oil extraction. *Mar. Pollut. Bull*. **44**: 1171–1172.

Grulke, E.A. 1989, Solubility Parameter Values. In *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E.H., Eds.; Wiley & Sons: New York, NY; Section 7, pp. 519–559.

Górecki, T. and Pawliszyn, J. 1997, Field-portable solid-phase microextraction/fast GC system for trace analysis. *Field Anal. Chem. Tech*. **1**: 227–284.

Harner, T. and Bidleman, T.F. 1996, Measurements of octanol-water partition coefficients for polychlorinated biphenyls. *J. Chem. Eng. Data*. **41**: 895–899.

Harner, T.; Farrar, N.J.; Schoeib, M.; Jones, K.C.; Gobas, F.A.P.C. 2003, Characterization of polymer-coated glass as a passive air sampler for persistent organic pollutants. *Environ. Sci. Technol.* **37**: 2486–2493.

Hassett, J.P.; Force, M.; Song, H. 1989, A Passive In situ Sampler for Organic Compounds in Water. *Extended Abstracts of the 198th National Meeting of American Chemical Society;* Miami Beach, FL; **5**: 496–397.

Huckins, J.N. 1988, Solvent and polymer interactions. USGS, Columbia Environmental Research Center, Columbia, MO; Unpublished work.

Huckins, J.N. 1989, A Novel Approach for Monitoring and Subsequent Cleanup of Nonpolar Contaminants in Water. *The 103rd Association of Official Analytical Chemists Annual International Meeting;* St. Louis, MO. Abstract **327**.

Huckins, J.N.; Tubergen, M.W.; Manuweera, G.K. 1990a, Semipermeable membrane devices containing model lipid: A new approach to monitoring the availability of lipophilic contaminants and estimating their bioconcentration potential. *Chemosphere* **20**: 533–552.

Huckins, J.N.; Tubergen, M.W.; Lebo, J.A.; Gale, R.W.; Schwartz, T.R. 1990b, Polymeric film dialysis in organic solvent media for cleanup of organic contaminants. *J. AOAC* **73**: 290–293.

Huckins, J.N.; Manuweera, G.K.; Petty, J.D.; Mackay, D.; Lebo, J.A. 1993, Lipid-containing semipermeable membrane devices for monitoring organic contaminants in water. *Environ. Sci. Technol.* **27**: 2489–2496.

Huckins, J.N. and Petty, J.D.1994a, Use of medical-grade silicone or silastic tubing alone as a passive sampler medium. USGS, Columbia Environmental Research Center, Columbia, MO; Unpublished work.

Huckins, J.N.; Petty, J.D.; Orazio, C.E. ; Lebo, J.A.; Clark R.C.; Haverland, P.S. 1994b, *A Laboratory Study to Demonstrate the Feasibility of the use of SPMD Permeability Reference*

Compounds (PRCs) to Correct for the Effects of Fouling on the Uptake of PAHs. USGS, Columbia Environmental Research Center, Columbia, MO; Unpublished report to American Petroleum Institute (API), Washington, DC.

Huckins, J.N.; Petty, J.D.; Prest, H.F.; Clark, R.C.; Alvarez, D.A.; Orazio, C.E.; Lebo, J.A.; Cranor, W.L.; Johnson, B.T. 2002a, *A Guide for the Use of Semipermeable Membrane Devices (SPMDs) as Samplers of Waterborne Hydrophobic Organic Contaminants;* Publication No. 4690; American Petroleum Institute (API): Washington, DC.

Huckins, J.N.; Petty, J.D.; Lebo, J.A.; Almeida, F.V.; Booij, K.; Alvarez, D.A.; Cranor, W.L.; Clark, R.C.; Mogensen, B.B. 2002b, Development of the permeability/performance reference compound (PRC) approach for in situ calibration of semipermeable membrane devices (SPMDs). *Environ. Sci. Technol.* **36**: 85–91.

Huckins, J.N.; Prest, H.F.; Petty, J.D.; Lebo, J.A.; Hodgins, M.M.; Clark, R.C.; Alvarez, D.A.; Gala, W.R.; Steen, A.; Gale, R.W.; Ingersoll, C.G. 2004, Overview and comparison of lipid-containing semipermeable membrane devices (SPMDs) and oysters (Crassostrea gigas) for assessing chemical exposure. *Environ. Toxicol. Chem.* **23**: 1617–1628.

Huebner, J.D. and Pynnönen, K.S. 1992, Viability of glochida of two species of Anodonta exposed to low pH and selected metals. *Can. J. Zool.* **70**: 2348–2354.

Hwang, S-T. and Kammermeyer, K. 1984, *Membranes in Separations*. Krieger Publishing: Malabar, FL.

Johnson, K.A.; Naddy, R.B.; Weisskopf, C.P. 1995, Passive sampling devices for rapid determination of soil contaminant distributions. *Toxicol. Environ. Chem.* **51**: 31–44.

Kingston, J.K.; Greenwood, R.; Mills, G.A., Morrison, G.M.; Björklund-Persson, L. 2000, Development of a novel passive sampling system for the time-averaged measurement of a range of organic pollutants in aquatic environments. *J. Environ. Monit.* **2**: 487–495.

Klein, A. W. and Schmidt-Bleek, F. 1982, Significance and Limitations of Environmental Compartmentalization Models in the Control of New Chemicals Based on the Organization for Economic Cooperation and Development Minimum Premarketing Set of Data. In *Modeling The Fate of Chemicals in the Aquatic Environment;* Dickson, K. L., Maki, A. W., Cairns, J. Jr., Eds.; Ann Arbor Science Publishers: Ann Arbor, MI.; pp. 73–92.

Kraut-Vass, A. and Thoma, J. 1991, Performance of an extraction disk in synthetic organic chemical analysis using gas chromatography-mass spectrometry. *J. Chromatogr.* **583**: 233–240.

Landrum, P.F.; Hayton, W.L.; Lee, H., II; McCarty, L.S.; Mackay, D.; McKim, J.M. 1994, Synopsis of Discussion Session on the Kinetics behind Environmental Bioavailability. In *Bioavailability: Physical, Chemical and Biological Interactions;* Hamelink, J.L., Landrum, P.F., Bergman, H.L., and Benson W., Eds.; CRC Press: Boca Raton, FL.; pp. 203–219.

Lefkovitz, L.F.; Crecelius, E.A.; Gilfcil, T.J. 1994, The Use of Semipermeable Membrane Devices to Predict Bioaccumulation of Hydrophobic Organic Contaminants. *The 15th Annual meeting of Society of Environmental Toxicology and Chemistry*, Denver, CO; Abstract WE25.

Leslie, A.L.; Oosthoek, A.J.P.; Busser, F.J.M.; Kraak, M.H.S.; Hermens, P.L.M. 2002, Biomimetic solid-phase microextraction to predict body residues and toxicity of chemicals that act by narcosis. *Environ. Toxicol. Chem.* **21**: 229–234.

Lieb, W.R. and Stein, W.D. 1969, Biological membranes behave as non-porous polymeric sheets with respect to the diffusion of non-electrolytes. *Nature* **224**: 240–243.

Litten, S.; Mead, B.; Hassett, J. 1993, Application of passive samplers (PISCES) to locating a source of PCBs on the Black River, New York, NY. *Environ. Toxicol. Chem.* **12**: 639–647.

Livingstone, D. R.; Moore, M.N.; Lowe, D.M.; Casci, C.; Farrar, S. 1985, Responses of the cytochrome P-450 monooxygenase system to diesel oil in the common mussel Mytilus edulis L. and the periwinkle, Littorina littorea L. *Aquat. Toxicol.* **7**: 79–91.

Mackay, D. and Paterson, S. 1981, Calculating fugacity. *Environ. Sci. Technol.* **15**: 1006–1013.

Mackay, D.; Shiu, W.Y.; Ma, K.C. 1992a, *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals: Monoaromatic Hydrocarbons, Chlorobenzenes, and PCBs*; Lewis Publishers: Chelsea, MI.; Vol. I.

Mackay, D.; Shiu, W.Y.; Ma, K.C. 1992b, *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals: Polynuclear Aromatic Hydrocarbons, Polychlorinated Dioxins, and Dibenzofurans*; Lewis Publishers: Chelsea, MI.; Vol. II.

Mackay, D. 1994, Unraveling the Choreography of Contaminant Kinetics: Approaches to Quantifying the Uptake of Chemicals by Organisms. In *Bioavailability: Physical, Chemical and Biological Interactions;* Hamelink, J.L., Landrum, P.F., Bergman, H.L., Benson W., Eds.; CRC Press: Boca Raton, FL.; pp. 171–177.

Mackay, D.; Shiu, W.Y.; Ma, K.C. 1997, *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals: Pesticide Chemicals*; Lewis Publishers: Boca Raton, FL; Vol. V.

Mayer, P.; Vaes, W.H.J.; Wijnker, F.; Legierse, K.C.H.M.; Kraaij, R.; Tolls, J.; Hermens, J.L. 2000, Sensing dissolved sediment porewater concentrations of persistent and bioaccumulative pollutants using disposable solid-phase microextraction fibers. *Environ. Sci. Technol.* **34**: 5177–5183.

Mayer, P. 2003, National Environmental Research Institute (NERI), Roskilde, Denmark. Personal communication.

McLachlan, M. 1999, Framework for the interpretation of measurements of SVOCs in plants. *Environ. Sci. Technol.* **33**: 1799–1804.

Meadows, J.C.; Tillitt, D.E.; Huckins, J.N.; Schroeder, D. 1993, Large-scale dialysis of sample lipids using a semipermeable membrane device. *Chemosphere* **26**: 1993–2006.

Moring, J.B. and Rose, D.R. 1997, Occurrence and concentration of polycyclic aromatic hydrocarbons in semipermeable membrane devices and clams in three urban streams of the Dallas-Fort Worth Metropolitan Area, Texas. *Chemosphere* **34**: 551–566.

Mueller, J. 2004, National Research Centre for Environmental Toxicology (NRCET), Coopers Plains, Australia. Personal communication.

Neely, W.B. 1980, *Chemicals in the Environment: Distribution, Transport, Fate and Analysis;* Marcel Dekker: New York, NY.

Ockenden, W.A.; Prest, H.F.; Thomas, G.O.; Sweetman, A.; Jones, K.C. 1998, Passive air sampling of PCBs: Field calculation of atmospheric sampling rates by triolein-containing semipermeable membrane devices. *Environ. Sci. Technol.* **32**: 1538–1543.

Paschke, A. and Popp, P. 2003, Solid-phase microextraction fibre-water distribution constants of more hydrophobic organic compounds and their correlations with octanol-water partition coefficients. *J. Chromatogr. A* **999**: 35–42.

Pauly, S. 1989, Permeability and Diffusion Data. In *Polymer Handbook*, 3rd ed., Brandrup, J. Immergut, E.H., Eds.; Wiley & Sons: New York.; Section 6, pp. 435–449.

Petty, J.D.; Huckins, J.N.; Zajicek, J.L. 1993, Application of semipermeable membrane devices (SPMDs) as passive air samplers. *Chemosphere* **27**: 1609–1624.

Petty, J.D. and Orazio, C.E. 1996, *Application of Semipermeable Membrane Devices (SPMDs) As Passive Monitors of the Environment of Antarctica*. USGS, Midwest Science Center, Columbia, MO; Unpublished report to National Science Foundation: Washington, DC.

Petty, J.D.; Huckins, J.N.; Alvarez, D.A.; Brumbaugh, W.G.; Cranor, W.L.; Gale, R.W.; Rastall, A.C.; Jones-Lepp, T.L.; Leiker, T.J.; Rostad C.E.; Furlong, E.T. 2004, A holistic passive integrative sampling approach for assessing the presence and potential impacts of waterborne environmental contaminants.*Chemosphere* **54**: 695–705.

Prest, H.F.; Jarman, W.M.; Burns, S.A.; Weismuller, T.; Martin, M.; Huckins, J.N. 1992, Passive water sampling via semipermeable membrane devices (SPMDs) in concert with bivalves in the Sacramento/San Joachin river delta. *Chemosphere* **25**: 1811–1824.

Rand, G.M. and Petrocelli, S.R., Eds. 1985, *Fundamentals of Aquatic Toxicology, Methods and Applications*; Hemisphere Publishing: Washington, DC.

Rantalainen, A.-L.; Ikonomou, M.G.; Rogers, I.H. 1998, Lipid-containing semipermeable-membrane devices (SPMDs) as concentrators of toxic chemicals in the Lower Fraser River, British Columbia.*Chemosphere* **37**: 1119–1138.

Rogers, C.E. 1985, Permeation of Gases Vapours in Polymers. In *Polymer Permeability*, Comyn, J., Ed.; Elsevier Applied Science LTD: London, England; pp. 11–73.

Sabaliūnas, D. and Sodergren, A. 1996, Uptake of organochlorine pesticides by solvent-filled cellulose and polyethylene membranes. *Ecotox. Environ. Safe.* **35**: 150–155.

Schnoor, J.L.; Rao, N.B.; Cartwright, K.J.; Noll, R.M. 1982, Fate and Transport Modeling for Toxic Substances. In *Modeling The Fate Of Chemicals In The Aquatic Environment;* Dickson, K. L., Maki, A. W., Cairns, j. Jr., Eds.; Ann Arbor Science Publishers: Ann Arbor, MI.; pp. 145–163.

Shoeib, M. and Harner, T. 2002, Characterization and comparison of three passive air samplers for persistent organic pollutants. *Environ. Sci. Technol.* **36**: 4142–4151.

Smedes, F. 2004, National Institute for Coastal and Marine Management (RIKZ), The Netherlands; Unpublished Work.

Södergren, A. 1987, Solvent filled dialysis membranes simulate uptake of pollutants by aquatic organisms. *Environ. Sci. Technol*. **21**: 855–859.

Strandberg, B.; Bergqvist, P.-A.; Rappe, C. 1998, Dialysis with semipermeable membranes as an efficient lipid removal method in the analysis of bioaccumulative chemicals. *Anal. Chem.* **70**: 526–533.

Vrana, B. and Schüürmann, G. 2002, Calibrating the uptake kinetics of semipermeable membrane devices in water: Impact of hydrodynamics. *Environ. Sci. Technol.* **36**: 290–296.

Wang, W-X. and Fisher, N.S. 1999, Assimilation efficiencies of chemical contaminants in aquatic invertebrates: A synthesis. *Environ. Toxicol. Chem.* **18**: 2034–2045.

Wania, F.; Shen, L.; Lei, Y.D.; Teixeira, C.; Muir, D.C.G. 2003, Development and calibration of a resin-based passive sampling system for monitoring persistent organic pollutants in the atmosphere. *Environ. Sci. Technol*. **37**: 1352–1359.

Wilcockson, J. B. and Gobas, F.A.P.C. 2001, Thin-film solid-phase extraction to measure fugacities of organic chemicals with low volatility in biological samples. *Environ. Sci. Technol*. **35**: 1425–1431.

Zabik, J.M.; Aston, L.S.; Seiber, J.N. 1992, Rapid characterization of pesticide residues in contaminated soils by passive sampling devices. *Environ. Toxicol. Chem*. **11**: 765–770.

Zabik, M. 1988, Michigan State University, East Lansing, MI. Personal communication.

Chapter 2

Fundamentals of SPMDs

2.1. SPMD DESCRIPTION AND RATIONALE

From the discussions thus far, the reader can infer that SPMDs are designed to mimic the passive diffusional and partitioning steps of bioconcentration while providing semi-quantitative to quantitative estimates of hydrophobic organic chemicals (HOC) concentrations in the ambient exposure medium. SPMDs (see Figure 1.1) generally consist of a thin film of the neutral triglyceride triolein (1,2,3-tri-[*cis*-9-octadecenoyl] glycerol) sealed in a layflat, thin-walled tube of low-density polyethylene (LDPE). Although fish lipid (Huckins et al., 1990a) and silicone fluids (Petty and Orazio, 1996) have been successfully used as SPMD liquid phases, triolein was chosen as the standard for use in SPMDs for the following reasons: 1) it is a major storage lipid found in most organisms; 2) its high-molecular weight (885.5 Daltons) results in extremely low LDPE membrane permeability, even during dialytic recovery of analytes; 3) triolein is commercially available in synthetic, high purity forms; 4) triolein-water partition coefficients and octanol-water partition coefficients (K_{ow}s) are similar in magnitude and are well correlated (Chiou, 1985); 5) it is a liquid down to about -4 °C; and 6) it provides a convenient reservoir for performance reference compounds (PRCs; for information on PRCs see Section 3.3.). Nonpolar liquid phases such as triolein have very low interfacial tension with LDPE, which enables the formation of a thin film with intimate membrane contact. Because solute diffusivity is 10^2 to 10^3 greater in liquids than in solids, the use of a liquid phase ensures rapid mixing of accumulated residues. In contrast, solid phase sorbents in LDPE and other nonporous hydrophobic polymer bags or enclosures are difficult to configure with

relatively high surface-area-to-sorbent-volume (AV^{-1}) ratios, and solutes in the membrane generally must vaporize to make contact with the sorbent. This step adds another potential barrier to the mass transfer or uptake of analytes.

As indicated earlier, the selection of nonporous LDPE layflat tubing for SPMDs was based on it's stability in organic solvents (required for dialysis and membrane cleaning), the low diffusion rates of triolein relative to HOCs in LDPE (both uptake and dialytic recovery processes), and it's resistance to abrasion and puncturing. The results of this research also enabled the development of polymeric film (LDPE) dialysis in organic solvent, which has been shown to be a highly effective method for separating organic contaminants from lipids (Huckins et al., 1990b; Meadows et al., 1993; Bergqvist et al., 1998). Thin-walled layflat LDPE is widely available and, because it is a thermoplastic, the lipid phase can be sealed inside the membrane tube using molecular welding (heat seals).

Although SPMDs are simple in design, the mechanisms governing their performance as passive samplers of HOCs can be quite complex (see Chapter 3). The underlying principle of molecular-size discrimination in the uptake and loss of chemicals by SPMDs is shown in Figure 2.1. The sizes of the molecules shown in the illustration are scaled to the postulated ≈10 Å diameter of the transient pores in the membrane. Temperature and the presence of plasticizers/solvent will affect the effective pore sizes.

In nonporous polymers such as LDPE, free volume is formed by random thermal motion of polymer chains in rubbery regions of the matrix (LDPE is about 50% crystalline and 50% rubbery). The volume associated with "fixed pores," which exist only in the crystalline regions of the polymer, is largely insignificant (Rogers, 1985) relative to the volume associated with the rubbery regions of the polymer. Thus, the passive sampling of dissolved and vapor phase analytes involves the dissolution of individual molecules into the rubbery regions of the polymer. The diameters of the transient polymeric cavities range up to ≈10 Å (Comyn, 1985), which precludes sampling of the waterborne residues associated with particulate organic carbon or dissolved organic carbon such as humic acids. The frequency of cavity formation is largely controlled by temperature-dependent chain segmental motility. Also, it is noteworthy that the postulated size of transient cavities in biomembranes is 9.8 Å (Opperhuizen et al., 1985). The molecular size limitation of nonporous polymers suggests that only readily bioavailable or dissolved chemicals (molecular weights <600 Daltons) will be sampled by SPMDs, which has been corroborated by the work of Ellis et al. (1995). This size exclusion characteristic of nonporous polymers is the reason for extremely low diffusion rates of triolein in LDPE (i.e., losses from SPMDs).

Ions of organic and inorganic chemicals are not sampled by SPMDs because charged species are hydrophilic and are essentially insoluble in nonpolar LDPE. Water quality variables, such as pH and salinity (Huckins et al., 1999), may affect the dissolved concentrations of some compounds in environmental waters (e.g., the residue concentrations of organic compounds with pK_as > 4 and < 9).

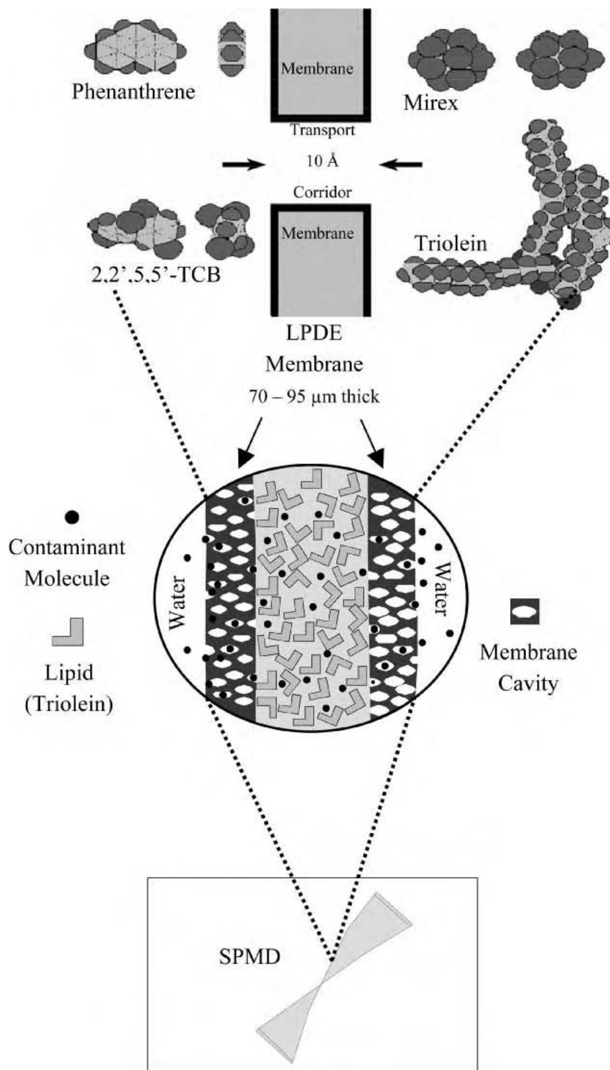

FIGURE 2.1 Exploded views showing the nonporous membrane size-exclusion phenomenon in the uptake and loss of organic compounds. Middle illustration shows the movement of contaminant molecules through transient pores in the membrane and retention (membrane exclusion) of much larger lipid molecules. Upper illustration shows similarly scaled space-filled molecular models of some organic contaminants and triolein, along with the hypothetical polymer pore (transient) size. Reprinted with permission from the American Petroleum Institute (Huckins et al., 2002).

Conceptually, SPMD data fills a gap between exposure assessments based on direct analytical measurement of total residues in water and air, and the analysis of residues present in biomonitoring organisms. SPMDs provide a biomimetic approach (i.e., processes in simple media that mimic more complex biological processes) for determining ambient HOC concentrations, sources, and gradients. Residues accumulated in SPMDs are representative of their environmental bioavailability (see Section 1.1.) in water and air and the encounter-volume rate as defined by Landrum et al. (1994) is expected to be proportional to the uptake rate. SPMD-based estimates of water concentrations can be readily compared to aquatic toxicity data (generally based on dissolved phase concentrations) and SPMD extracts can be used to screen for toxic concentrations of HOCs using bioassays or biomarker tests.

2.2. APPLICABILITY OF SPMDs

Although SPMDs concentrate a very wide range of hydrophobic organic compounds, they are not suitable for all environmental contaminants. Table 2.1 lists chemicals classes or selected compounds shown to concentrate in SPMDs, but is not all inclusive.

Examination of Table 2.1 shows that SPMDs are not suitable for sampling very large organic molecules, ionized organic compounds, and metals. For compounds such as chlorinated phenols with different pK_as, the environmental pH determines the ratio of ionized to neutral species, which directly impacts the capacity of an SPMD to concentrate the chemical. Thus, the selectivity of SPMD sampling is limited to size exclusion properties of the low density polyethylene membrane (see Figure 2.1) and the polarity/ionization potential of the analyte. Hydrophobic or nonpolar compounds are characterized by a lack of polar functional groups and a very low potential for ionization at environmental pHs (i.e., a range of about 4.5 to 9). SPMDs will significantly concentrate ambient levels of nearly all

Table 2.1 Classes or Specific Chemicals Known to Concentrate in SPMDs

priority pollutant PAHs and alkylated PAHs	chlorinated dibenzodioxins, including 2,3,7,8-TCDD
many heterocyclic aromatics, cyclic hydrocarbons (e.g., decalin and alkylated decalins) and aliphatics	polybrominated diphenyl ethers
organochlorine pesticides	chlorinated benzenes
other pesticides: includes diazinon, endosulfans, pyrethroids, toxaphene, and trifluralin	chlorinated anisoles and veratroles
PCB congeners	alkyl phenols (nonyl phenol)
chlorinated naphthalenes	triclosan
chlorinated dibenzofurans, including 2,3,7,8-TCDF	tributyl tin
	sulfur
	essentially, any compound with log $K_{ow} \geq 3.0$[a]

[a] See Table 8.1 for additions to this list.

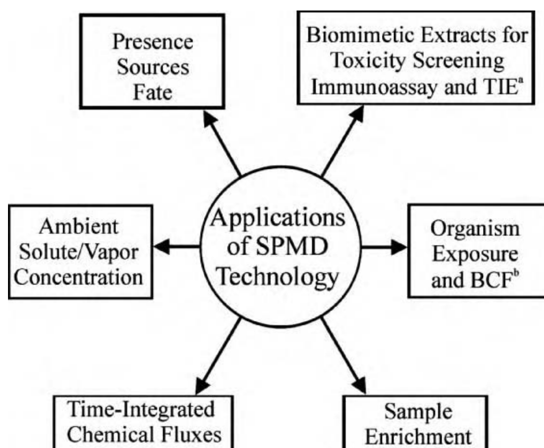

FIGURE 2.2 Various applications of SPMDs reported in the literature.

hydrophobic compounds with log K_{ow}s ≥ 3 and the sampling rates (R_ss) of most HOCs are controlled by the "encounter volume", as defined for aquatic organisms in Chapter 1. Water quality variables, such as salinity (Brown, 1978), can affect the dissolved concentrations of hydrophobic compounds in environmental waters, and thus the amounts of residues accumulated by an SPMD. However, water quality should have no effect on sampling rate constants (see Section 2.3.).

For compounds with log K_{ow}s < 3, SPMDs may not perform as well as other sampling procedures such as purge and trap methods for volatile organic compounds and the polar organic chemical integrative sampler (POCIS) for hydrophilic organic compounds (Alvarez et al., 2004). Also, for compounds with log K_{ow}s and octanol-air partition coefficients (K_{oa}s) larger than about 7.5 and 10.5, respectively, only vanishingly small amounts will be available for uptake, because of sorption to particulates and dissolved organic carbon. However, SPMDs have been successfully used for determining chemicals with very high K_{ow}s and K_{oa}s in environmental systems (McCarthy and Gale, 2001; Booij et al., 2002; Bartkow et al., 2004) but may require the use of composite SPMD samples (e.g., three to nine 1-mL triolein SPMDs).

Figure 2.2 illustrates a number of potential SPMD applications. More specifically, SPMD technology has been used for the following: 1) determination of the presence, sources, and the transport/fate of hydrophobic semi-volatile organic pollutants; 2) estimation of ambient time-weighted average (TWA) dissolved or vapor phase chemical concentrations; 3) determination of time-integrated fluxes of dissolved and vapor phase chemicals in environmental media; 4) *in situ* biomimetic sample extracts of readily available chemicals for toxicity screening (bioassays or

biomarkers), immunoassay, and toxicity identification evaluation; 5) estimation of organism exposure and bioconcentration factors (*BCF*s) for dissolved and vapor phase compounds; and 6) polymeric membrane organic solvent dialysis for enriching a wide variety of hydrophobic analytes in environmental sample extracts. Some of these applications and example studies are covered in subsequent Chapters. Herein, we briefly discuss some general considerations associated with SPMD applications.

Before choosing SPMDs for a project, data quality requirements must be considered. Two extreme levels are litigation quality data (i.e., legally admissible) and screening data (note that rigorous quality control can be applied to screening tests). The SPMD approach can be readily used in screening projects, such as the presence/absence, sources, and relative amounts of chemicals (ranking) measured in SPMDs at different sites, to more in-depth studies designed to estimate the ambient concentrations of chemicals. For projects in the USA requiring litigation quality data, study results are typically generated by the US EPA or industry standard methods in conjunction with a formal set of quality assurance (QA) and quality control (QC) guidelines/parameters. Particular attention must be made to security issues (QA) such as sample chain of custody. Because US EPA and industry standard methods are often more than a decade behind the best available technology, there has been increased use of more current, but well-established, nonstandard methods (so-called "performance based methods") in litigation.

The SPMD approach is widely used by environmental investigators and is beginning to gain acceptance from regulatory and resource management agencies (e.g., certain EPA regions and states, the United Kingdom, and the Czech Republic). However, the authors are not aware of any studies conducted with protocols adequate for litigation. The SPMD studies presented herein may meet the criteria based on QC parameters but typically fail to meet the QA requirements for litigation, such as chain of custody documentation. However, as *a priori* acceptance of SPMD technology becomes more widespread, and studies are conducted with more stringent QA standards, the likelihood of the successful incorporation of SPMD data in litigation will increase.

Other issues of SPMD applicability relate to the type of matrix sampled. In particular, the ability to extrapolate ambient concentrations from analyte concentrations in SPMDs differs significantly depending on the matrix sampled and the variables affecting analyte concentrations in the matrix. An assumption, fundamental to the use of mathematical models for concentration extrapolations, is that the sampling process does not significantly alter ambient solute or vapor concentrations of analytes. Theory and studies to date show that this assumption is not violated when sampling surface waters and the atmosphere. However, some exceptions may occur when sampling sediments, groundwater and small, enclosed indoor spaces. To maintain pore water concentration during sampling, solute resupply via desorption from particulate and dissolved organic carbon phases of sediment must be faster than the sampler uptake rates. In the only test of this assumption in the literature, Booij et al. (2003) used LDPE strip samplers in sediments (collected

from two marine harbors) and found that pore water concentration estimates, based on linear uptake rates and PRC loss rates, corresponded well to those based on sediment-pore water equilibrium partition coefficients. These data suggest that chemical resupply of the pore water was rapid enough to offset sampler uptake or clearance rates. Because SPMDs and LDPE strips with similar surface areas sample at essentially the same rate during linear uptake, this finding likely applies to SPMDs as well (see Chapter 3 for more details).

Monitoring wells in fine grained strata often have low coefficients of permeability or recharge rates or hydraulic conductivities (see Chapter 3 for more details). In this case, SPMD sampling may significantly reduce well water concentrations of the chemicals of concern. However, knowledge of SPMD uptake rates for target compounds (see Appendix A), the groundwater hydraulic conductivity at the well site, the cross-sectional surface area of the well and the approximate volume of water in the well, should enable investigators to determine if water concentration will be significantly reduced during sampling. If so, the size (i.e., surface area) or numbers of SPMDs used in a well can be reduced as long as acceptable detection and quantitation limits can be achieved. When very low quantitation limits are required and the well's hydraulic conductivity is low, it may be possible to increase the numbers or the surface area of the SPMDs used to ensure that the extraction efficiency of target compounds from well water (dissolved phase) is $>90\%$ during an exposure period. Thus, depending on the nature of the well, SPMD sampling may deplete, moderately affect or have little effect on groundwater concentrations of target solutes.

SPMDs are biomimetic only when partitioning-diffusion processes mediate bioconcentration. The appropriateness of using SPMD data to predict equilibrium concentrations of bioconcentratable contaminants in aquatic organisms is dependent on a number of factors, as discussed in Chapter 7 and by Huckins et al. (2004). Briefly, SPMDs and other passive samplers cannot account for physiological and behavioral differences among species such as residue metabolism, dietary uptake and trophic transfer, which can cause residue concentrations in tissues to vary considerably from equilibrium partition levels (Connell, 1990; Huckins et al., 2004). Also, unlike many aquatic invertebrates, shellfish and finfish, SPMDs generally do not reach equilibrium with hydrophobic chemicals (i.e., for compounds with log K_{ow}s >5) during exposures of 42 d or less. Thus, direct comparisons of SPMD-water partition coefficients (K_{sw}s) and *BCF*s often are not feasible. However, SPMDs provide reasonably accurate estimates of *in situ* TWA concentrations of dissolved-phase chemical concentration. Use of SPMD-derived water concentrations and biomonitoring organism (BMO) tissue concentrations may enable the development of improved regression models for estimating HOC *BCF*s. This statement is based on the assumption that some of the scatter in *BCF*s derived from existing regression models relates to the inability of previous investigators to determine TWA concentrations of bioavailable residues in exposure waters. Regardless of the difficulties in directly relating SPMD concentrations to *BCF*s, SPMDs provide reasonable estimates of aquatic organism exposure to

persistent HOCs (e.g., Meadows et al., 1998; Huckins et al., 2004), via the dissolved phase.

The case for using SPMDs as a biomimetic device for estimating TWA atmospheric exposure of HOCs to terrestrial organisms is less well developed. The possible exception to this statement is the exposure of humans to semi-volatile organic compounds (SVOCs) in indoor air. Determination of TWA values for volatile organic compounds using passive samplers is widely accepted as the method of choice for assessing occupational exposure. Because K_{oa}s are very large for hydrophobic SVOCs, sampling is generally integrative for months. Note that TWAs can only be determined by integrative passive samplers. Furthermore, the sampling rates and capacities of SPMDs for vapors of SVOCs are much higher than traditional passive samplers. This permits the isolation of sufficient target compound mass for bioassay and lower quantitation limits.

2.3. ACCUMULATION OF CHEMICALS BY SPMDs

Although "Theory and Modeling" is more extensively discussed in Chapter 3, it is helpful to briefly discuss some basic concepts related to the accumulation of chemicals by SPMDs. Huckins et al. (1993) have shown that the uptake process obeys first-order kinetics (Figure 2.3). This type of exchange kinetics is characterized by "half-lives" ($t_{1/2}$), which are constant for a particular set of conditions and

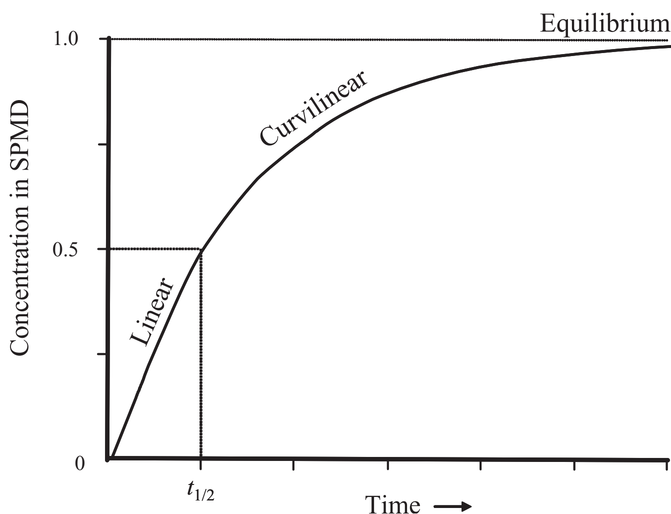

FIGURE 2.3 Plot of the three phases of SPMD uptake, illustrating first-order exchange kinetics. Time is given in halflives or $t_{1/2}$, which in this case is the time required to reach half of the equilibrium concentration of a chemical. This figure is reproduced courtesy of the American Petroleum Institute (Huckins et al., 2002).

chemicals, and "rate constants" that are independent of chemical concentration. In this case, the rate of change of the concentration in an SPMD (C_s) is given by

$$dC_s/dt = k_u C_w - k_e C_s \tag{2.1}$$

where k_u is the uptake rate constant, k_e is the elimination rate constant, C_w is the concentration in the water phase, and t is time. In the case of SPMD-air exchange, it is only necessary to replace the subscript "w" by "a". In the initial stages of the uptake, the term $k_e C_s$ is much smaller than $k_u C_w$ and Eq. 2.1 reduces to

$$dC_s/dt \approx k_u C_w \tag{2.2}$$

Equation 2.2 shows that C_s increases linearly with time when the aqueous concentration is constant. This is why the initial stage of the uptake process is called the "linear uptake phase" (Figure 2.3). Integrating Eq. 2.2 over time shows that sampling is "integrative", and that C_s is linearly proportional to the TWA concentration in the water phase ($C_{w,TWA}$)

$$C_s(t) = \int dC_s = k_u \int C_w \, dt \equiv k_u C_{w,TWA} t \tag{2.3}$$

When equilibrium is attained, the rate of uptake balances the rate of loss, and Eq. 2.1 reduces to

$$C_s = C_w k_u / k_e \tag{2.4}$$

This stage of the uptake process is therefore called the "equilibrium sampling phase".

The time it takes to reach 50% of the equilibrium concentration ($t_{1/2}$) is related to the elimination rate constant (k_e) by

$$t_{1/2} = \ln 2 / k_e \tag{2.5}$$

where ln 2 is the natural logarithm of 2. Figure 2.3 shows that analytes accumulated by an SPMD may be in the linear (integrative), curvilinear, or equilibrium partitioning phases of uptake, depending on the chemical sampled, environmental conditions, and the duration of the exposure. Also, Figure 2.3 shows that sampling is essentially integrative up to $t < t_{1/2}$. For $t > 4t_{1/2}$, equilibrium is essentially complete (>94%). Although the limits between the linear uptake phase, the curvilinear phase, and the equilibrium phase are somewhat arbitrary, these times can be used to get a feeling for the extent to which sampling is integrative.

Modeling SPMD residue exchange as two compartments (membrane and lipid) adds complexity (Huckins et al., 1993, 1999). A single compartment model can be applied to SPMD residue exchange when using K_{sw}, resistance is controlled by the boundary layer, and equilibrium exists between the membrane and lipid phases. The K_{sw} is the volume-averaged partition coefficient of the membrane and lipid phases and is given by Eq. 3.11. In simple one-compartment models (Figure 2.4), the concentration at any moment in time is determined by competing

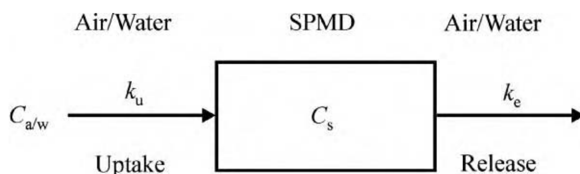

FIGURE 2.4 Single compartment model for the uptake and release of hydrophobic organic compounds. The a/w subscript refers to air or water.

rates of chemical uptake and release, as given in Eq. 2.1. This common modeling approach is widely used for estimates of the concentration of hydrophobic chemicals in the lipids of aquatic organisms.

2.4. PASSIVE SAMPLER FUNDAMENTALS AND TERMINOLOGY

Until the advent of SPMDs and solid phase microextraction (SPME) fibers, passive sampling devices were generally limited to integrative "diffusion" or "permeation" samplers (Fowler, 1982), with engineered barriers that control uptake rates. The engineered rate-limiting barriers of these classical samplers consist of a structural feature with stagnant air or water (diffusional samplers) or a nonporous polymeric membrane (permeation samplers). In both cases, these barriers are designed to account for >90% of the total resistance to solute or vapor uptake by the sampler. The advantage of using the engineered barrier approach is that changes in facial velocity and turbulence have little effect on sampling rates and thus can be neglected. Also, the diffusion samplers are relatively simple to calibrate because equations for calculating diffusion coefficients in air and water are well developed and the relevant diffusional pathway or length is fixed by design. The disadvantage of both of these engineered diffusion and permeation samplers is that their uptake fluxes (e.g., ng cm^{-2} d^{-1}) are generally more than an order of magnitude lower than the uptake rates of samplers under external boundary layer control such as SPMEs and SPMDs.

All passive monitoring devices operate on the basis of diffusive transfer, regardless of whether they are classified as diffusion, permeation or unclassified (e.g., SPMDs), and the rate-limiting barrier is the step with the greatest resistance to mass transfer (see Figure 3.1). Fick's first law is the fundamental law of diffusion. It states that the flux of a chemical in the x-direction (j_x, e.g., ng cm^{-2} d^{-1}) is proportional to the concentration gradient ($\partial C/\partial x$)

$$j_x = -D_i(\partial C/\partial x) = -D_i \Delta C/\delta_i \tag{2.6}$$

where D_i is the diffusion coefficient in the rate limiting barrier, δ_i is the effective thickness of the rate limiting barrier, and ΔC is the concentration difference across the barrier. Fick's first law appears to apply to diffusion of trace levels of HOCs through SPMD membranes and associated boundary layers. However,

the polymer permeability literature contains many references (e.g., Comyn, 1985) where membrane-diffusion coefficients are not constant, requiring the application of Fick's second law.

Unlike the aforementioned classical samplers, the barrier limiting chemical uptake by SPMDs is dependent on physicochemical properties of the target compound and the exposure conditions. For example, under conditions of low water flows and turbulence (i.e., <1 cm s^{-1}), the water boundary layer (WBL) is relatively thick and compounds with log K_{ow}s ≥ 4.5 are generally under WBL control and δ_w represents the effective thickness of the WBL. In this case, SPMDs act as diffusion samplers (Huckins et al., 1999). However, under the same conditions, compounds with log K_{ow}s < 4.5 are under membrane control (δ_m), and SPMDs act as permeation samplers. The reason for this bimodal rate control is that the magnitude of the membrane-water or membrane-air partition coefficient affects the resistance to mass transfer across the membrane (Eqs. 3.8 and 3.9). More specifically, high membrane-water partition coefficients effectively reduce resistance to mass transfer across the membrane. The transition point between membrane and boundary layer rate control varies (see Figure 7.2) depending on flow and turbulence conditions at the external surface of the membrane (i.e., thinning of the boundary layer reduces resistance to mass transfer). Because SPMD sampling rates are affected by environmental conditions, *in situ* sampling rates may vary greatly (see Section 3.6.) across sites. As mentioned in Chapter 1 and discussed in Chapter 3, PRCs were developed to provide a means of determining the effects of environmental exposure conditions on SPMD sampling rates.

Some introductory comments on the conceptual basis of SPMD uptake (k_u) and release (k_e) rate constants and the associated sampling rates (i.e., R_s) are in order. The k_u can be conceptualized as the volume of air or water cleared of chemical per unit sampler mass or volume per unit time (e.g., mL g^{-1} d^{-1} or mL mL^{-1} d^{-1}) and R_s is the volume of air or water cleared per unit time (e.g., L d^{-1}). Thus, the only difference between k_u and R_s is that R_s is not normalized to a unit mass or unit volume of sampler. In the context of organism exposure (see Section 1.1.), the SPMD k_u is equivalent to the "encounter volume" times the fractional bioavailability of the chemical (which excludes dietary uptake). The release rate constant (d^{-1}) is equal to $k_u K_{sw}^{-1}$.

Equation 1.1 gives the "clearance or sorption capacity" (E_v) of a thin polymeric film sampler for nonpolar organic compounds, which equals $V_s K_{sw}$ in the case of water sampling by SPMDs. E_v can be visualized as the volume of water cleared of a target compound, when an SPMD has attained equilibrium with the ambient environment. For moderate to high K_{ow} compounds, the E_v of an SPMD is generally not approached in most exposures, but E_v is often attained for relatively low K_{ow} compounds, exposed under similar conditions. In these cases, an investigator can estimate E_v volumes by using measured or estimated values of K_{sw}, or by assuming that $K_{ow} \approx K_{sw}$. The E_v volumes thus derived can be used to compare to the volumes of air or water extracted by other methods, to determine if

analyte mass is sufficient for analytical determination or bioassay screening, and to evaluate the need for compositing SPMDs. For the case of air sampling, Cao (1991) has proposed that sorbents capable of clearing >0.1 m^3 g^{-1} (i.e., SPMD-air partition coefficient [K_{sa}] $\approx 10^5$) are suitable for the integrative sampling of organic vapors. In aquatic environments, the minimal value is equivalent to about 0.12 L g^{-1} (i.e., $K_{sw} \approx 120$). For most passive samplers, this $K_{s(a/w)}$ value is far too low to maintain linear uptake for periods greater than one week and the corresponding E_vs would be inadequate to accumulate sufficient residues for trace to ultra-trace analyses.

If the aim of a study is to estimate TWA concentrations, an integrative sampler must be used. In this case, the response time (t_r) provides useful information on sampler performance in environments where concentrations vary through time. Following a step change in ambient exposure concentration, t_r can be defined as the time required for the sampling flux ($R_s C_w$) of a passive monitoring device to largely adjust to the full concentration change in the ambient environment (Fowler, 1982). Values of t_r are representative of the average time an analyte spends within the rate-limiting barrier. If a linear concentration gradient is assumed across the rate-limiting barrier, then

$$t_r = \delta_i^2 / 2D_i \tag{2.7}$$

where t_r is the response time for both integrative and steady state samplers and subscripts were defined earlier. Other non-linear derivations of t_r using Fick's second law show that t_r is the time required to achieve approximately 63% increase (relative to full change induced) in the concentration of a chemical in the rate limiting zone or region due to a step change in ambient exposure concentration. Using Eq. 2.7, values of D in water for phenanthrene, benzo[*g,h,i*]perylene and decachlorobiphenyl (PCB congener 209) from Hofmans (1998), and an estimate of SPMD boundary layer thickness under low flow conditions (<1 cm s^{-1}) by Gale (1998), t_rs for these compounds were 131, 157 and 197 s, respectively. Note that the compounds used in this example are known to be under WBL control at low-flow rates. Under higher flow conditions, these response times would be expected to be reduced by at least 4-fold. Fowler (1982) has suggested that a t_r of a few minutes or less is satisfactory for most applications of passive samplers.

If the aim of an investigator is to determine equilibrium concentrations in samplers, then the "residence time" (t_m) is a logical parameter to compare among samplers. The t_m is the mean length of time that a molecule spends in a passive sampling device, where solute exchange follows first-order kinetics. Residence time is given by

$$t_m = 1/k_e \tag{2.8}$$

where t_m is about 1.5 $t_{1/2}$s. This parameter can be determined by curve fitting when analyte concentrations reach the curvilinear or equilibrium phases of exchange kinetics (Figure 2.3) or it can be calculated when the k_u and K_{sw} are known. Residence times of chemicals in an SPMD are much larger than response times.

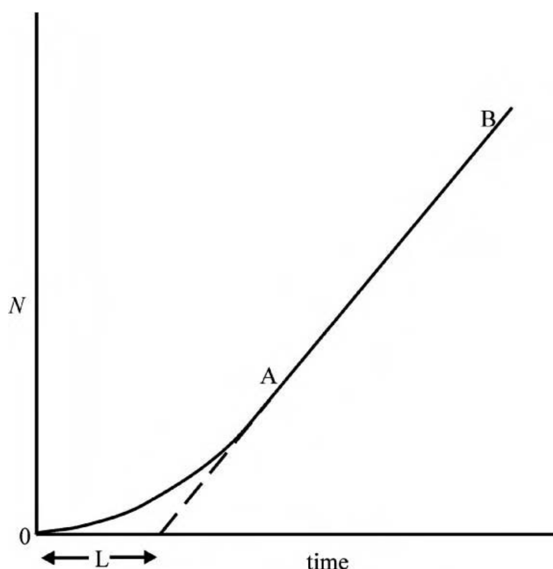

FIGURE 2.5 The amount of a chemical absorbed by a sampler through time, where the lag time (L) is the time represented by the x-intercept of the extension (dashed line) of the steady state line AB.

For example, under low flow conditions and at a temperature of 18 °C, the SPMD residence time for phenanthrene is 45.4 d and k_e values for benzo[*g,h,i*]perylene are too small to measure, which suggests a residence time of $>10^3$ d.

The lag time t_L is a closely related parameter to t_r but is generally used for diffusional processes under membrane control. This term is given by

$$t_L = \delta_i^2/6D_i \tag{2.9}$$

The meaning of this term is shown by Figure 2.5 and it is essentially the time required to attain steady state flux across a barrier. When the resistance in the boundary layer is negligible, the lag-time equation provides a convenient means of calculating membrane or polymer-diffusion coefficients.

2.5. REFERENCES

Alvarez, D.A.; Petty, J.D.; Huckins, J.N.; Jones-Lepp, T.L.; Getting, D.C.; Goddard, J.P.; Manahan, S.E. 2004, Development of a passive, in situ, integrative sampler for hydrophilic organic contaminants in aquatic environments. *Environ. Toxicol. Chem.* **23**: 1640–1648.

Bartkow, M.E.; Huckins, J.N.; Müller, J.F. 2004, Field-based evaluation of semipermeable membrane devices (SPMDs) as passive air samplers of polyaromatic hydrocarbons (PAHs). *Atmos. Environ.* **38**: 5983–5900.

Bergqvist, P.-A.; Strandberg, B.; Rappe, C. 1998, Lipid removal using semipermeable membranes in PCDD and PCDF analysis of fat-rich environmental samples. *Chemosphere* **38**: 933–943.

Booij, K.; Zegers, B.N.; Boon, J.P. 2002, Levels of some polybrominated diphenyl ether (PBDE) flame retardants along the Dutch coast as derived from their accumulation in SPMDs and blue mussels (Mytilus edulis). *Chemosphere* **46**: 683–688.

Booij, K.; Hoedemaker, J.R.; Bakker, J.F. 2003, Dissolved PCBs, PAHs, and HCB in pore waters and overlying waters of contaminated harbor sediments. *Environ. Sci. Technol.* **37**: 4213–4220.

Brown, R.A. 1978, *Fate and Effects of Polynuclear Aromatic Hydrocarbons in the Aquatic Environment*. Report No. 4297; American Petroleum Institute (API): Washington, DC.

Cao, X-L.; 1991, Determination of specific retention volumes at 20 °C for hydrocarbons on microporous carbons. *J. Chromatogr.* **586**: 161–165.

Chiou, C.T. 1985, Partition coefficients of organic compounds in lipid-water systems and correlations with fish bioconcentration factors. *Environ. Sci. Technol.* **19**: 57–62.

Comyn, J , Ed. 1985, *Polymer Permeability*; Elsevier Applied Science LTD: London, England.

Connell, D.W. 1990, *Bioaccumulation of Xenobiotic Compounds*. CRC Press: Boca Raton, FL.

Ellis, G.S.; Huckins, J.N.; Rostad, C.E.; Schmitt, C.J.; Petty J.D.; MacCarthy, P. 1995, Evaluation of lipid-containing semipermeable membrane devices (SPMDs) for monitoring organochlorine contaminants in the Upper Mississippi River. *Environ. Toxicol. Chem.* **14**: 1875–1884.

Fowler, W.K. 1982, Fundamentals of passive vapor sampling. *Am. Lab.* **14**: 80–87.

Gale, R.W. 1998, Three-compartment model for contaminant accumulation by semipermeable membrane devices. *Environ. Sci. Technol.* **32**: 2292–2300.

Hofmans, H.E. 1998, *Numerical Modeling of the Exchange Kinetics of Semipermeable Membrane Devices*. M.S. Thesis, Netherlands Institute for Sea Research: Den Burg, The Netherlands.

Huckins, J.N.; Tubergen, M.W.; Manuweera, G.K. 1990a, Semipermeable membrane devices containing model lipid: A new approach to monitoring the availability of lipophilic contaminants and estimating their bioconcentration potential. *Chemosphere* **20**: 533–552.

Huckins, J.N.; Tubergen, M.W.; Lebo, J.A.; Gale, R.W.; Schwartz, T.R. 1990b, Polymeric film dialysis in organic solvent media for cleanup of organic contaminants. *J. AOAC* **73**: 290–293.

Huckins, J.N.; Manuweera, G.K.; Petty, J.D.; Mackay, D.; Lebo, J.A. 1993, Lipid-containing semipermeable membrane devices for monitoring organic contaminants in water. *Environ. Sci. Technol.* **27**: 2489–2496.

Huckins, J.N.; Petty, J.D.; Prest, H.F.; Clark, R.C.; Alvarez, D.A.; Orazio, C.E.; Lebo, J.A.; Cranor, W.L.; Johnson, B.T. 2002, *A Guide for the Use of Semipermeable Membrane Devices (SPMDs) as Samplers of Waterborne Hydrophobic Organic Contaminants*; Publication No. 4690; American Petroleum Institute (API): Washington, DC.

Huckins, J.N.; Petty, J.D.; Orazio, C.E.; Lebo, J.A.; Clark, R.C.; Gibson, V.L.; Gala, W.R.; Echols, K.R. 1999, Determination of uptake kinetics (sampling rates) by lipid-containing semipermeable membrane devices (SPMDs) for polycyclic aromatic hydrocarbons (PAHs) in water. *Environ. Sci. Technol.* **33**: 3918–3923.

Huckins, J.N.; Prest, H.F.; Petty, J.D.; Lebo, J.A.; Hodgins, M.M.; Clark, R.C.; Alvarez, D.A.; Gala, W.R.; Steen, A.; Gale, R.W.; Ingersoll, C.G. 2004, Overview and comparison of lipid-containing semipermeable membrane devices (SPMDs) and oysters (Crassostrea gigas) for assessing chemical exposure. *Environ. Toxicol. Chem.* **23**: 1617–1628.

Landrum, P.F.; Hayton, W.L.; Lee, H., II; McCarty, L.S.; Mackay, D.; McKim, J.M. 1994, Synopsis of Discussion Session on the Kinetics behind Environmental Bioavailability. In *Bioavailability: Physical, Chemical and Biological Interactions*; Hamelink, J.L., Landrum, P.F., Bergman, H.L., and Benson W., Eds.; CRC Press: Boca Raton, FL.; pp. 203–219.

McCarthy, K.A. and Gale, R.W. 2001, Evaluation of persistent hydrophobic organic compounds in the Columbia River Basin using semipermeable membrane devices. *Hydrol. Process* **15**: 1271–1283.

Meadows, J.C.; Tillitt, D.E.; Huckins, J.N.; Schroeder, D. 1993, Large-scale dialysis of sample lipids using a semipermeable membrane device. *Chemosphere* **26**: 1993–2006.

Meadows, J.C.; Echols, K.R.; Huckins, J.N.; Borsuk, F.A.; Carline, R.F.; Tillitt, D.E. 1998, Estimation of uptake rate constants for PCB congeners accumulated by semipermeable membrane devices and brown trout (Salmo trutta). *Environ. Sci. Technol.* **32**: 1847–1852.

Opperhuizen, A.; van der Velde, E.W.; Gobas, F.A.P.C.; Liem, A.K.D.; van der Steen, J.M.D.; Hutzinger, O.; 1985, Relationship between bioconcentration in fish and steric factors of hydrophobic chemicals. *Chemosphere* **14**: 1871–1896.

Petty, J.D. and Orazio, C.E. 1996, *Application of Semipermeable Membrane Devices (SPMDs) As Passive Monitors of the Environment of Antarctica*. USGS Midwest Science Center, Columbia, MO; Unpublished report to National Science Foundation, Washington, DC.

Rogers, C.E. 1985, Permeation of Gases Vapours in Polymers. In *Polymer Permeability*, Comyn, J., Ed.; Elsevier Applied Science LTD: London, England; pp. 11–73.

Chapter 3

Theory and Modeling

3.1. UPTAKE MODELS

In this section we focus on solute exchange between SPMDs and water, but the general scheme can be easily extended to vapor exchange between SPMDs and air. Before going into details on the mathematical formulation of the exchange kinetics between SPMDs and the sample medium, it is instructive to have a look at the successive transport resistances that dissolved contaminants must overcome to be absorbed by exposed SPMDs. A few mm from the SPMD surface, all transport is dominated by eddy diffusion and convection (Figure 3.1). When solutes approach the SPMD surface, molecular diffusion becomes increasingly important relative to eddy diffusion and convection. The region where molecular diffusion dominates the transport is commonly referred to as the "aqueous diffusion layer", but other names are used as well, such as "water boundary layer" (WBL), "diffusive sub-layer", and "diffusive boundary layer". After crossing the WBL, contaminant molecules may encounter a potentially complex layer of periphyton, macrofauna, imbibed and surficial particulates, and in some cases, calcareous precipitates. We refer to this layer or coating on the external surface of the SPMD membrane as the "biofilm", bearing in mind that material composition in this layer may be organic and/or inorganic depending on the exposure site and on the season. Also, the biofilm thickness, composition, and membrane coverage generally varies and may even be absent. Contaminant transport through the biofilm takes place via molecular diffusion, or in some cases by internal ventilation by the organisms present. After crossing the biofilm, the solutes arrive at the membrane surface, diffuse through and concentrate in the LDPE phase, and finally are concentrated in the triolein.

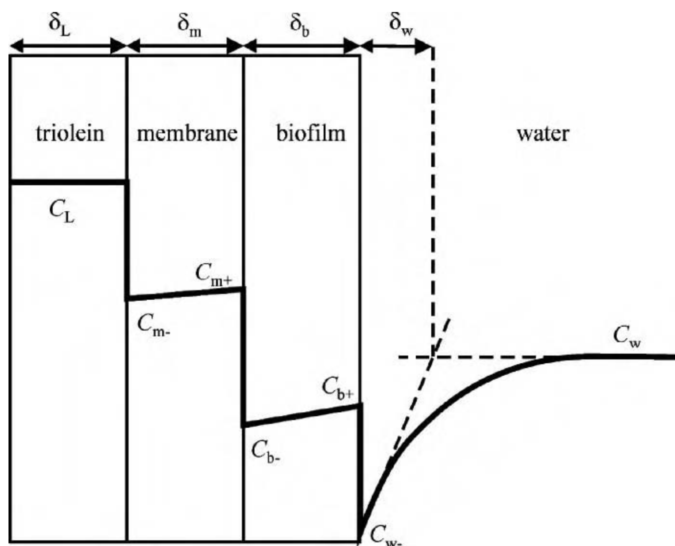

FIGURE 3.1 Schematic overview of the concentration distribution inside and outside SPMDs. The deltas (δ) represent the effective thickness of each region and the associated subscripts denote the region.

Two types of models are used to quantitatively describe the SPMD-water exchange of hydrophobic organic chemical (HOC) solutes. These models can easily be inter-converted, and differ only in the definition of the rate constants used. The fact that various authors have used the same symbols to denote different kinds of rate constants is a complicating factor that requires a careful inspection by the reader to delineate the meaning and assumptions of the respective authors.

3.1.1. Chemical Reaction Kinetics (CRK) Model

The first type of model is based on models describing bioconcentration, which in turn are based on an analogy with chemical reaction kinetics. For this reason we will refer to this type of model as the chemical-reaction kinetics (CRK) model. The exchange process is thought of as the net result of a forward (uptake) and a backward (release) reaction that is first order with respect to reactant concentration. Hence, the rate of change of the solute concentration in the SPMD (C_s) is given by

$$\frac{dC_s}{dt} = k_u C_w - k_e C_s \tag{3.1}$$

where C_w is the aqueous concentration, k_u is the rate constant for the uptake process, and k_e is the rate constant for the release process (k_u and k_e are often named k_1 and k_2 when describing bioconcentration). Solving Eq. 3.1 for the initial condition $C_s = 0$ at $t = 0$, gives

$$C_s = K_{sw} C_w[1 - \exp(-k_e t)] \tag{3.2}$$

where the SPMD-water partition coefficient (K_{sw}) equals the ratio of the two rate constants (k_u/k_e). The only assumption underlying this CRK model is that both the uptake and the release are first order processes. Equation 3.2 is useful for comparing the kinetics of SPMD uptake and bioconcentration, and can be used to determine the extent to which SPMDs are biomimetic (i.e., similar to contaminant uptake by biota) for a particular exposure scenario (Huckins et al., 2004). This model is highly empirical, and other models are needed to examine the uptake and release rate constants in terms of fundamental processes.

3.1.2. Mass Transfer Coefficient (MTC) Model

The second type of model is a mass-transfer coefficient (MTC) model, which is based on a mathematical description of solute-mass transfer through sequential but distinct physical environments (phases or regions). In the case of SPMD exposures, these environments include the WBL, the biofilm (not always present), the membrane, and the triolein. The MTC (k) can be viewed as the velocity (e.g., cm s^{-1}) of a solute moving through a region, and k is equivalent to D/δ, where D is the diffusion coefficient and δ is the effective thickness of a particular phase. With the MTC model, it is assumed that the fluxes through the successive regions are linearly proportional to the concentration difference between the end points of the phases (Figure 3.1).

The flux (j_w: mass per unit surface area per unit time) through the WBL is assumed to be proportional to the concentration difference between bulk water (C_w) and the water side of the biofilm-water interface (C_{w-})

$$j_w = k_w (C_w - C_{w-}) \tag{3.3}$$

where k_w is the MTC for the WBL. Similarly, the flux through the biofilm (j_b) equals

$$j_b = k_b (C_{b+} - C_{b-}) \tag{3.4}$$

where C_{b+}, C_{b-} are the concentrations in the biofilm at the water side and at the membrane side, respectively, and k_b is the MTC for the biofilm. Finally, the flux through the membrane (j_m) is given by

$$j_m = k_m (C_{m+} - C_{m-}) \tag{3.5}$$

where C_{m+}, C_{m-} are the concentrations in the membrane at the biofilm side and at the triolein side, respectively, and k_m is the MTC for the membrane. To use the MTC model, it is assumed that sorption equilibrium exists at all interfaces, that the fluxes through the various phases are equal ($j_w = j_b = j_m$), and that the triolein phase is well mixed as shown in Figure 3.1. The assumptions of interfacial equilibrium and equality of the fluxes through the phases can be used to eliminate the contaminant concentrations at the interfaces (Flynn and Yalkowsky, 1972),

yielding an expression for the solute flux (j) between the phases

$$j = k_o \left(C_w - \frac{C_L}{K_{Lw}} \right) \tag{3.6}$$

where C_L is the concentration in the lipid phase, K_{Lw} is the lipid-water partition coefficient, and k_o is the overall MTC. The k_o is also known as the overall conductivity, because it is the proportionality constant between the flux and the effective concentration or fugacity difference that drives this flux. Similarly, $1/k_o$ is known as the overall transport resistance (or impedance, I_o), which is the sum of the transport resistances for the successive phases (I_w, I_b, I_m).

$$I_o = I_w + I_b + I_m \tag{3.7}$$

$$\frac{1}{k_o} = \frac{1}{k_w} + \frac{1}{k_b\, K_{bw}} + \frac{1}{k_m\, K_{mw}} \tag{3.8}$$

From Eq. 3.8, it follows that transport resistances are additive and that high partition coefficients (K_{bw} and K_{mw}) reduce the resistance to mass transfer in the respective phases. As discussed earlier, MTCs can be written as D/δ (Figure 3.1 illustrates the hypothetical δ of each SPMD related barrier to mass transfer). The importance of barrier thickness in resistance to mass transfer is more explicit in the following version of Eq. 3.8.

$$\frac{1}{k_o} = \frac{\delta_w}{D_w} + \frac{\delta_b}{D_b K_{bw}} + \frac{\delta_m}{D_m K_{mw}} \tag{3.9}$$

From Eq. 3.9, the greater the thickness (δ) of each phase the larger the resistance to solute transfer. Although the use of δ_w is convenient for modeling and conceptualizing WBL resistance, it is largely fictitious, as complex hydrodynamics control resistance to mass transfer across the WBL in environmental exposures (see Section 3.6.5. for a more in- depth discussion on this phenomenon).

It is now common practice to analyze HOC residues in the membrane and lipid phases together, as opposed to analyzing the lipid phase alone. Assuming that the concentrations in the lipid and in the membrane are close to equilibrium, Eq. 3.6 can be written as

$$j = k_o \left(C_w - \frac{C_s}{K_{sw}} \right) \tag{3.10}$$

where C_s is the concentration in the whole SPMD, and K_{sw} is

$$K_{sw} = \frac{V_m K_{mw} + V_L K_{Lw}}{V_m + V_L} \tag{3.11}$$

which is the volume weighted average of the membrane-water and the lipid-water partition coefficients. From Eq. 3.10, the rate of change of the solute concentration in the SPMD (C_s) is given by

$$\frac{dC_s}{dt} = \frac{Aj}{V_s} = \frac{Ak_o}{V_s} \left(C_w - \frac{C_s}{K_{sw}} \right) \tag{3.12}$$

where A is the SPMD surface area, and V_s its volume. With the initial condition $C_s = 0$ at $t = 0$, the solution to Eq. 3.12 is

$$C_s = K_{sw} C_w [1 - \exp(-k_e t)] \quad (3.13)$$

which is identical to Eq. 3.2. The exchange rate constant k_e is given by

$$k_e = \frac{A k_o}{V_s K_{sw}} \quad (3.14)$$

The advantage of the MTC model, as opposed to the CRK model, is that the exchange rate constant k_e is no longer an empirical constant, but is now defined in terms of more fundamental processes that can be separately modeled. Equations 3.1 and 3.12 are linked via the equality

$$k_u = \frac{k_o A}{V_s} \quad (3.15)$$

Caution is needed regarding the units of k_u. Eq. 3.15 gives k_u in units of reciprocal time (e.g., d^{-1}). This is a result of expressing C_s on a volume basis. In the case that C_s is expressed on an SPMD mass basis, k_u has units of volume per mass per time (e.g., mL g^{-1} d^{-1}). An uptake rate constant given in these units can be converted to k_u in d^{-1} by multiplying with the SPMD density (0.91 g mL^{-1}), as further discussed in Appendix A.

A number of authors have presented models of somewhat higher mathematical complexity. Hofmans (1998) presented an uptake model based on Fick's second law. Using the results obtained after numerical integration of the partial differential equations, she confirmed the validity of the assumptions that the triolein phase is well mixed, and that the C_L/C_m ratio equals the triolein-membrane partition coefficient after 1 to 13 days for phenanthrene and polychlorinated biphenyl (PCB) congener 209, respectively. Gale (1998) presented a pseudo-steady state numerical model that allowed for studying the effects of transient exposure concentrations, changes in analyte physicochemical properties, and modifications in SPMD design. Booij et al. (2003a) have given an analytical solution of the uptake equation for the case of aqueous concentrations that vary linearly with time.

3.2. KINETIC AND EQUILIBRIUM SAMPLING

Equation 3.13 shows that the concentration in SPMDs gradually increases with time until equilibrium is attained. When $k_e t \gg 1$, C_s attains its equilibrium value

$$C_s = K_{sw} C_w \quad (3.16)$$

In this case, the exposure mode is called "equilibrium sampling". When $k_e t \ll 1$ (short exposure times and/or highly hydrophobic compounds), the group between

square brackets in Eq. 3.13 is approximately equal to $k_e t$, and C_s is given by

$$C_s = K_{sw} C_w k_e t \tag{3.17}$$

Because C_s increases linearly with time, this phase of an exposure is called "kinetic sampling", or the "linear uptake mode", and sampling is time-integrative. The amount (N) absorbed by SPMDs during kinetic sampling equals

$$N = V_s K_{sw} k_e C_w t \tag{3.18}$$

$$N = R_s C_w t \tag{3.19}$$

which defines the apparent water sampling rate (R_s) for kinetic sampling.

$$R_s = V_s K_{sw} k_e \tag{3.20}$$

The sampling rate provides a conceptual link between classical batch extraction techniques and passive sampling with SPMDs, because $R_s t$ equals the equivalent extracted water volume. For distinguishing between the kinetic- and equilibrium-sampling modes, limits must be set that are (unavoidably) arbitrary in nature. The errors involved depend on the degree of equilibrium attained during sampling. However, there is no reason to use either approximation. By substituting the definition of R_s (Eq. 3.20) into the full model (Eq. 3.13), one establishes the links among the calibration data (R_ss and K_{sw}s), the absorbed amounts after the exposure, and the aqueous concentration.

$$N = V_s K_{sw} C_w \left(1 - \exp\left(-\frac{R_s t}{V_s K_{sw}}\right)\right) \tag{3.21}$$

The aqueous concentration can therefore be calculated from the absorbed amounts by

$$C_w = \frac{N}{V_s K_{sw} \left(1 - \exp\left(-\frac{R_s t}{V_s K_{sw}}\right)\right)} \tag{3.22}$$

In the limiting cases, where $t \to 0$ or $t \to \infty$, Eq. 3.22 reduces to the special cases of sampling during the linear uptake kinetic phase and equilibrium-sampling phase (Eqs. 3.16 and 3.19), respectively. The advantage of Eq. 3.22 is that no arbitrary limits have to be set for the two sampling modes. Thus, slightly more complex mathematics is the price paid for avoiding this ambiguity.

3.3. DISSIPATION OF PERFORMANCE REFERENCE COMPOUNDs (PRCs)

In order to assess an analyte's *in situ* SPMD-water exchange kinetics, performance reference compounds (PRCs; as described in Chapter 1) are added to SPMD triolein prior to an exposure (Ellis et al., 1995; Booij et al., 1998; Ockenden et al., 2001; Huckins et al., 2002a). To use this approach, the investigator must be

sure that the PRCs do not occur in the environment (e.g., certain non-labeled or native compounds such as PCB congeners 14, 29, 50, and a variety of compounds labeled with deuterium, ^{13}C, or ^{14}C generally can be used). PRC dissipation is governed by

$$N = N_0 \exp(-k_e t) \tag{3.23}$$

where N_0 is the amount present at $t = 0$. If N and N_0 are measured, the PRC release rate constant (k_e) can be estimated using

$$k_e = -\frac{\ln(N/N_0)}{t} \tag{3.24}$$

When the k_e and SPMD-water partition coefficient of the PRC are known, its R_s can be calculated from Eq. 3.20. More precisely, we assume that the PRC R_s is representative of the *in situ* sampling rates of target compounds with similar physicochemical properties as the PRC. Various approaches have been used to estimate sampling rates for all analytes from the PRC-derived sampling rates (see Section 3.6.).

3.4. POTENTIAL EFFECTS OF DISSOLVED ORGANIC CARBON (*DOC*) ON SPMD CALIBRATION DATA

Because SPMD sampling rates are independent of chemical concentration, the attenuation of dissolved phase concentrations by *DOC* (including colloids) or particulate organic carbon (*POC*: particle size >0.45 μm) should have no measurable effect on actual analyte R_s values. In practice, the fractional amount of chemical sorbed to *DOC* can affect the accuracy of SPMD calibration experiments, which in turn can affect SPMD-derived estimates of dissolved environmental concentrations. Even in the laboratory, measurements of the true dissolved-phase concentrations of test chemicals are especially difficult for compounds with high octanol-water (K_{ow}s) partition coefficients. When batch extraction methods (i.e., liquid-liquid extraction) are used for sampling water for SPMD calibration, the fractional amounts of a compound sorbed to *POC* and *DOC* are recovered along with the dissolved fraction. This results in an overestimation of dissolved-phase concentrations. Pre-filtration of water samples with glass fiber filters (GFFs) is effective in removing *POC*, but this step may result in attenuation of dissolved phase concentration due to adsorption of solutes on the GFF. To circumvent this problem, cartridges or columns of solid phase sorbents (SPE) equipped with GFF pre-filters have been used to measure dissolved-phase water concentrations. This approach is largely based on the results of one study, which showed that *DOC* associated chemicals are not extracted during SPE extraction of dissolved residues (Landrum et al., 1984). However, Mackay (1994) has suggested that desorption times for very small particles (i.e., <1 μm) are on the order of a few seconds for compounds with particle-water partition coefficients of about 10^4. Based on this

study, SPE sampling of *DOC*-associated residues cannot be ruled out. Also, no data are available on the potential of the surficial retention of colloids or *DOC* by the SPE sorbent. These factors would lead to an overestimation of dissolved concentrations. Other sampling equipment may also yield inaccurate measurements of dissolved concentrations. Pre-equilibration of laboratory exposure systems is a separate issue related to attainment of steady-state water concentrations in the exposure system prior to initiation of the test. Clearly, the issue of *DOC* or colloidally sorbed contaminants deserves additional discussion.

Recently, Burkhard (2000) reviewed contaminant sorption by dissolved organic matter. Using several hundreds of *DOC*-water partition coefficients (K_{DOC}) reported in these studies, he found that *DOC*-water partition coefficients for naturally occurring *DOC* (humic and fulvic acids, sediment pore water, soil pore water, groundwater, and surface water) was best described by

$$\log K_{\mathrm{DOC}} = \log K_{\mathrm{ow}} - 1.11 \quad s = 0.66, n = 127 \tag{3.25}$$

The 95% confidence interval amounted to 1.3 log units, which corresponds to a scatter in the K_{DOC} values by a factor of 20. Burkhard (2000) argues that the uncertainty in Eq. 3.25 originates partly from inter-laboratory variation, and partly from differences in *DOC* quality. In view of the wide range of *DOC* sources included in Eq. 3.25, it does not seem likely that the uncertainties in any K_{DOC} encountered would be more than 1.3 log units. Hence, the worst-case estimate (maximum sorption of dissolved phase residues by *DOC*) can be described by

$$\log K_{\mathrm{DOC}} = \log K_{\mathrm{ow}} + 0.20 \tag{3.26}$$

When *DOC*-bound residues are extracted along with the dissolved phase (i.e., the total concentrations are measured), then the ratio of the truly dissolved concentrations (C_{w}) to the total concentration (C_{t}) of an HOC can be estimated by

$$\frac{C_{\mathrm{w}}}{C_{\mathrm{t}}} = \frac{1}{1 + [DOC]K_{\mathrm{DOC}}} \tag{3.27}$$

where the brackets represent the concentration of *DOC*. Only few authors report *DOC* concentrations in their SPMD calibration studies. Meadows et al. (1998) and Huckins et al. (1999; 2002b) found *DOC* values to be below detection limits of <1 mg L^{-1}. In a later study, the *DOC* content of deep-well water used by Huckins et al. (1999) was quantified as 0.26 mg L^{-1} (McCarthy, 2004). Luellen and Shea (2002) report values of 0.3 and 1.3 mg L^{-1} in two separate experiments. Rantalainen et al. (2000) argued that *DOC*-bound contaminants did not contribute to their C_{w} estimates because the fine fraction of the sediment (<63 μm) in their exposure system was sieved out, and because the XAD-2 resin used to extract the water would not retain *DOC*-bound contaminants, but no experimental values of *DOC* concentrations are available for this study. Booij et al. (2003a) used ultra pure Milli-Q water with a specified *DOC* content <0.01 mg L^{-1}, but did not measure the actual *DOC* concentrations in their system.

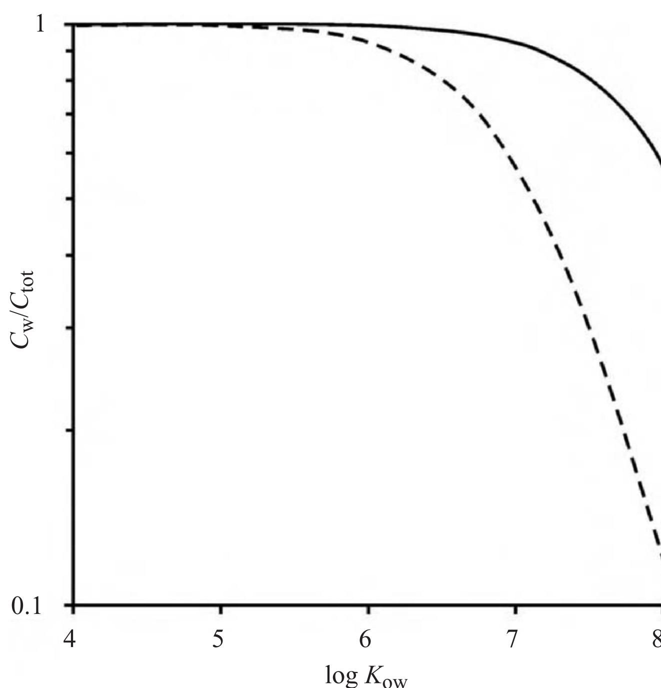

FIGURE 3.2 Reduction of concentrations of dissolved compounds due to sorption to *DOC*, for *DOC* levels of 0.1 (solid line) and 1 mg L^{-1} (dashed line).

The effect of binding to *DOC* on the freely dissolved contaminant concentration is shown for *DOC* concentrations of 0.1 and 1 mg L^{-1} in Figure 3.2, using Eqs. 3.25 and 3.27. At *DOC* concentrations of 1 mg L^{-1}, a two-fold reduction in C_w can be expected at log $K_{ow} = 7.3$. Because of the uncertainties associated with the Burkhard equation (1.3 log units), this reduction could occur in the range of $6 < \log K_{ow} < 8.6$ at this *DOC* level.

3.5. SPMD-WATER PARTITION COEFFICIENTS

Because both LDPE and triolein are non-polar organic phases, it can be expected that SPMD-water partitioning is driven by hydrophobic interactions, and that strong correlations will exist between K_{sw} values and K_{ow}s. Experimental values of K_{sw} are available for polycyclic aromatic hydrocarbons (PAHs), PCBs, chlorobenzenes, and nonpolar and moderately polar pesticides (Figure 3.3). The experimental evidence suggests that K_{sw} values are not temperature dependent in the 2 to 30 °C temperature range. Huckins et al. (2002a) reported that phenanthrene deviates from this general rule (0.4 log units decrease between 8 to 30 °C), whereas

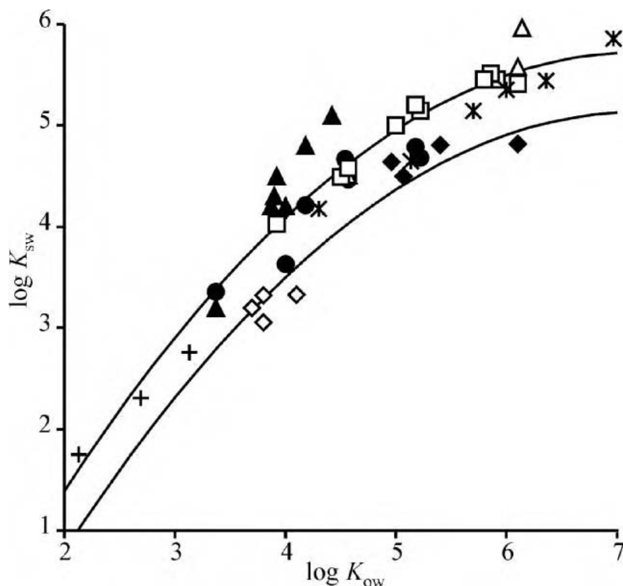

FIGURE 3.3 SPMD-water partition coefficients (mL mL^{-1} units) as a function of log K_{ow} for PAHs—filled circles: Huckins et al. (1999), filled triangles: Huckins et al. (2004); phenanthrene, PCB 52, and p,p′-DDE—open triangles: Huckins et al. (2002a); chlorobenzenes, PAHs, and PCBs—squares: Booij et al. (2003a); pesticides—filled diamonds: Sabaliunas and Södergren (1997); and HCHs—open diamonds: Vrana and Schüürmann (2002). Additional K_{sw} data were calculated for PCBs (asterisks) and alkylated benzenes (crosses) using the K_{mw} data from Lefkovitz et al. (1996) and Reynolds et al. (1990), and the K_{LW} data from Chiou (1985).

PCB 52 and p,p'-DDE did not. However, Booij et al. (2003a) reported the log K_{sw} value for phenanthrene to be constant within 0.17 log units in the temperature range 2 to 30 °C. Additional K_{sw} values for mono- to hexachlorobiphenyls can be determined by combining the LDPE-water partition coefficients of PCB congeners 1, 5, 29, 47, 98, and 154 (Lefkovitz et al., 1996) with the triolein-water partition coefficients of PCBs with an equal number of chlorine atoms (Chiou, 1985), and adopting a triolein mass fraction of 0.20 in standard SPMDs. All log K_{sw} data are plotted as a function of log K_{ow} in Figure 3.3. When applicable, the average log K_{sw} values over different temperatures (within a single study) are plotted. Log K_{ow} values were adopted as specified in Appendix A (Tables A.1 to A.3). The log K_{sw} data could best be described by a quadratic equation in log K_{ow}. The inclusion of a different intercept for moderately polar and nonpolar compounds resulted in a significantly better fit ($p < 0.001$).

$$\log K_{sw} = a_0 + 2.321 \log K_{ow} - 0.1618 (\log K_{ow})^2 \tag{3.28}$$

$$\text{PCBs, PAHs, 4,4'-DDE} \quad : a_0 = -2.61$$

$$\text{polar pesticides} \quad : a_0 = -3.20$$

$$n = 45, s = 0.25, r = 0.97$$

The inclusion of a third-order term did not yield a significantly better fit ($p > 0.6$). There are no indications that PAHs and nonpolar chlorinated hydrocarbons have a different $K_{sw} - K_{ow}$ dependence. By contrast, the moderately polar pesticides such as hexachlorocyclohexanes (HCHs), dieldrin, chlorpyrifos, heptachlor, and trifluralin (open and closed diamonds in Figure 3.3) have K_{sw} values that are 0.6 log units lower than PAHs and PCBs with similar K_{ow} values ($p < 0.001$).

Figure 3.3 shows that the log K_{ow}-log K_{sw} plot for compounds with log $K_{ow} > 5$ deviates from linearity. This phenomenon is also observed for plots of log bioconcentration factor (*BCF*) versus log K_{ow} (Connell, 1990). Chiou (1985) has shown that a similar deviation occurs in a triolein-water system alone, at log $K_{ow} > 5.5$, as a result of solute-triolein incompatibility. Similarly, Banerjee and Baughman (1991) argued that *BCFs* of large molecules are smaller than expected on the basis of their hydrophobicity as a result of their disrupting effect on the structure of the lipid phase. The curvilinearity is not likely to be caused by sorption to *DOC* in the experimental systems (Section 3.4.), because deviations from linearity already occur at log $K_{ow} \approx 5$, whereas the effect of *DOC*-bound contaminants can only be expected at log K_{ow} values > 7.

3.6. WATER SAMPLING RATES

Sampling rates have been determined for a large number of compounds, representing several compound classes, and include PAHs (Huckins et al., 1993; 1999, 2004; Luellen and Shea, 2002; Booij et al., 2003a), PCBs (Huckins et al., 1993; Meadows et al., 1998; Booij et al., 2003a), chlorobenzenes (Vrana and Schüürmann, 2002; Booij et al., 2003a), PCDDs/PCDFs (Rantalainen et al., 2000), and a number of polar pesticides (Sabaliūnas and Södergren, 1997; Vrana and Schüürmann, 2002), both in the lab and in the field. A comparison of experimental sampling rates is hindered by the differences in experimental conditions, such as temperature, flow rates, and geometry of the mounting cages. The sorption of analytes to *DOC* may result in an overestimation of the dissolved concentrations, and hence to an underestimation of the sampling rates.

3.6.1. Temperature Effects

Sampling rates at different temperatures have been determined by Huckins et al. (1999) for PAHs at 10, 18, and 26 °C, by Rantalainen et al. (2000) for PCDDs, PCDFs, and non-*ortho* chlorine substituted PCBs at 11 and 19 °C, and by Booij et al. (2003a) for chlorobenzenes, PCBs, and PAHs at 2, 13 and 30 °C. The effect of temperature on the sampling rates can be quantified in terms of activation energies (ΔE_a) for mass transfer, as modeled by the Arrhenius equation

$$R_s = R_{s,\infty} \exp\left(-\frac{\Delta E_a}{RT}\right) \tag{3.29}$$

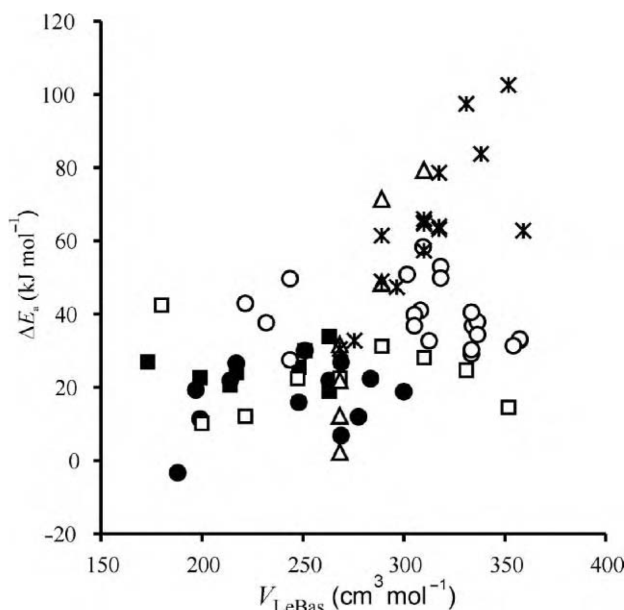

FIGURE 3.4 Activation energies of contaminant sampling by SPMDs as a function of molar volume (LeBas method). PAHs—filled circles: Huckins et al. (1999); filled squares: Booij et al. (2003a); pesticides—open circles: Huckins et al. (2002b); chlorobenzenes and PCBs—open squares: Booij et al. (2003b); planar PCBs—triangles: Rantalainen et al. (2000); and PCDD/Fs—asterisks: Rantalainen et al. (2000).

where $R_{s,\infty}$ is the sampling rate at the hypothetical upper limit where temperature is infinite, R is the gas constant, and T is the absolute temperature.

Values of ΔE_a can be determined by plotting the natural logarithm of R_s (ln R_s) versus the reciprocal absolute temperature ($1/T$). The activation energy can then be calculated by multiplying the slope of the regression line with the gas constant. Figure 3.4 shows a plot of ΔE_a as a function of molar volume, estimated using the LeBas method (Reid et al., 1987; Mackay et al., 1992a, 1992b). Activation energies range between -3 and 103 kJ mol^{-1}. For PAHs, good correspondence exist for the ΔE_a values estimated from the data reported by Huckins et al. (1999) and Booij et al. (2003a). The activation energies reported by Rantalainen et al. (2000) for tetrachlorobiphenyls with non-*ortho* Cl atoms show good correspondence with the values for PCBs reported by Booij et al. (2003a). For penta- and hexachlorobiphenyls, the ΔE_a values reported in both studies differ by 40 to 60 kJ mol^{-1}. This difference may be related to differences in planarity for the PCBs used in both studies. A number of non-polar and moderately polar pesticides (HCB, DDT-like compounds, HCHs, dieldrin, endrin, chlordanes) have activation energies that are similar to those of PAHs and PCBs. Taking all data together, ΔE_a values seem to increase slightly from about 20 kJ mol^{-1} at $V_m = 180$ cm^3 mol^{-1} (log $K_{ow} \approx 4$) to about 40 kJ mol^{-1} at $V_m = 350$ cm^3 mol^{-1} (log $K_{ow} \approx 7$),

with the exception of the data on PCDDs/PCDFs and non-*ortho* substituted PCBs reported by Rantalainen et al. (2000), which are in the range 40 to 100 kJ mol^{-1}. The activation energies of 23-64 kJ mol^{-1} obtained from the dissipation of trichlorobenzene, PCB congeners 4 and 29 in the field are in line with the values shown in Figure 3.4 (Booij and van Drooge, 2001). The average of all ΔE_a values is 37 kJ mol^{-1} with a standard deviation of 21 kJ mol^{-1}. This means that a temperature increase from 10 to 20 °C causes an increase in sampling rate by a factor of about 1.7. The highest (103 kJ mol^{-1}) and lowest (−3 kJ mol^{-1}) ΔE_a value observed would correspond to a change in sampling rate by a factor of 4.5 and 1 over this temperature range, respectively. Therefore, the effect of temperature on SPMD sampling rates in the field appears to be modest, unless large temperature differences exist between exposure sites or exposure periods.

3.6.2. R_s Calibration Data

A selection of published R_s values is shown as a function of log K_{ow} in Figure 3.5. Only data from calibration studies conducted at 15 ± 4 °C were considered, in order to eliminate the temperature effect as much as possible. When

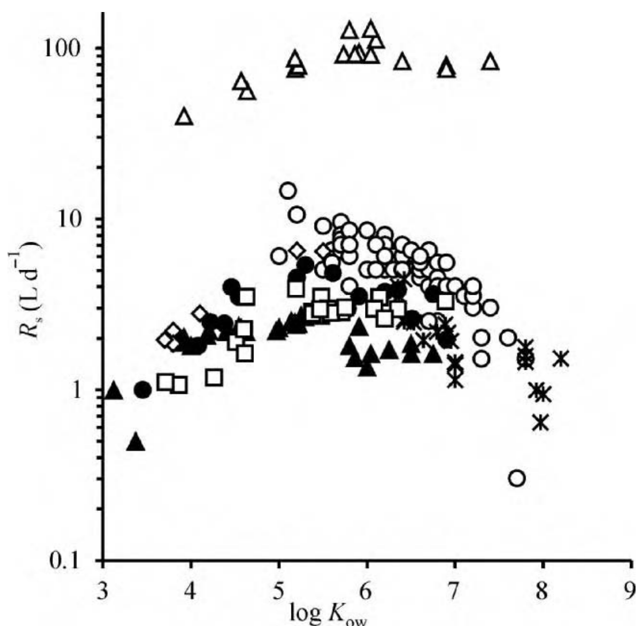

FIGURE 3.5 Sampling rates at 15 ± 4 °C as a function of log K_{ow} for PCBs—open circles: Meadows et al. (1998), PAHs—closed circles: Huckins et al. (1999), closed triangles: Huckins et al. (2004); chlorobenzenes/PCBs/PAHs—open triangles: Booij et al. (2003a); HCHs/HCB—diamonds: Vrana and Schüürmann (2002); non-ortho PCBs/PCDDs/PCDFs—asterisks: Rantalainen et al., 2000); and pesticides—squares: Huckins et al. (2002b).

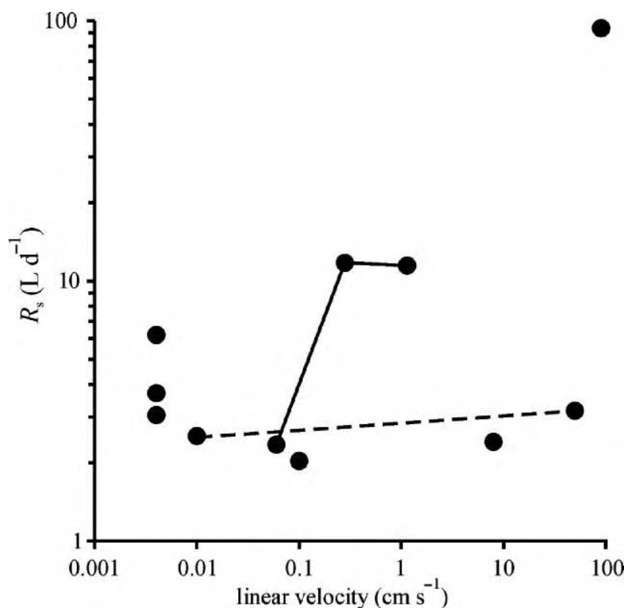

FIGURE 3.6 Sampling rates of compounds in the log K_{OW} range 6 to 7 as a function of water flow velocity. Connected data points represent measurements within single studies (dashed line: Luellen and Shea, 2002; solid line: Vrana and Schüürmann, 2002).

calibration data at multiple temperatures existed, the temperature-interpolated values at 15 °C were calculated from Eq. 3.29. For compounds that are low to moderately hydrophobic (log $K_{ow} = 3$ to 5), log R_s values increase linearly with log K_{ow}. A maximum in R_s values is reached for compounds with log $K_{ow} = 5$ to 6, and thereafter, compound R_s values decrease with increasing log K_{ow}. Although the shape of the log R_s versus log K_{ow} curves is similar for all studies, the sampling rates among studies appear to be shifted by a relatively constant factor.

In order to check if this shift is related to flow velocity, the geometric mean of R_s values for compounds with log $K_{ow} = 6$ to 7 was plotted versus the reported linear flow velocity (Figure 3.6). The linear flow velocity seems to be a poor predictor of sampling rates. At flow velocities below 10 cm s^{-1}, three values cluster around 10 ± 3 L d^{-1} and 6 values fall in the range 3 ± 1 L d^{-1}. The highest sampling rates (≈100 L d^{-1}) are reported by Booij et al. (2003a) at a flow velocity of about 90 cm s^{-1}. The lack of correlation between linear flow velocity and R_s values is not surprising. The linear flow velocity is typically calculated from the volumetric rate of flow and the cross-sectional area of the exposure chamber, which is only a crude measure of the hydrodynamical conditions prevailing at the SPMD-water interface. At low flow velocities, inertial currents originating from the inflow-orifices may be much larger than calculated linear velocities. Moreover, it is the flow at the membrane-water interface that controls the exchange rates in the boundary layer, rather than the flow at larger distance from the

interface. For fully developed linear flow that is parallel to semi-infinite flat plates these two flow characteristics are closely related (Bird et al., 1960; Levich, 1962), but this is seldom the case in relatively small exposure chambers, with water entering at discrete spots, and SPMDs that are mounted in widely different exposure configurations.

A general conclusion that can be drawn from Figure 3.6 is that sampling rates of compounds with log K_{ow} values between 6 and 7 are in the range 2 to 12 L d^{-1} at flow velocities below 10 cm s^{-1}, with a geometric mean of 4.2 L d^{-1}. These data underscore the importance of using PRCs for a site- and SPMD-specific assessment of the effects of exposure conditions.

3.6.3. Empirical Uptake Rate Model

Booij et al. (1998) and Huckins et al. (2002a) showed that differences in exposure conditions cause sampling rates to be shifted by a constant factor for all compounds. Building upon this observation, and acknowledging that the log R_s-log K_{ow} plots in Figure 3.5 have highly similar shapes, the sampling rate of a particular compound (i) in an exposure (j) can be written as

$$R_{i,j} = R_{s,ref}\,\alpha_i \beta_j \tag{3.30}$$

where $R_{s,ref}$ is the sampling rate of a model or reference compound exposed under standard conditions, α_i is a unitless compound-specific effect and β_j is a unitless exposure-specific effect. It is of little concern which standard compound is selected and how "standard exposure conditions" are defined, as explained below.

The relative sampling rate of a single compound (i) that is exposed under different site conditions (j = 1, 2) equals

$$\frac{R_{i,2}}{R_{i,1}} = \frac{\beta_2}{\beta_1} = EAF \tag{3.31}$$

where *EAF* is the exposure adjustment factor introduced by Huckins et al. (2002a). In this case, both the reference sampling rate ($R_{s,ref}$) and the compound-specific effect α_i are divided out. Huckins et al. (2002a) showed for a number of cases that *EAF*s are relatively independent of the physicochemical properties of the analytes. They therefore proposed to estimate the *EAF* for a specific exposure from the ratio of PRC-based sampling rates in the field and in the laboratory. A problem with the original *EAF* method is that sampling rate calibration data for PRCs and many other analytes often are not available. As a result, the sampling rates for these compounds have to be estimated from the listed values for compounds with similar properties. The fact that some compounds were included in more than one calibration study, introduces an additional ambiguity, because SPMD users may choose one or the other calibration study as a basis for estimating the sampling rates in the field. These ambiguities can be removed if Eq. 3.30 can be applied. In

this case, the *in situ* sampling rate of a PRC is given by

$$R_{\mathrm{PRC,j}} = R_{\mathrm{s,ref}}\,\alpha_{\mathrm{PRC}}\,\beta_{\mathrm{j}} \tag{3.32}$$

Dividing Eq. 3.30 by Eq. 3.32 gives the sampling rate of compound i in exposure j

$$R_{\mathrm{i,j}} = R_{\mathrm{PRC,j}}\frac{\alpha_{\mathrm{i}}}{\alpha_{\mathrm{PRC}}} \tag{3.33}$$

The reference sampling rate ($R_{\mathrm{s,ref}}$) as well as the exposure-specific effect β_{j} are divided out. For practical applications, it therefore suffices to know how the compound-specific effect depends on the properties of the analytes. Observing that the experimental sampling rates have a similar dependence on log K_{ow}, but show a varying offset for the different studies, the log-transformed sampling rates observed in 19 calibration experiments in 9 studies were fitted as a third order polynomial in log K_{ow}:

$$\log R_{\mathrm{i,j}} = 0.0130\,\log K^{3}_{\mathrm{ow,i}} - 0.3173\,\log K^{2}_{\mathrm{ow,i}} + 2.244\,\log K_{\mathrm{ow,i}} + a_{0,\mathrm{j}} \tag{3.34}$$
$$n = 412,\ s = 0.17,\ r = 0.91$$

where $a_{0,\mathrm{j}}$ is the intercept that is observed for calibration experiment j. Comparing Eq. 3.34 with the log-transformed Eq. 3.30 shows that the compound-specific effect can be modeled by

$$\log \alpha_{\mathrm{i}} = 0.0130\,\log K^{3}_{\mathrm{ow}} - 0.3173\,\log K^{2}_{\mathrm{ow}} + 2.244\,\log K_{\mathrm{ow}} \tag{3.35}$$

A plot of log α_{i} (= log $R_{\mathrm{ij}} - a_{0\mathrm{j}}$) is shown in Figure 3.7. The standard deviation of the fit (0.17 log units) corresponds to an uncertainty factor of about 1.5, which is quite good considering the large differences in exposure conditions involved (flow rates between 0.004 and 90 cm s^{-1}, temperature range 2 to 30 °C). Thus, when PRC-derived sampling rates are available, Eq. 3.35 can be used to calculate reasonably accurate relative sampling rates for all the analytes plotted in Figure 3.7. Box 3.1 shows an example of how to calculate *in situ* R_{s} values of a target compound.

A brief discussion is warranted on the physical interpretation of the shape of the regression curve in Figure 3.7. For compounds with log $K_{\mathrm{ow}} < 4.5$, sampling rates rise with K_{ow}, indicating that a significant portion of the overall resistance to mass transfer lies in the SPMD membrane under the conditions of the tests (see discussion on membrane control in Section 3.6.4.). As can be deduced from Eqs. 3.7 and 3.8, an increase in K_{mw} causes a decrease of the resistance to mass transfer across the membrane, resulting in a concomitant increase in sampling rate, until rate control switches to the WBL. Under WBL control, R_{s} values of compounds with increasing K_{ow} values are expected to gradually decline due to small reductions in their D_{w} (see Section 3.6.5.). However, the apparent steepness in the decline of R_{s} values is more than predicted (Huckins et al., 1998). Several potential factors for this decline in sampling rate of high K_{ow} compounds are subsequently discussed.

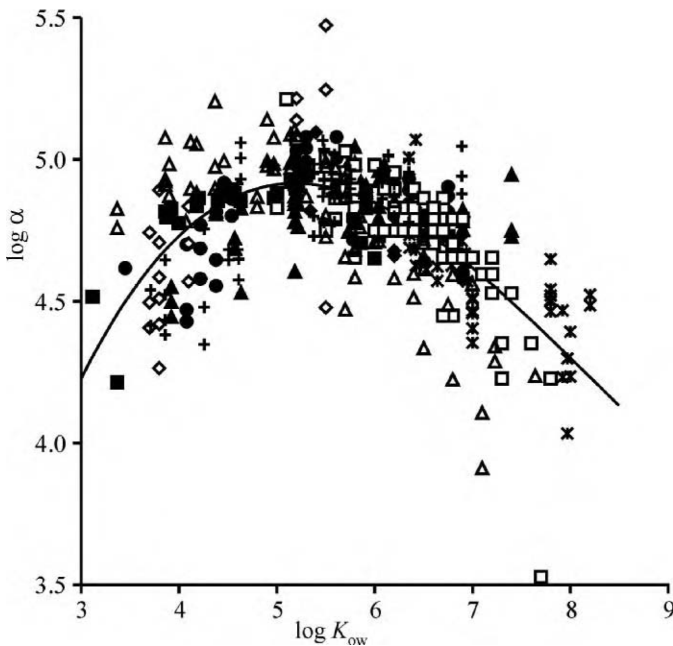

FIGURE 3.7 Compound-specific effect (α) on the sampling rate as a function of log K_{ow} for PCBs—open squares: Meadows et al. (1998); PAHs—filled circles: Huckins et al. (1999), open triangles: Luellen and Shea (2002), filled squares: Huckins et al. (2004); HCHs/chlorobenzenes—open diamonds: Vrana and Schüürmann (2002); chlorobenzenes/PAHs/ PCBs—filled triangles: Booij et al. (2003a); PCDDs/PCDFs/PCBs—asterisks: Rantalainen et al. (2000); and pesticides—filled diamonds: Sabaliunas and Södergren (1997), crosses: Huckins et al. (2002b).

3.6.4. Theoretical Uptake Model: Membrane-Controlled Uptake

In order to properly interpret differences in sampling rates among compounds and among exposure conditions, it is important to discriminate between membrane-controlled uptake and WBL-controlled uptake. From Eq. 3.8 (in the absence of biofouling), contaminant uptake is rate-limited by the membrane when

$$k_m K_{mw} \ll k_w \tag{3.36}$$

Because neither k_m nor k_w are strong functions of the physical-chemical properties of the analytes (see below), the issue of which phase controls the uptake rate is primarily governed by the membrane-water partition coefficient, which varies between compounds by many orders of magnitude (Reynolds et al., 1990; Lefkovitz et al., 1996; Booij et al., 2003a). With increasing log K_{ow}, there always will be a critical log K_{ow} value where the uptake rates will be controlled by the WBL instead of by the membrane. Next to K_{mw} (which is a compound specific property) it is important to note that rate control is also dependent on the magnitude of k_w, which is determined by the hydrodynamical conditions prevailing at the membrane-water

Box 3.1 Example of the Calculation of Sampling Rates from a PRC-Derived Sampling Rate, Using the Empirical Uptake Model (Eqs. 3.33 and 3.35)

Input data

$V_s = 4.95\ \text{cm}^3$
exposure time = 42 d

chrysene-$d12$ amounts per SPMD:
118 ng at t = 0
84 ng at t = 42 d

log K_{ow} values:
chrysene-$d12$: 5.8
pyrene : 5.2
PCB 153 : 6.9

accumulated amounts:
pyrene : 264 ng
PCB153 : 13 ng

Step 1. Calculate the R_s of the PRC

from Eq. 3.24: $k_e = -\ln(84/118)/42 = 0.0081\ \text{d}^{-1}$
from Eq. 3.28: $\log K_{sw,\text{chrysene-}d12} = 5.41$
from Eq. 3.20: $R_{s,\text{chrysene-}d12} = 4.95 \cdot 10^{5.41} \cdot 0.0081 = 10306\ \text{cm}^3\,\text{d}^{-1} \approx 10.3\ \text{L d}^{-1}$

Step 2. Calculate the relative R_s of analyte and PRC

from Eq. 3.35:
chrysene-$d12$: $\log \alpha_{\text{chrysene-}d12} = 4.88 \Rightarrow \alpha_{\text{chrysene-}d12} = 75454$
pyrene : $\log \alpha_{\text{pyrene}} = 4.92 \Rightarrow \alpha_{\text{pyrene}} = 82587$
PCB153 : $\log \alpha_{\text{PCB153}} = 4.65 \Rightarrow \alpha_{\text{PCB153}} = 44419$

Step 3. Calculate R_s of the analyte

from Eq. 3.33:
$R_{s,\text{pyrene}} = R_{s,\text{chrysene-}d12} \cdot (\alpha_{\text{pyrene}}/\alpha_{\text{chrysene-}d12}) = 10.3 \times 82587 \div 75454 = 11.3\ \text{L d}^{-1}$
$R_{s,\text{PCB153}} = R_{s,\text{chrysene-}d12} \cdot (\alpha_{\text{PCB153}}/\alpha_{\text{chrysene-}d12}) = 10.3 \times 44419 \div 75454 = 6.1\ \text{L d}^{-1}$

Step 4. Calculate the aqueous concentrations

from Eq. 3.28:
$\log K_{sw,\text{pyrene}} = 5.08$
$\log K_{sw,\text{PCB153}} = 5.70$

$$C_{w,\text{pyrene}} = \frac{264}{4.95 \cdot 10^{5.08}\left(1 - \exp\left(-\dfrac{11300 \cdot 42}{4.95 \cdot 10^{5.08}}\right)\right)} = 0.81\ \text{ng L}^{-1}$$

$$C_{w,\text{PCB153}} = \frac{13}{4.95 \cdot 10^{5.70}\left(1 - \exp\left(-\dfrac{6100 \cdot 42}{4.95 \cdot 10^{5.70}}\right)\right)} = 0.053\ \text{ng L}^{-1}$$

interface. For a given log K_{ow} range, all compounds could be membrane-controlled at very high flow rates. The same set of compounds could also be boundary-layer controlled at very low flow rates (e.g., quiescent conditions). Hence, specification of the exposure conditions must be included if an investigator wants to pin-point the critical log K_{ow} value where rate control changes from one phase to the other. For example, under relatively low flow-turbulence conditions (i.e., <1 cm s^{-1} flow velocity), rate control likely switches from the membrane to the WBL for compounds with log K_{ow} values in the range 4 to 4.5.

Membrane-controlled sampling rates can be modeled by

$$R_s = k_o A \approx k_m K_{mw} A \tag{3.37}$$

Because δ_m is well defined, k_m can be written as

$$k_m = D_m/\delta_m \tag{3.38}$$

where D_m is the diffusion coefficient in the LDPE phase. On the polymer side, diffusion rates increase with increasing segmental motility of the polymer chains and free volume (Moisan, 1981; Lloyd and Meluch, 1985; Asfour et al., 1989; Saleem et al., 1989; Reynolds et al., 1990). Both of these related factors control the availability of cavities that are needed for diffusional jumps. Diffusion coefficients are inversely related to molecular volume and molecular weight (Lieb and Stein, 1969; Möller and Gevert, 1994), but it is recognized that for a given size class, more elongated diffusants with greater conformational freedom have larger diffusion coefficients than rigid molecules with large cross sectional diameters (Lloyd and Meluch, 1985; Asfour et al., 1989; Saleem et al., 1989; Reynolds et al., 1990). Hofmans (1998) used molecular weight (M) to correlate diffusion coefficients (m^2 s^{-1} units) in LDPE obtained from five literature sources (Figure 3.8).

$$\log D_m = -7.47 - 2.33 \log M \tag{3.39}$$
$$n = 42, s = 0.44, 70 < M < 655$$

Distinguishing between rigid molecules and those with a high degree of conformational freedom within this data set, showed that the more flexible compounds had diffusion coefficients that were higher by a factor of 1.7, but this difference was not statistically significant. Because molecular weight and log K_{ow} are closely related quantities for non-polar analytes, Booij et al. (2003a) argued that sampling rates for membrane-controlled uptake can be modeled by

$$R_s = A k_m = A B_m K_{ow}^{0.682} \tag{3.40}$$

where B_m is a temperature-dependent proportionality constant that is inversely proportional to the membrane thickness. For SPMDs with a 70 μm LDPE wall thickness these authors arrived at B_m estimates of 14 nm s^{-1} at 2 °C and 50 nm s^{-1} at 30 °C.

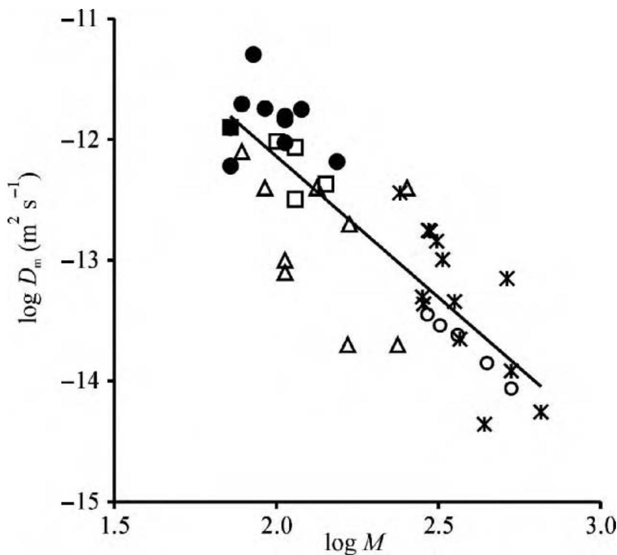

FIGURE 3.8 Diffusion coefficients in LDPE at 22–25 °C, as a function of molecular weight. Filled circles: Saleem et al. (1989), triangles: Reynolds et al. (1990), open circles: Möller and Gevert (1994), asterisks: Moisan (1981).

3.6.5. Theoretical Uptake Model: WBL-Controlled Uptake

Sampling rates that are controlled by the WBL can be modeled by

$$R_s = k_w A \tag{3.41}$$

where k_w is the mass transfer coefficient of the WBL. In general, k_w increases when flow rates and turbulence intensities increase. However, because of the complexity of the flow around exposed SPMDs, it is quite difficult to estimate the magnitude of k_w from first principles, except for some simple configurations, such as SPMDs that are mounted parallel to a fully developed unidirectional flow (Bird et al., 1960; Levich, 1962). In a typical SPMD exposure study, however, the samplers are mounted in a zigzag or twisted fashion with a random orientation relative to the main water flow and placed in exposure cages that contain sharp edges and orifices. Similar problems are often encountered by chemical engineers, when ill-defined flows characterize the system of interest (e.g., in the case of mass transfer in reactor beds that are packed with irregularly shaped packing material). Chemical engineers have worked their way around the problem of determining precise hydrodynamical conditions at solid-water interfaces by establishing semi-empirical correlations between three dimensionless groups of variables, the Sherwood (Sh), Reynolds (Re) and Schmidt (Sc) numbers

$$\mathrm{Sh} = k\,d/D_w \tag{3.42}$$

$$\mathrm{Re} = u\,d/\nu \tag{3.43}$$

$$\mathrm{Sc} = \nu/D_w \tag{3.44}$$

where k is the mass transfer coefficient at the surface, d is a characteristic length scale (e.g. a particle diameter), D_w was defined earlier, u is a characteristic velocity (e.g. the interstitial flow rate, or the flow velocity at infinite distance from the surface) and ν is the kinematic viscosity (ratio of a fluid's viscosity to its density) of the fluid. Typically, the Sherwood number is proportional to $Sc^{1/3}$ (Bird et al., 1960; Levich, 1962; Boudreau and Guinasso, 1982; Worch, 1993). However, Levich (1962) argues that there are reasons to believe that $Sh \sim Sc^{1/4}$. We find that the $1/3$ power dependence occurs more frequently in the engineering literature than the $1/4$ power, and will leave the discussion on this issue to the hydrodynamicists. The typical relation between k_w and the diffusion coefficient can then be summarized as

$$k_w \sim D_w^{2/3} \tag{3.45}$$

Diffusion coefficients may be estimated using the Wilke-Chang equation (Danckwerts, 1970), the Sutherland-Einstein equation (Gobas et al., 1986), or the Hayduk-Laudie equation (Tucker and Nelken, 1982), which state that D_w values decrease with the molar volume (V_m) to the power 0.3 to 0.6. Alternatively, the semi-empirical Worch relation may be used (Worch, 1993), which predicts diffusion coefficients to decrease with increasing molar mass to the power of 0.53. These four equations yield very similar D_w estimates (factor of 1.2 difference). Using the D_w estimates from the most commonly used Hayduk-Laudie equation ($D_w \sim V_m^{-0.589}$), and combining Eqs. 3.41 and 3.45, SPMD sampling rates for WBL-controlled uptake would vary according to

$$R_s \sim V_m^{-0.39} \tag{3.46}$$

where V_m is the LeBas molar volume. Over the molar volume range 199 cm^3 mol^{-1} (phenanthrene) to 480 cm^3 mol^{-1} (fenvalerate), Eq. 3.46 predicts a reduction in sampling rates by a factor of 1.4.

Because sampling rates are commonly given as a function of log K_{ow}, Booij et al. (2003a) expressed log D_w for PCBs, PAHs and chlorobenzenes as a function of log K_{ow}, and obtained

$$R_s = A B_w K_{ow}^{-0.044} \tag{3.47}$$

where B_w is a constant for a given exposure, but may vary among exposures according to differences in hydrodynamical conditions, and sampler geometry.

3.6.6. Combined Theoretical Uptake Model

Combining the models for membrane-controlled and boundary layer-controlled uptake (Eqs. 3.40 and 3.47) for nonpolar compounds yields (Booij et al., 2003a)

$$R_s = k_o A = \frac{1}{\dfrac{1}{A B_m K_{ow}^{0.682}} + \dfrac{1}{A B_w K_{ow}^{-0.044}}} \tag{3.48}$$

A qualitative comparison of Eq. 3.48 with the measured uptake rates (Figure 3.5) reveals a number of features that are worth noting. First, one would expect the sampling rates for membrane-controlled uptake to fall on the same straight line. This expectation is met for all studies, except for the sampling rates reported by Booij et al. (2003a). However, the slope of the log R_s versus log K_{ow} lines attains similar values for all studies. Second, one would also expect the sampling rates to weakly decrease with increasing log K_{ow} in the high log K_{ow} range. Based on Eq. 3.47, sampling rates at log $K_{ow} = 8$ can be expected to be about 80% of the sampling rates at log $K_{ow} = 6$. This weak log K_{ow}-dependence of the sampling rates was observed in some studies (Huckins et al., 2002b, 2004; Booij et al., 2003a), but in several other studies a decrease in sampling rates over this log K_{ow} range by a factor of 3 to 8 was observed (Meadows et al., 1998; Huckins et al., 1999; Rantalainen et al., 2000; Luellen and Shea, 2002). A possible reason for a large drop in measured sampling rates of very hydrophobic compounds may be the overestimation of aqueous concentrations due to sorption to *DOC*. This was first acknowledged by Meadows et al. (1998), who adopted a hypothetical *DOC* concentration of 0.5 mg L^{-1} and assumed that the contaminant affinity for *DOC* was similar to that for octanol, i.e., $K_{DOC} = K_{ow}$. Luellen and Shea (2002) measured the *DOC* concentrations and applied the Burkhard equation (Burkhard, 2000) to predict *DOC* sorption affinities. Adopting Eq. 3.48 for the sampling rate of truly dissolved analytes, and the Burkhard relationship for sorption to *DOC*, the apparent sampling rate ($R_{s,app}$) is given by

$$R_{s,app} = \frac{R_s}{1 + [DOC]K_{DOC}} = \frac{1}{\left(\frac{1}{AB_m K_{ow}^{0.682}} + \frac{1}{AB_w K_{ow}^{-0.044}}\right)(1 + [DOC]QK_{ow})} \quad (3.49)$$

where Q is dependent on *DOC* quality ($Q = 10^{-1.11} \approx 0.078$ for *DOC* of average quality, see Eq. 3.25). In order to check if Eq. 3.49 sufficiently explains the observed sampling rates, this model was fitted to the calibration data from 19 experiments in 9 studies, using log AB_m, log AB_w, and log $Q[DOC]$ as adjustable parameters, and assuming a log normal distribution of errors.

The results are summarized in Table 3.1. Inclusion of a *DOC*-sorption term in the model significantly improved the $R_s - K_{ow}$ fit for the studies by Huckins et al. (1999, 2004), Rantalainen et al. (2000), Meadows et al. (1998), and Luellen and Shea (2002). The non-significance of *DOC* sorption in the studies by Vrana and Schüürmann (2002) and by Sabaliūnas and Södergren (1997) may be related to the fact that highly hydrophobic compounds were not included in these studies. The sampling rate data for organochlorine pesticides (OCPs) by Huckins et al. (2002b) gave no indication of sorption to *DOC*, even though the log K_{ow} range for this data set was similar to the range covered by PAHs studied by these authors (Huckins et al., 1999). However, it should be stressed that the *DOC* concentration of 0.26 mg L^{-1} was determined in a separate sample taken from the same

Table 3.1 Parameter Estimates Obtained by Fitting Experimental Sampling Rates to the Membrane-WBL-DOC Model (Eq. 3.49)

Sources	Flow Rate (cm s^{-1})	Temperature °C	n	log K_{ow} range	log AB_m (L d^{-1})	log AB_w (L d^{-1})	log Q [DOC]	[DOC] (mg L^{-1})	log Q (cm^3 g^{-1})
Huckins et al. (1999)	0.004	10	16	3.5–6.9	-1.91 ± 0.10[a]	0.82 ± 0.04	-7.10 ± 0.19	0.26	−0.5
”	0.004	18	15	3.5–6.9	-2.36 ± 0.11	0.97 ± 0.08	-6.90 ± 0.27	0.26	−0.3
”	0.004	26	15	3.5–6.9	-2.29 ± 0.12	1.15 ± 0.11	-6.71 ± 0.28	0.26	−0.1
Vrana and Schüürmann (2002)	0.06	19	6	3.7–5.5	ns[b]	0.60 ± 0.14	ns	—	—
”	0.28	19	6	3.7–5.5	-2.17 ± 0.03	1.52 ± 0.07	ns	—	—
”	1.14	19	6	3.7–5.5	-2.52 ± 0.13	ns	ns	—	—
Booij et al. (2003a)	90	2	16	3.9–7.4	-1.26 ± 0.10	2.06 ± 0.04	ns	—	—
”	90	13	14	3.9–7.4	-0.77 ± 0.05	2.30 ± 0.01	-8.07 ± 0.20	—	—
”	90	30	17	3.9–7.4	-0.70 ± 0.05	2.49 ± 0.03	ns	—	—
Rantalainen et al. (2000)	8	11	23	6.4–8.2	ns	0.60 ± 0.06	-7.86 ± 0.22	—	—
”	8	19	23	6.4–8.2	ns	0.83 ± 0.03	-8.49 ± 0.23	—	—
Huckins et al. (2004)	0.1	16	32	3.1–6.8	-2.06 ± 0.08	0.63 ± 0.03	-6.94 ± 0.21	0.26	−0.4
Meadows et al. (1998)	0.004	12	73	5.0–7.8	ns	1.08 ± 0.02	-7.09 ± 0.08	<1	> -1.1
Sabaliūnas and Södergren (1997)	0.006	?	6	5.0–6.2		0.85 ± 0.16	ns	—	—
Luellen and Shea (2002)	50	25	47	3.4–7.6	-1.27 ± 0.20	0.92 ± 0.02	-6.88 ± 0.09	0.35	−0.4
”	0.01	25	32	3.4–7.6	ns	0.86 ± 0.04	-6.32 ± 0.14	1.29	−0.4
Huckins et al. (2002b)	0.004	10	22	3.7–6.9	-2.69 ± 0.06	0.71 ± 0.03	ns	0.26	—
”	0.004	18	20	3.7–6.9	-2.24 ± 0.11	0.66 ± 0.03	ns	0.26	—
”	0.004	26	23	3.7–6.9	-2.19 ± 0.08	1.07 ± 0.04	ns	0.26	—

[a] Standard error of the estimated parameter.
[b] Parameters that did not significantly ($p < 0.05$) improve the quality of the fit are listed as “ns”.

water source (a deep well), after the exposure experiments had finished. The *DOC* quality can be estimated for those studies where *DOC* concentrations are reported. Values of log Q fall within the 95% confidence range of log Q values (-2.4 to $+0.2$) reported by Burkhard (2000). Although the evidence is indirect, sorption to *DOC* may have caused an underestimation of the sampling rates of highly hydrophobic compounds in many studies. An underestimation of the sampling rate by a factor of 2 occurs when $Q\,[DOC]\,K_{ow} = 1$. Inspection of Table 3.1 shows that sampling rates of compounds with log K_{ow} values > 6.3 to 8.5 may have been underestimated, depending on the experiment. Thus, investigators should consider including methods for independently measuring the extent of sorption to *DOC* in future calibration experiments. A potential approach would be to measure the water solubility enhancement of the most hydrophobic analyte of the calibration set, relative to that of ultra-pure water.

An alternative explanation for the lower sampling rates of very hydrophobic compounds is that the membrane may become rate limiting again for compounds with large molar volumes and low conformational freedom, due to the fact that molecular size may be too large to fit into the transient cavities in the LDPE. Combining Eqs. 3.36 and 3.38 gives the condition for membrane controlled uptake

$$k_m K_{mw} = \frac{D_m K_{mw}}{\delta_m} \ll k_w \qquad (3.50)$$

Diffusion coefficients in LDPE steadily decrease with increasing molecular weight (Figure 3.8), and LDPE-water partition coefficients increase with increasing molecular weight. In general, the increase in K_{mw} with molecular size is much larger than the decrease in D_m. In the case of acenaphthene and benzo[*a*]pyrene, for example, D_m can be expected to decrease by a factor of about 3 (Eq. 3.39), but this decrease is more than offset by a 350 fold increase in K_{mw} (Booij et al., 2003a). Although membrane-controlled uptake cannot be excluded for very large hydrophobic molecules, the drop in D_m and/or K_{mw} for these compounds would have to be very sharp indeed.

3.6.7. Implications of *DOC* Sorption in the Lab for *In Situ* Sampling Rate Estimates

The underestimation of laboratory-derived sampling rates due to analyte sorption to *DOC* has no counterpart in PRC-derived sampling rates in the field, since aqueous PRC concentrations are zero anyway, and sorption to *DOC* would not change that. This implies that PRC-derived sampling rates in the field may be more accurate than laboratory-derived sampling rates for highly hydrophobic compounds (log $K_{ow} > 7$). For typical SPMD deployments without intermediate sampling, PRC-derived sampling rates can only be estimated for a limited number of PRCs (log $K_{ow} \approx 5$ to 6, for a typical exposure period of 3 to 6 weeks). PRCs with low K_{ow} values will have dissipated to below the detection level. For highly hydrophobic PRCs, the dissipated amount is usually too small to quantify. This raises

the question of how PRC-based sampling rates should be extrapolated into the high and low log K_{ow} range. Verweij et al. (2004) argued that for WBL-controlled uptake, the decrease in sampling rates with molecular size is small enough to be neglected. Booij et al. (2003a, 2003b) proposed to calculate R_s values from the PRC-derived sampling rate using an equation similar to Eq. 3.46 when the exchange kinetics of PRCs and analytes are WBL-controlled. This procedure relies on theoretical considerations and on the observation that accounting for sorption to *DOC* may bridge the gap between theory and experimental sampling rates, as indicated above. Therefore, the sampling rate of a WBL-controlled PRC may be used to calculate R_s values for more hydrophobic analytes, by adopting Eq. 3.46.

$$R_s = R_{s,PRC} \left(\frac{V_{PRC}}{V} \right)^{0.39} \tag{3.51}$$

Subsequent application of these estimated R_s values in Eq. 3.22 then allows for estimating the aqueous concentrations (Box 3.2).

Sampling rate extrapolation into the low log K_{ow} range is more difficult, because of the increasing resistance of the membrane, which causes the sampling rates to fall below the values that are predicted by Eq. 3.51. Fortunately, this extrapolation is less critical, because compounds that are less hydrophobic than the PRCs typically have attained a substantial degree of equilibrium. As a result, aqueous concentration estimates for these compounds are quite insensitive to uncertainties in the sampling rates. Alternatively, when the log K_{ow} interval between successive PRCs is small, the degree of equilibrium attained by analytes with intermediate log K_{ow} values may be obtained by interpolation. The aqueous concentrations may be subsequently calculated from the partition coefficients and corrected for partial equilibrium attainment.

3.6.8. Biofouling

The thickness of the biofilm on exposed SPMDs varies not only from exposure to exposure, but varies from spot to spot on the same membrane as well. Biofilms as thick as about 1 mm have been observed on SPMD membranes in extended (>30 d) warm water exposures. The composition of biofilms can vary significantly, depending on the aquatic system. For example, the biofilm may not only consist of periphytic communities, but may contain imbibed particles and mineral precipitates as well. Huckins et al. (1997) determined PAH sampling rates using SPMDs that were heavily biofouled in a control pond before use, relative to unfouled SPMDs. Sampling rate ratios (fouled divided by unfouled) ranged between 0.7 at log $K_{ow} = 4$ to 0.3 at log $K_{ow} = 7$ (Figure 3.9). As far as organic contaminant transport is concerned, a biofilm may be viewed as a layer of immobilized water with dispersed organic carbon sorption sites. From Eq. 3.8, the conductivity of the biofilm is given by

$$1/I_b = k_b K_{bw} \tag{3.52}$$

Box 3.2 Example of the Calculation of Sampling Rates from a PRC-Derived Sampling Rate, Using the WBL-Model (Eq. 3.51)

Input data

$V_s = 4.95\ \text{cm}^3$
exposure time = 42 d

chrysene-*d*12 amounts per SPMD:
  118 ng at $t = 0$
  84 ng at $t = 42$ d

log K_{ow} values:
  chrysene-*d*12 : 5.8
  pyrene : 5.2
  PCB 153 : 6.9

LeBas volume ($\text{cm}^3\ \text{mol}^{-1}$):
  chrysene-*d*12 : 251
  pyrene : 214
  PCB153 : 310

accumulated amounts:
  PCB 153 = 13 ng
  pyrene = 264 ng

Step 1. Calculate the R_s of the PRC

from Eq. 3.24: $k_{e,\text{chrysene-}d12} = -\ln(84/118)/42 = 0.0081\ \text{d}^{-1}$
from Eq. 3.28: $\log K_{sw,\text{chrysene-}d12} = 5.41$
from Eq. 3.20: $R_{s,\text{chrysene-}d12} = 4.95 \cdot 10^{5.41} \cdot 0.0081 = 10306\ \text{cm}^3\text{d}^{-1} \approx 10.3\ \text{L d}^{-1}$

Step 2. Calculate the R_s of the analytes

from Eq. 3.51:

$$R_{s,\text{ pyrene}} = 10.3(251 \div 214)^{0.39} = 11.0\ \text{L d}^{-1}$$

$$R_{s,\text{ PCB153}} = 10.3(251 \div 310)^{0.39} = 9.5\ \text{L d}^{-1}$$

Step 3. Calculate the aqueous concentrations
from Eq. 3.28:
  $\log K_{sw,\text{ pyrene}} = 5.08$
  $\log K_{sw,\text{ PCB153}} = 5.70$

$$C_{w,\text{pyrene}} = \frac{264}{4.95 \cdot 10^{5.08}\left(1 - \exp\left(-\frac{11000 \cdot 42}{4.95 \cdot 10^{5.08}}\right)\right)} = 0.82\ \text{ng L}^{-1}$$

$$C_{w,\text{PCB153}} = \frac{13}{4.95 \cdot 10^{5.70}\left(1 - \exp\left(-\frac{9500 \cdot 42}{4.95 \cdot 10^{5.70}}\right)\right)} = 0.035\ \text{ng L}^{-1}$$

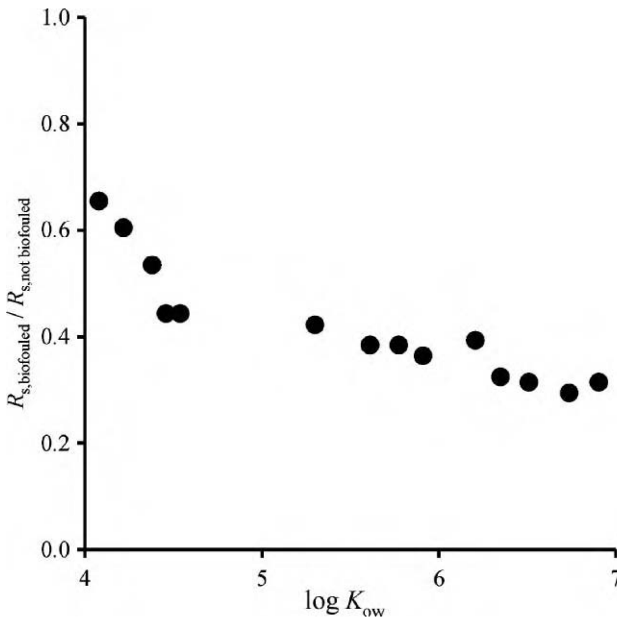

FIGURE 3.9 Ratio of sampling rates with biofouled and non-biofouled SPMDs as a function of log K_{ow}.

Because of the similarity of transport in biofilms and in stagnant sediments, information on the parameters that control the conductivity of the biofilm can be obtained from diagenetic models for contaminant diffusion in pore waters. Assuming that molecular diffusion is the dominant transport mechanism, and that instantaneous sorption equilibrium exists between dissolved and particle-bound solutes, the vertical flux (j) through a stagnant sediment is given by (Berner, 1980)

$$j = \phi \frac{D_w}{\theta(1+K)} \frac{dC}{dz} \tag{3.53}$$

where ϕ is the porosity, θ is the tortuosity of the sediment diffusional pathways, D_w is the molecular diffusion coefficient in particle-free water and K is the bulk sediment-water partition coefficient, defined as the concentration ratio of sorbed and dissolved solutes (both on a bulk sediment volume basis). Since K_{bw} is defined as the concentration ratio of sorbed plus dissolved contaminants (on a biofilm volume basis) and dissolved contaminants (on a particle-free water volume basis), the factor $1 + K$ is given by

$$1 + K = K_{bw}/\phi \tag{3.54}$$

Combining Eqs. 3.53 and 3.54, and assuming a linear concentration gradient over a biofilm with thickness δ_b, the flux through the biofilm can be written as

$$j = \frac{\phi^2 D_w}{\theta K_{bw} \delta_b} \Delta C = k_b \, \Delta C \tag{3.55}$$

From Eq. 3.55, the conductivity of the biofilm is given by

$$\frac{1}{I_b} = \frac{\phi^2 D_w}{\theta \delta_b} \tag{3.56}$$

Equation 3.56 indicates that the biofilm essentially behaves like an immobilized water layer, with a resistance that is independent of the biofilm-water partition coefficient. Evidently, when the growth rate of the biofilm and the diffusion rate of the contaminants are of similar magnitude, this highly idealized model breaks down, and it can be expected in those cases that highly hydrophobic compounds will have more difficulty in reaching the membrane than less hydrophobic (more mobile) compounds. Also, Eq. 3.56 will likely fail to predict solute transport in biofilms with sizable populations of invertebrates because of bioturbation.

The sampling rate reduction that is shown in Figure 3.9 is relatively independent of the hydrophobicity for compounds with log K_{ow} values between 4.5 and 7, in accordance with Eq. 3.56. The initial rapid fall in the magnitude of the R_s ratios of PAHs up to log $K_{ow} = 4.5$ is indicative of the reduced importance of membrane-controlled uptake and an increasing dependence on WBL and biofilm control. The 3-fold reduction in uptake rates due to biofouling clearly is important. It can be expected that the dissipation of PRCs is similarly reduced, although only very limited experimental evidence is available. Huckins et al. (1994, 2002b) showed for biofouled SPMDs that PRC-based sampling rates, obtained from the dissipation of perdeuterated acenaphthene, phenanthrene, and pyrene, were within 1.5 fold of the R_s values of the corresponding native compounds.

3.7. PORE WATER SAMPLING

Investigators have used SPMDs buried in fresh water sediments and shore soils to determine the relative contamination by chlorinated hydrocarbon contaminants (Rantalainen et al., 1998, 2000) and PAHs (Williamson et al., 2002). Rantalainen et al. (2000) have suggested that, at the points of contact between the SPMD membrane and sediment particles, the aqueous film thickness is very small, giving rise to high initial uptake rates. Huckins et al. (1996) and Rantalainen et al.(2000) reported that the initial rapid rise in SPMD concentrations ($<$1 week), is followed by a less rapid linear uptake of hydrophobic chemicals by buried SPMDs. When mixing of particles and pore water by waves, currents, and biota can be neglected, transport of solutes from the sediment to the SPMD surface takes place by molecular diffusion only. In the initial stages of the uptake, the contaminant distribution in sediment and pore water is relatively homogeneous. During the uptake process, dissolved contaminants are removed from the pore water in the immediate vicinity of the SPMD surface. The resulting concentration gradients induce desorption from contiguous particles, and trigger diffusional fluxes from the pore waters at larger distances from the SPMD surface (Booij et al., 2003b). These processes result in a relatively slow but progressive contaminant depletion of both the pore

water and the particulate phase. This causes the contaminants to be transported to the membrane over increasingly large distances, preventing the establishment of a steady-state flux. As a result, the uptake rates decrease with time, even when the concentrations in the SPMD are far below their equilibrium value. The growth of the effective thickness of the WBL with time is counteracted by contaminant desorption from the particulate phase. Sediments with high sorption capacities will be able to efficiently replenish the pore water, whereas sediments with low sorption coefficients will quickly be depleted themselves. A complicating factor in this respect is that desorption rates may become rate limiting once the quickly equilibrating fractions of the sediment have been depleted (Cornelissen et al., 1998, 2000, 2001; ten Hulscher et al., 1999).

Booij et al. (2003b) made an effort to model contaminant uptake by buried passive samplers. The major assumptions underlying this model are that the sampler can be regarded as an infinite sink for target contaminants, that the depletion of the bulk sediment phase is insignificant, and that the contaminant desorption kinetics are not rate-limiting.

$$N = \frac{2\phi A C_{\mathrm{w}} \sqrt{D_{\mathrm{w}}(1+K)}}{\sqrt{\pi\theta}} \sqrt{t} \tag{3.57}$$

where A is the SPMD surface area, ϕ is the porosity, θ was defined earlier, D_{w} is the molecular diffusion coefficient in particle-free water and K is defined as the concentration ratio of sorbed and dissolved solutes (both on a bulk sediment volume basis). This model predicts that the absorbed amounts increase with the square root of time, and with the square root of K. Thus, aqueous concentrations can in principle be calculated from the amount absorbed by SPMDs when the porosity, torturosity, and molecular diffusion coefficients are known. Unfortunately, the calculations require a number of estimates or measurements, and are rather tedious. In addition, the requirement that the concentrations in SPMDs are far below their equilibrium values is not always satisfied for compounds with low and intermediate log K_{ow} values. For these reasons, Booij et al. (2003b) recommended that SPMDs be incubated in slowly stirred sediment slurries. In this case, the modeling of contaminant uptake is the same as for uptake from the water phase (Eq. 3.13), although the reported sampling rates are much higher than with exposures to particle-free water ($\approx 30 - 300$ L d^{-1} for 460 cm^2 samplers).

The assumptions that the depletion of the sediment phase is insignificant, and that the contaminant desorption kinetics are not rate-limiting for exposures to sediment slurries, are only valid if some critical conditions regarding experimental design are met. For compounds that attain equilibrium, the total amount in the SPMDs should be much smaller than the total amount in the sediment phase. This condition can be expressed as

$$V_{\mathrm{s}} C_{\mathrm{s}} \ll m_{\mathrm{oc}} C_{\mathrm{oc}} f_{\mathrm{r}} \tag{3.58}$$

where m_{oc} is organic carbon mass of sediment present in the incubation vessel, C_{oc} is the contaminant concentration in the sediment phase on an organic carbon

basis, and f_r is the contaminant fraction that quickly (i.e. on the time scale of the experiment) equilibrates with the pore water. Introducing the partition coefficients of sediment organic carbon-water (K_{oc}) and K_{sw}, and rearranging gives a criterion for the ratio of SPMD volume to organic carbon mass

$$\frac{V_s}{m_{oc}} \ll \frac{K_{oc}}{K_{sw}} f_r \tag{3.59}$$

Since the right hand side of Eq. 3.59 would typically approximate 1, a V_s/m_{oc} ratio of 0.05 mL g^{-1} seems to be a safe choice.

For compounds that do not reach a significant degree of equilibrium during the exposure, the absorption rate by the SPMD should be much smaller than the desorption rate by the sediment (Booij et al., 2003b)

$$R_s \ll m_{oc} k_2 K_{oc} \tag{3.60}$$

where k_2 is the first-order desorption rate constant of the sediment phase, which typically attain values of 0.1–1 h^{-1} and 10^{-3} h^{-1} for the rapidly and the slowly equilibration sediment fraction, respectively (Cornelissen et al., 1998, 2000, 2001; ten Hulscher et al., 1999). Based on a number of model calculations, using literature values for k_2 and K_{oc}, Booij et al. (2003b) recommend that sampler volume to organic carbon mass ratios of 0.05 mL g^{-1} would be a safe choice in this case as well.

3.8. GROUNDWATER SAMPLING

Considerations for the deployment of SPMDs in groundwater wells have been described by Gustavson and Harkin (2000), who also presented a comparison of SPMD-derived and batch extraction-derived PAH concentrations in groundwater. The sampling of water in subterranean strata with SPMDs is generally straightforward, as environmental conditions are usually more constant than surface water, and biological growths on the SPMD membrane surface are minimal. However, permeability in fine-grained strata can be very low, which may result in the depletion of target solutes at the membrane surface in a similar fashion as with the exposure of SPMDs in stagnant sediments. In this case, the uptake rate is limited by the groundwater flow. Groundwater fluxes can be estimated from Darcy's Law, which links well flow rates (F_w; volume per time) or recharge rates to the local pressure gradients and the hydraulic permeability/conductivity (P_{hc}; distance per time) of the strata (Gustavson and Harkin, 2000).

$$F_w = P_{hc} A \Delta h / L_f \tag{3.61}$$

where Δh is the difference in the hydraulic head over the water bearing strata, and L_f is the length of the strata. When SPMDs are placed in wells, F_w should be compared to the sampling rate of the analyte of interest. If $F_w \gg R_s$, then the methods described for SPMDs exposed to HOCs in surface waters can be applied.

When $F_w \ll R_s$, groundwater sampling is essentially equivalent to the exposure of an SPMD in a small volume of well water in a closed system (V_{gw}). Assuming that residue contributions from suspended particulates or colloids and dissolution of non-aqueous phase liquids is insignificant, the aqueous concentrations may be calculated from

$$C_w = N / V_{gw} \tag{3.62}$$

When F_w is not known, using both Eqs. 3.22 and 3.62 to compute groundwater concentrations of analytes, provides an investigator with defined limits of the range of potential analyte concentrations.

3.9. AIR SAMPLING

Because processes such as diffusion and partitioning are fundamentally the same in water and air, equations that describe uptake from air can be obtained by replacing the subscripts in equations for water with those appropriate for air

$$C_s = K_{sa} C_a \left(1 - \exp\left(-\frac{R_s t}{V_s K_{sa}}\right)\right) \tag{3.63}$$

$$R_s = V_s K_{sa} k_e \tag{3.64}$$

$$k_e = \frac{A k_o}{V_s K_{sa}} \tag{3.65}$$

$$\frac{1}{k_o} = \frac{1}{k_a} + \frac{1}{k_m K_{ma}} + \frac{1}{k_{Ld} K_{Lda}} \tag{3.66}$$

where all parameters have the same meaning as described earlier, and the subscript "a" and "Ld" refer to the air phase and the lipid derived film on the exterior surface of SPMDs exposed for extended periods, respectively. Physical chemical properties of organic contaminants differ widely for water and air. Diffusion coefficients in air are larger than in water by about four orders of magnitude, and SPMD partition coefficients for air are two to three orders of magnitude higher than for water. Flow velocities in air (1–20 m s^{-1}) are typically much higher than in water (0.001–1 m s^{-1}), and air and water viscosities differ by a factor of about 60. Because of these differences, the general lack of biofouling, and the common presence of a surficial lipid-derived film, a separate discussion on air sampling by SPMDs is required.

3.9.1. SPMD-Air Partition Coefficients

No published values of SPMD-air partition coefficients (K_{sa}) exist. These values therefore have to be calculated from published values of K_{sw} and Henry's law constants (H) using

$$K_{sa} = \frac{K_{sw} RT}{H} \tag{3.67}$$

where R is the gas law constant, and T is the absolute temperature. Henry's law constants (Pa m^3 mol^{-1}) are available for a wide range of contaminants at various temperatures (ten Hulscher et al., 1992; Alaee et al., 1996; de Maagd et al., 1998; Paasivirta et al., 1999; Bamford et al., 1999, 2002; Shiu and Ma, 2000; Staudinger and Roberts, 2001; Sander, 2003; US EPA, 2003), including a large number of polar pesticides. Sometimes, Henry's law constants are given in the dimensionless form (H/RT), which is the air-water partition coefficient. The temperature dependence of H is well-documented for nonpolar compounds like chlorobenzenes, PCBs, PAHs, PCDDs, PCDFs, and the classical OCPs like DDTs, chlordanes, and HCHs. Typically, values of H increase by 0.3 log units (range 0.06 to 0.6 log units), when the temperature increases from 10 to 20 °C. Bearing in mind that K_{sw} is virtually temperature-independent, a decrease in K_{sa} values by a factor of about 2 (range 1.1 to 4) can be expected for each 10 °C temperature increase, due to the temperature dependence of H.

3.9.2. Air Sampling Rates

In a number of field studies, sampling rates were obtained by parallel deployment of SPMDs and high-volume active air samplers (HiVols) for PCBs (Petty et al., 1993; Prest et al., 1995; Ockenden et al., 1998; Shoeib and Harner, 2002), and polychlorinated naphthalenes (Shoeib and Harner, 2002). Lohman et al. (2001) reported sampling rates of PAHs and PCDDs/PCDFs that were based on SPMD and HiVol data obtained during different periods of the year. Laboratory-derived sampling rates have been reported for PCBs (Huckins et al., 1994), and for PAHs and a number of moderately polar pesticides (Robertson, 2004). In a similar laboratory experiment, Huckins et al. (2001) followed the dissipation of phenanthrene, diazinon and chlorpyrifos at two flow velocities and two temperatures. In addition, Ockenden et al. (2001) compared the kinetics of SPMD-air equilibration of native PCBs and the dissipation rate of ^{13}C-labeled PCBs, but no sampling rates were reported due to the absence of HiVol data. A summary of SPMD sampling rates is shown as a function of the octanol-air partition coefficient in Figure. 3.10. Log K_{oa} values were adopted as specified in Appendix A (Tables A.13–A.16). Sampling rates could be described by

$$\log R_s = 0.154 \log K_{oa} - 0.80 \tag{3.68}$$
$$n = 75, s = 0.20, r = 0.64$$

No large variation in sampling rates is observed among the different studies, despite differences in exposure conditions, such as wind speeds, temperature, and SPMD mounting layout. It should be noted, however, that the effect of temperature is partially accounted for by our use of temperature-corrected log K_{oa} values. An example of the application of Eq. 3.68 for calculating atmospheric concentrations is given in Box 3.3.

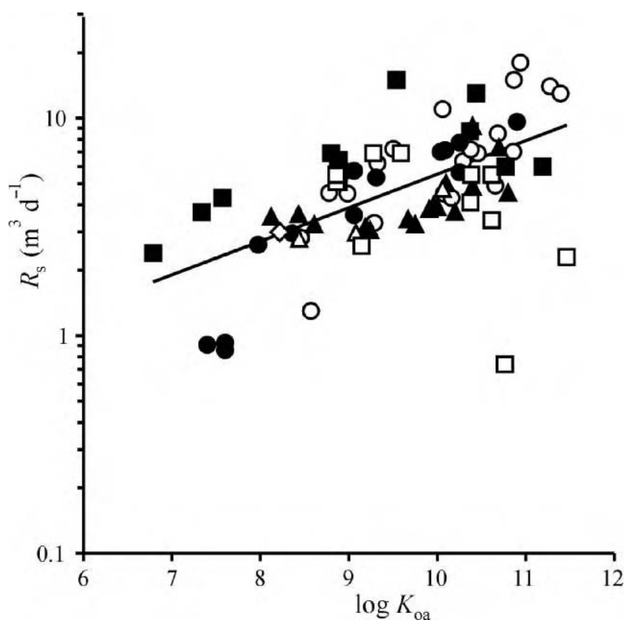

FIGURE 3.10 Experimental air sampling rates as a function of log K_{oa} for PCBs—open circles: Ockenden et al. (1998), diamond: Petty et al. (1993), closed circles: Huckins et al. (1994), closed triangles: Shoeib and Harner (2002); polychlorinated naphthalenes—open triangles: Shoeib and Harner (2002); PAHs—closed squares: Robertson (2004); and pesticides—open squares: Robertson (2004).

The small value of the log R_s versus log K_{oa} slope indicates that the uptake is partially membrane controlled and partially air boundary layer (ABL) controlled. Applying the same line of reasoning as for SPMD-water exchange, membrane-controlled uptake would result in log R_s − log K_{oa} slopes close to (but smaller than) one. On the other hand, ABL controlled sampling rates would be proportional to the compound's diffusion coefficient to the power of 2/3. Since diffusion coefficients in air are only weak functions of molecular size (Tucker and Nelken, 1982; Shoeib and Harner, 2002), a log R_s − log K_{oa} slope of about 0 would be expected in this case. Because the slope obtained in Eq. 3.68 is between these two limiting slopes, we suggest that the uptake generally is partially controlled by the membrane, and partially by the ABL. However, the fine structure in the individual data series is worth noting. Sampling rates reported by Ockenden et al. (1998) seem to level off to a constant value for log $K_{oa} > 9.5$ in the 14 °C, 18 °C series, and for log $K_{oa} > 11$ in the 4 °C series. For the data reported by Huckins et al. (1994) a less steep slope is observed for log $K_{oa} > 9$. A similar trend was observed for sampling rates of PAHs and moderately polar pesticides, which level off to a nearly constant R_s value for compounds with log $K_{oa} > 9$, albeit with a relatively large

Box 3.3 Example of the Calculation of Atmospheric Concentrations of Vapor-Phase Compounds Using Eq. 3.68

Input data

$V_s = 4.95\ \text{cm}^3$
exposure time = 50 d
exposure temperature 4 to 16 °C

$\log K_{ow} = 5.5$
$\log K_{oa} = -6.3 + 3928\text{T}^{-1}$ (Harner and Mackay, 1995)
Henry's law coefficient at 20 °C 41 Pa $m^3\ mol^{-1}$ (ten Hulscher et al., 1992)
water-air transfer enthalpy: 49 kJ mol^{-1} (ten Hulscher et al., 1992)
HCB accumulated per SPMD = 107 ng

Step 1. Calculate R_s

estimate $\log K_{oa}$ at the average exposure temperature of 10 °C, using the data given by Harner and Mackay (1995). $\log K_{oa}$ (283 K) = 7.6
from Eq. 3.68: $\log R_s = 7.6 * 0.154 - 0.80 = 0.37 \Rightarrow R_s = 2.3\ \text{m}^3\ \text{d}^{-1}$

Step 2. Calculate K_{sa}

from Eq. 3.28: $\log K_{sw} = 5.3$
from ten Hulscher et al. (1992):
$\ln H\ (283\ \text{K}) = \ln H\ (293\ \text{K}) - 49000/8.314\ (1/283 - 1/293) = 3.0$
$H = 20\ \text{Pa m}^3\ \text{mol}^{-1}$
from Eq. 3.67 : $\log K_{sa} = 7.4$

Step 3. Calculate C_{air}

$$C_{a,HCB} = \frac{107}{4.95 \cdot 10^{7.4}\left(1 - \exp\left(-\frac{2.3 \cdot 10^6\ 50}{4.95 \cdot 10^{7.4}}\right)\right)}$$
$$= 1.4 \cdot 10^{-6}\ \text{ng cm}^{-3} = 1.4\ \text{ng m}^{-3}$$

The exponential factor (−0.92) indicates that HCB has attained $[1-\exp(-0.92)] \cdot 100\% = 60\%$ of its equilibrium value.

scatter (Robertson, 2004). Sampling rates reported by Shoeib and Harner (2002) are relatively constant in the range of $8 < \log K_{oa} < 10$, and show a modest increase at $\log K_{oa} > 10$. Again, the constancy of sampling rates with $\log K_{oa}$ is indicative of ABL controlled uptake. Huckins et al. (2001) showed that the k_e of phenanthrene and diazinon increased by a factor of 2.2 and 1.5, respectively, when the air-flow rate increased from <15 cm s^{-1} to about 60 cm s^{-1}. The suggestion that sampling rates are under partial membrane control and boundary layer control is supported

by the Ockenden et al. (2001) observation that PCB amounts sampled by shielded SPMDs was slightly less than for fully exposed SPMDs (smaller than a factor of 1.5, depending on the compound). These authors conclude that the effect of wind speed on the sampling rates is insufficient to explain the earlier observation by Ockenden et al. (1998) that sampling rates were higher in winter than in summer, and that the increase of sampling rates at lower temperature implies membrane-controlled uptake.

The temperature dependence of R_s yields additional information on the issue of whether the membrane or the ABL controls the uptake rates. In the case of membrane-controlled uptake, the sampling rates are given by

$$R_s \approx Ak_m K_{ma} \approx \frac{Ak_m K_{mw} RT}{H} \tag{3.69}$$

Activation energies for membrane-controlled uptake rates from water attain values of about 20 kJ mol^{-1} (Figure 3.4). Because membrane-controlled water sampling rates are proportional to $k_m K_{mw}$, and because the temperature dependence of the LDPE-water partition coefficient (K_{mw}) is quite weak (≈ -0.3 kJ mol^{-1}, Booij et al., 2003a), these activation energies are almost entirely related to k_m. For that reason, the value of k_m derived from water sampling rates can be adopted for k_m when analyzing air sampling rate data. This logic indicates that k_m values increase by a factor of about 1.3 when the temperature increases from 10 to 20 °C in air exposures. This increase in k_m is offset by a decrease of K_{ma}, caused by the increase of Henry's law constant, as illustrated for PCB congeners 28 and 153. These compounds have water-air transfer enthalpies of 41 and 27 kJ mol^{-1}, respectively (Bamford et al., 2002), indicating that a temperature increase from 10 to 20 °C causes H to increase by about 1.8 fold for PCB 28 and by about 1.5 fold for PCB 153. A 10 °C temperature increase therefore causes both k_m and H to increase. As a result, sampling rates for PCB congeners 28 and 153 can be expected to change by a factor of $1.3/1.8 = 0.7$ and $1.3/1.5 = 0.9$, respectively, if the uptake would be membrane-controlled for these compounds.

Sampling rates for the case of total boundary layer-control can be expected to be nearly independent of temperature, since both the diffusion coefficients in air, and the kinematic viscosity of air are only weak functions of temperature (Shoeib and Harner, 2002). This leaves the air-flow velocity as the major factor that can be responsible for the seasonal differences among sampling rates observed by Ockenden et al. (1998). The absence of large R_s differences between indoor and outdoor exposures may be indicative of membrane-control, but it may also reflect the efficient damping of high flow velocities by the deployment devices used for SPMD air exposures (Ockenden et al., 2001).

Summarizing, some of the evidence indicates membrane-controlled uptake. Other evidence suggests ABL controlled uptake. However, the reasonably small variance in the available sampling rates obtained under widely differing flow and temperature conditions suggests that relatively accurate R_s values for PCBs and related compounds may be estimated from Eq. 3.68.

A more complicated situation exists for particle-associated contaminants. Lohman et al. (2001) report that predominantly (>95%) particle-associated contaminants (5- and 6-ring PAHs, hepta- and octachloro dibenzo-*p*-dioxins) are efficiently sampled by SPMDs. This observation has been supported by other research (Bartkow, 2004). In both studies, it appears that the surficial film was not removed prior to dialytic recovery of analytes. Particle sampling is likely mediated by the presence of a sticky triolein related film on the exterior of SPMDs exposed to air. The time-dependent development of this film has been documented by Petty et al. (1993) for SPMDs that contained 95% pure triolein. After a 28 day exposure to indoor air at 25 °C, the mass of the exterior film amounted to 3% of the triolein mass. The authors suggest that it likely consisted of lower molecular weight triolein impurities, such as methyl oleate, oleic acid, and glyceryl (di-)oleate. Lebo et al. (2004) have subsequently shown that 4% of the impurities in one lot of 95% triolein was methyl oleate. Also, unsaturated lipids are known to oxidize over time and reaction rates are enhanced by light (Dobarganes and Marquez-Ruiz, 1998). The oxidation of unsaturated lipids generally produces epoxides, ketones, and in the case of triglycerides, monomers, dimers and oligomers can be produced as well. The reactivity of unsaturated lipids on the exterior surface of the membrane is expected to be much higher than for membrane enclosed triolein, because supplies of oxygen and water are not limited by membrane permeation. In regard to membrane-enclosed lipids, exposure temperature is a critical parameter in that it affects both reaction rates and the diffusivity of oxidation products through the membrane. The availability of oxygen in the SPMD interior during air exposures may be a limiting factor for several days, since the permeability of oxygen in LDPE has been shown to be relatively low (Pauly, 1989; Divine and McCray, 2004). To our knowledge, no published data exists on the potential for the autoxidation of LDPE enclosed triolein during long-term air exposures. However, we report that 82 d air exposures (≈25 °C) of standard SPMDs ($A = 460$ cm^2) containing 1-mL of high purity triolein (Lebo et al., 2004) in a dark room, resulted in only a very slight surficial film with a residue mass of ≈13 mg ± 2.5 ($n = 4$). These data suggest that autoxidation of membrane enclosed high purity triolein (99%) does occur very slowly, but for exposures of moderate duration (<60 d) and temperature (≤25 °C), and in the absence of light, oxidation products of triolein should contribute only slightly to the development of a surficial film.

Although R_s values of high K_{sa} compounds derived from Eq. 3.68 may have been partly influenced by particle sampling, it is unlikely that the equation can accurately predict the summed vapor plus particulate phase concentrations, because transport rates through the boundary layer and through the membrane are different for the vapor-phase fraction and the particle-bound fraction, due to differences in effective diffusion coefficients between molecules and small particles. In addition, it will be difficult to define universally applicable calibration curves for the sampling rate of total (particle + vapor) atmospheric contaminants. At this stage of development, results obtained with SPMDs for particle-associated compounds provides valuable information on source identification and temporal

trends (Lohman et al., 2001), but these results can only be considered to be qualitative or semi-quantitative. However, Eq. 3.68 can be used to set an upper limit to vapor-phase concentrations.

An additional complicating factor with respect to air sampling rate calibration is the uncertainty associated with determinations of vapor-phase and particle sorbed concentrations of analytes by HiVol sampling. These systems suffer from artifacts such as the volatilization of particle-bound contaminants, insufficient retention of small particles, and adsorption of vapor-phase contaminants on the GFFs (Ockenden et al., 1998; Lohman et al., 2001). These artifacts may cause concentrations in the vapor-phase to be overestimated or underestimated, which results in sampling rates that are too low or too high.

3.9.3. The Use of PRCs in Atmospheric Sampling

The use of PRCs in atmospheric sampling has been fairly limited. Booij and van Drooge (2001) have used 1,3,5-trichlorobenzene, and the PCB congeners 4, 29, 155, and 204 as PRCs in SPMD exposures to coastal air for three weeks. No measurable loss was observed for PCB congeners 155 and 204. Ockenden et al. (2001) studied the dissipation of ^{13}C-labelled PCBs (congeners 28, 52, 101, 138, 153, and 180) for 120 days. The ratios of PRC-based sampling rates and the sampling rates of native PCBs were in the range 0.8 for PCB 28 to 3.6 for PCB 153. No measurable losses were observed for ^{13}C-labelled PCB congeners 138 and 180. Although the calibration data available give no reason to assume that sampling rates need a correction for differences in exposure conditions, the use of PRCs may provide a useful check on the correctness of the proposed calibration model. In addition, the use of PRCs may allow for correcting the results obtained after more calibration data becomes available.

3.10. REFERENCES

Alaee, M.; Whittal, R.M.; Strachan, M.J. 1996, The effect of water temperature and composition on Henry's law constants for various PAH's. *Chemosphere* **32**: 1153–1164.

Asfour, A.-F.; Saleem, M.; De Kee, D. 1989, Diffusion of saturated hydrocarbons in low density polyethylene (LDPE) films. *J. Appl. Polym. Sci.* **38**: 1503–1514.

Bamford, H.A.; Poster, D.L.; Baker, J.E. 1999, Temperature dependence of Henry's law constants of thirteen polycyclic aromatic hydrocarbons between 4 °C and 31 °C. *Environ. Toxicol. Chem.* **18**: 1905–1912.

Bamford, H.A.; Poster, D.L.; Huie, R.E.; Baker, J.E. 2002, Using extrathermodynamic relationships to model the temperature dependence of Henry's law constants of 209 PCB congeners. *Environ. Sci. Technol.* **36**: 4395–4402.

Banerjee, S. and Baughman, G.L. 1991, Bioconcentration factors and lipid solubility. *Environ. Sci. Technol.* **25**: 536–539.

Bartkow, M. 2004, ENTOX, Queensland, Australia. Personal communication.

Berner, R.A. 1980, *Early Diagenisis. A Theoretical Approach.* Princeton University Press: Princeton, NJ.

Bird, R.B.; Stewart, W.E.; Lightfoot, E.N. 1960, *Transport Phenomena.* John Wiley & Sons: New York, NY.

Booij, K.; Sleiderink, H.M.; Smedes, F. 1998, Calibrating the uptake kinetics of semipermeable membrane devices using exposure standards. *Environ. Toxicol. Chem.* **17**: 1236–1245.

Booij, K. and van Drooge, B.L. 2001, Polychlorinated biphenyls and hexachlorobenzene in atmosphere, sea-surface microlayer, and water measured with semi-permeable membrane devices (SPMDs). *Chemosphere* **44:** 91–98.

Booij, K.; Hofmans, H.E.; Fischer, C.V.; van Weerlee, E.M. 2003a, Temperature-dependent uptake rates of nonpolar organic compounds by semipermeable membrane devices and low-density polyethylene membranes. *Environ. Sci. Technol.* **37**: 361–366.

Booij, K.; Hoedemaker, J.R.; Bakker, J.F. 2003b, Dissolved PCBs, PAHs, and HCB in pore waters and overlying waters of contaminated harbor sediments. *Environ. Sci. Technol*. **37**: 4213–4220.

Boudreau, B.P. and Guinasso, N.L. 1982, The influence of a diffusive sublayer on accretion, dissolution, and diagenisis at the sea floor. In *The Dynamic Environment of the Ocean Floor.* Fanning, K.A., Manheim, F.T., Eds.; Lexington Books: Toronto.

Burkhard, L.P. 2000, Estimating dissolved organic carbon partition coefficients for nonionic organic chemicals. *Environ. Sci. Technol.* **34**: 4663–4668.

Chiou, C.T. 1985, Partition coefficients of organic compounds in lipid-water systems and correlations with fish bioconcentration factors. *Environ. Sci. Technol*. **19**: 57–62.

Connell, D.W. 1990, *Bioaccumulation of Xenobiotic Compounds*. CRC Press: Boca Raton, FL.

Cornelissen, G.; Rigterink, H.; Ferdinandy, M.M.A.; Van Noort, P.C.M. 1998, Rapidly desorbing fractions of PAHs in contaminated sediments as a predictor of the extent of bioremediation. *Environ. Sci. Technol.* **32**: 966–970.

Cornelissen, G.; Rigterink, H.; Van Noort, P.C.M.; Govers, H.A.J. 2000, Slowly and very slowly desorbing organic compounds in sediments exhibit Langmuir-type sorption. *Environ. Toxicol. Chem.* **19**: 1532–1539.

Cornelissen, G.; Rigterink, H.; ten Hulscher, D.E.M.; Vrind, B.A.; Van Noort, P.C.M. 2001, A simple Tenax extraction method to determine the availability of sediment-sorbed organic compounds. *Environ. Toxicol. Chem.* **20**: 706–711.

Danckwerts, P.V. 1970, *Gas-Liquid Reactions.* McGraw-Hill: New York, NY.

de Maagd, P.G.J.; ten Hulscher, D.T.E.M.; van den Heuvel, H.; Opperhuizen, A.; Sijm, D.T.H.M. 1998, Physicochemical properties of polycyclic aromatic hydrocarbons: Aqueous solubilities, n-octanol/water partition coefficients, and Henry's law constants. *Environ. Toxicol. Chem.* **17**: 251–257.

Divine, C.E. and McCray, J.E. 2004, Estimation of membrane diffusion coefficients and equilibration times for low-density polyethylene passive diffusion samplers. *Environ. Sci. Technol.* **38**: 1849–1857.

Dobarganes, M.C. and Marquez-Ruiz, G. 1998, Analytical evaluation of fats and oils by size-exclusion chromatography. *Analusis* **26**: M61–65.

Ellis, G.S.; Huckins, J.N.; Rostad, C.E.; Schmitt, C.J.; Petty J.D.; MacCarthy, P. 1995, Evaluation of lipid-containing semipermeable membrane devices (SPMDs) for monitoring organochlorine contaminants in the Upper Mississippi River. *Environ. Toxicol. Chem.* **14**: 1875–1884.

Flynn, G.L. and Yalkowsky, S.H. 1972, Correlation and prediction of mass transport across membranes I: Influence of alkyl chain length on flux-determining properties of barrier and diffusant. *J. Pharm. Sci*. **61**: 838–852.

Gale, R.W. 1998, Three-compartment model for contaminant accumulation by semipermeable membrane devices. *Environ. Sci. Technol.* **32**: 2292–2300.

Gobas, F.A.P.C.; Opperhuizen, A.; Hutzinger, O. 1986, Bioconcentration of hydrophobic chemicals in fish: Relationship with membrane permeation. *Environ. Toxicol. Chem.* **5**: 637–646.

Gustavson, K.E. and Harkin, J.M. 2000; Comparison of sampling techniques and evaluation of semipermeable membrane devices (SPMDs) for monitoring polynuclear aromatic hydrocarbons (PAHs) in groundwater. *Environ. Sci. Technol.* **34**: 4445–4451.

Harner, T. and Mackay, D. 1995, Measurement of octanol-air partition coefficients for chlorobenzenes, PCBs, and DDT. *Environ. Sci. Technol.* **29**: 1599–1606.

Hofmans, H.E. 1998, Numerical Modeling of the Exchange Kinetics of Semipermeable Membrane Devices. MSc Thesis, Netherlands Institute for Sea Research: Den Burg, The Netherlands.

Huckins, J.N.; Manuweera, G.K.; Petty, J.D.; Mackay, D.; Lebo, J.A. 1993, Lipid-containing semipermeable membrane devices for monitoring organic contaminants in water. *Environ. Sci. Technol.* **27**: 2489–2496.

Huckins, J.N.; Petty, J.D.; Orazio, C.E.; Zajicek, J.L.; Gibson, V.L.; Clark, R.C.; Echols, K.R. 1994, Semipermeable Membrane Device (SPMD) Sampling Rates for Trace Organic Contaminants in Air and Water. *Abstract of the 15th Annual meeting of Society of Environmental Toxicology and Chemistry;* Denver, CO.; Abstract MB01.

Huckins, J.N.; Petty, J.D.; Lebo, J.A.; Orazio, C.E.; Prest, H.F.; Tillitt, D.E.; Ellis, G.S.; Johnson, B.T.; Manuweera, G.K. 1996, Semipermeable Membrane Devices (SPMDs) for the Concentration and Assessment of Bioavailable Organic Contaminants in Aquatic Environments. In *Techniques in Aquatic Toxicology*; Ostrander, G.K., Ed.; CRC Press: Boca Raton, FL; pp. 625–655.

Huckins, J.N.; Petty, J.D.; Prest, H.F.; Lebo, J.A.; Orazio, C.E.; Gale, R.W.; Clark, R.C. 1997, Important Considerations in Semipermeable Membrane Devices (SPMDs) Design, Performance, and Data Comparability. Presented at the 18th Annual Meeting of Society of Environmental Toxicology and Chemistry; San Francisco, CA; November 16, 1997; Abstract PTP055.

Huckins, J.N.; Petty, J.D.; Gale, R.W.; Booij, K.; Prest, H.F.; Clark, R.C. 1998, Observations on Declining SPMD Sampling Rates for High Kow Compounds. Presented at the 19th Annual Meeting of Society of Environmental Toxicology and Chemistry; November 15, 2004; Charlotte, NC; Abstract PWA173.

Huckins, J.N.; Petty, J.D.; Orazio, C.E.; Lebo, J.A.; Clark, R.C.; Gibson, V.L.; Gala, W.R.; Echols, K.R. 1999, Determination of uptake kinetics (sampling rates) by lipid-containing semipermeable membrane devices (SPMDs) for polycyclic aromatic hydrocarbons (PAHs) in water. *Environ. Sci. Technol.* **33**: 3918–3923.

Huckins, J.N.; Petty, J.D.; Robertson, G.L.; Clark, R.C.; Cranor, W.L.; Alvarez, D.A.; Gale, R.W. 2001, Calibration of Lipid-containing Semipermeable Membrane Devices (SPMDs) for Vapor-phase Contaminants. Presented at the 22nd Annual Meeting of Society of Environmental Toxicology and Chemistry; Baltimore, MD; November 11, 2001; Abstract PT258.

Huckins, J.N.; Petty, J.D.; Lebo, J.A.; Almeida, F.V.; Booij, K.; Alvarez, D.A.; Cranor, W.L.; Clark, R.C.; Mogensen, B.B. 2002a, Development of the permeability/performance reference compound (PRC) approach for in situ calibration of semipermeable membrane devices (SPMDs). *Environ. Sci. Technol.* **36**: 85–91.

Huckins, J.N.; Petty, J.D.; Prest, H.F.; Clark, R.C.; Alvarez, D.A.; Orazio, C.E.; Lebo, J.A.; Cranor, W.L.; Johnson, B.T. 2002b, *A Guide for the Use of Semipermeable Membrane Devices (SPMDs) as Samplers of Waterborne Hydrophobic Organic Contaminants*; Publication No. 4690; American Petroleum Institute (API): Washington, DC.

Huckins, J.N.; Prest, H.F.; Petty, J.D.; Lebo, J.A.; Hodgins, M.M.; Clark, R.C.; Alvarez, D.A.; Gala, W.R.; Steen, A.; Gale, R.W.; Ingersoll, C.G. 2004, Overview and comparison of lipid-containing semipermeable membrane devices (SPMDs) and oysters (Crassostrea gigas) for assessing chemical exposure. *Environ. Toxicol. Chem.* **23**: 1617–1628.

Landrum, P.F.; Nihart, S.R.; Eadie, B.J.; Gardner, W.S. 1984, Reverse-phase separation method for determining pollutant binding to Aldrich humic acid and dissolved organic carbon of natural waters. *Environ. Sci. Technol.* **18**: 187–192.

Lebo, J.A.; Almeida, F.V.; Cranor, W.L.; Petty, J.D.; Huckins, J.N.; Rastall, A.; Alvarez, D.A.; Mogensen, B.B.; Johnson, B.T. 2004, Purification of triolein for use in semipermeable membrane devices (SPMDs). *Chemosphere* **54**: 1217–1224.

Lefkovitz, L.; Crecelius, E.; McElroy, N. 1996, The use of Polyethylene Alone to Predict Dissolved-phase Organics in the Columbia River. Presented at the 17th annual meeting Society of Environmental Toxicology Chemistry; November 17–21, 1996; Washington, D.C.

Levich, V.G. 1962, *Physicochemical Hydrodynamics.* Prentice Hall, Inc.: Englewood Cliffs, NJ.

Lieb, W.R. and Stein, W.D. 1969, Biological membranes behave as non-porous polymeric sheets with respect to the diffusion of non-electrolytes. *Nature* **224**: 240–243.

Lloyd, D.R. and Meluch, T.B. 1985, Selection and evaluation of membrane materials for liquid separations. In *Materials Science of Synthetic Membranes*; Lloyd, D.R., Ed.; American Chemical Society: Washington, DC.

Lohman, R.; Corrigan, B.P.; Howsam, M.; Jones, K.C.; Ockenden, W.A. 2001, Further developments in the use of semipermeable membrane devices (SPMDs) as passive air samplers for persistent organic pollutants: Field application in a spatial survey of PCDD/Fs and PAHs. *Environ. Sci. Technol.* **35**: 2576–2582.

Luellen, D.A. and Shea, D. 2002, Calibration and field verification of semipermeable membrane devices for measuring polycyclic aromatic hydrocarbons in water. *Environ. Sci. Technol.* **36**: 1791–1797.

Mackay, D.; Shiu, W.Y.; Ma, K.C. 1992a, *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals: Monoaromatic Hydrocarbons, Chlorobenzenes, and PCBs*; Lewis Publishers: Chelsea, MI.; Vol. I.

Mackay, D.; Shiu, W.Y.; Ma, K.C. 1992b, *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals: Polynuclear Aromatic Hydrocarbons, Polychlorinated Dioxins, and Dibenzofurans*; Lewis Publishers: Chelsea, MI.; Vol. II.

Mackay, D. 1994, Unraveling the Choreography of Contaminant Kinetics: Approaches to Quantifying the Uptake of Chemicals by Organisms. In *Bioavailability: Physical, Chemical and Biological Interactions*; Hamelink, J.L., Landrum, P.F., Bergman, H.L., Benson W., Eds.; CRC Press: Boca Raton, FL.; pp. 171–177.

McCarthy, J. 2004, Oak Ridge National Laboratory, Oak Ridge, TN. Personal communication.

Meadows, J.C.; Echols, K.R.; Huckins, J.N.; Borsuk, F.A.; Carline, R.F.; Tillitt, D.E. 1998, Estimation of uptake rate constants for PCB congeners accumulated by semipermeable membrane devices and brown trout (Salmo trutta). *Environ. Sci. Technol.* **32**: 1847–1852.

Moisan, J.Y. 1981, Diffusion des additives du polyethylene-IV. *Eur. Polym. J.* **17**: 857–864.

Möller, K. and Gevert, T. 1994, An FTIR solid-state analysis of the diffusion of hindered phenols in low-density polyethylene (LDPE): the effect of molecular size on the diffusion coefficient. *J. Appl. Polym. Sci.* **51**: 895–903.

Ockenden, W.A.; Prest, H.F.; Thomas, G.O.; Sweetman, A.; Jones, K.C. 1998, Passive air sampling of PCBs: Field calculation of atmospheric sampling rates by triolein-containing semipermeable membrane devices. *Environ. Sci. Technol.* **32**: 1538–1543.

Ockenden, W.A.; Corrigan, B.P.; Howsam, M.; Jones, K.C. 2001, Further developments in the use of semipermeable membrane devices as passive air samplers: Application to PCBs. *Environ. Sci. Technol.* **35**: 4536–4543.

Paasivirta, J.; Sinkkonen, S.; Mikkelson, P.; Rantio, T.; Wania, F. 1999, Estimation of vapor pressures, solubilities and Henry's law constants of selected persistent organic pollutants as functions of temperature. *Chemosphere* **39**: 811–832.

Pauly, S. 1989, Permeability and Diffusion Data. In *Polymer Handbook*, 3rd ed., Brandrup, J. Immergut, E.H., Eds.; Wiley & Sons: New York, NY; Section 6, pp. 435–449.

Petty, J.D.; Huckins, J.N.; Zajicek, J.L. 1993, Application of semipermeable membrane devices (SPMDs) as passive air samplers. *Chemosphere* **27**: 1609–1624.

Prest, H.F.; Jacobson, L.A.; Huckins, J.N. 1995, Passive sampling of water and coastal air via semipermeable membrane devices. *Chemosphere* **30**: 1351–1361.

Rantalainen, A.-L.; Ikonomou, M.G.; Rogers, I.H. 1998, Lipid-containing semipermeable-membrane devices (SPMDs) as concentrators of toxic chemicals in the Lower Fraser River, British Columbia.*Chemosphere* **37**: 1119–1138.

Rantalainen, A.-L.; Cretney, W.; Ikonomou, M.G. 2000, Uptake rates of semipermeable membrane devices (SPMDs) for PCDDs, PCDFs, and PCBs in water and sediment. *Chemosphere* **40**: 147–158.

Reid, R.C.; Prausnitz, J.M.; Poling, B.E. 1987, *The Properties of Gases and Liquids.* 4th Edition;. McGraw-Hill: New York, NY.

Reynolds, G.W.; Hoff, J.T.; Gillham, G.W. 1990, Sampling bias caused by materials used to monitor halocarbons in groundwater. *Environ. Sci. Technol.* **24**: 135–140.

Robertson, G, 2004, U.S. EPA, National Exposure Research Laboratory: Las Vegas, NV; Personal communication.

Sabaliūnas, D. and Södergren, A. 1997, Use of semipermeable membrane devices to monitor pollutants in water and assess their effects: A laboratory test and field verification. *Environ. Pollut.* **96**: 195–205.

Saleem, M.; Asfour, A.A.; De Kee, D. 1989, Diffusion of organic penetrants through low density polyethylene (LDPE) films: Effect of size and shape of the penetrant molecules. *J. Appl. Polym. Sci.* **37**: 617–625.

Sander, R. 2003, Compilation of Henry's Law Constants for inorganic and organic species of potential importance in environmental chemistry (version 3). Max Planck Institute for Chemistry, Mainz, Germany. http://www.mpch-mainz. mpg.de/~sander/res/henry.html (accessed November, 2004)

Shiu, W.Y. and Ma, K.C. 2000, Temperature dependence of physical-chemical properties of selected chemicals of environmental interest. II. Chlorobenzenes, polychlorinated biphenyls, polychlorinated dibenzo-*p*-dioxins, and dibenzofurans. *J. Phys. Chem. Ref. Data* **29**: 387–462.

Shoeib, M. and Harner, T. 2002, Characterization and comparison of three passive air samplers for persistent organic pollutants. *Environ. Sci. Technol.* **36**:4142–4151.

Staudinger, J. and Roberts, P.V. 2001, A critical compilation of Henry's law constant temperature dependence relations for organic compounds in dilute aqueous solutions. *Chemosphere* **44**: 561–576.

ten Hulscher, Th.E.M.; van der Velde, L.E.; Bruggeman, W.A. 1992, Temperature dependence of Henry's Law constants for selected chlorobenzenes, polychlorinated biphenyls, and polycyclic aromatic hydrocarbons. *Environ. Toxicol. Chem.* **11**: 1595–1604.

ten Hulscher, Th.E.M.; Vrind, B.A.; van den Heuvel, H.; van der Velde, L.E.; van Noort, P.C.M.; Beurskens, J.E.M.; Govers, H.A.J. 1999, Triphasic desorption of highly resistant chlorobenzenes, polychlorinated biphenyls, and polycyclic aromatic hydrocarbons in field contaminated sediment. *Environ. Sci. Technol.* **33**: 126–132.

Tucker, W.A. and Nelken, L.H. 1982, Diffusion coefficients in air and water. In *Handbook of Chemical Property Estimation Methods.* Lyman, W.J., Reehl, W.F., Rosenblatt, D.H., Eds.; McGraw-Hill: New York, NY.

US EPA 2003, Estimation Program Interface (EPI) Suite. Version 3.11; U.S. Environmental Protection Agency; http://www.epa.gov/opptintr/exposure/docs/episuite.htm (accessed on November, 2004).

Verweij, F.; Booij, K.; Satumalay, K.; van der Molen, N.; van der Oost, R. 2004, Assessment of bioavailable PAH, PCB, and OCP concentrations in water using semipermeable membrane devices (SPMDs), sediments and caged carp. *Chemosphere* **11**: 1675–1689.

Vrana, B. and Schüürmann, G. 2002, Calibrating the uptake kinetics of semipermeable membrane devices in water: Impact of hydrodynamics. *Environ. Sci. Technol.* **36**: 290–296.

Williamson, K.S.; Petty, J.D.; Huckins, J.N.; Lebo, J.A.; Kaiser, E.M. 2002, Sequestration of priority pollutant PAHs from sediment pore water employing semipermeable membrane devices. *Chemosphere* **49**: 717–729.

Worch, E. 1993, Eine neue gleichung zur berechnung von diffusionskoeffizienten gelöster Stoffe. *Vom Wasser* **81**: 289–297.

Chapter 4

Study Considerations

4.1. OVERVIEW

Before deploying SPMDs, it is important that users are aware of a number of study considerations and quality control (QC) issues. Some of the QC issues apply to environmental sampling in general, whereas some are specifically related to SPMDs and to a few other passive samplers. For example, SPMDs generally have relatively large surface areas (e.g., $\approx$460 cm^2 cm^{-3} of triolein) to enhance uptake rates of solutes or vapor phase chemicals. Thus, special care must be used to prevent contamination of the SPMDs or the loss of target compounds (e.g., through pervaporation or photodegradation) during SPMD assembly, transport, deployment, recovery and storage. Potential pitfalls that specifically relate to SPMD processing, cleanup and analysis are discussed in Chapter 5.

4.2. SOURCES OF SPMDs

The SPMD technology is the subject of two United States Government Patents, (Huckins et al.,1992, 1995a) and a Canadian Patent (Huckins et al., 1996). The United States Department of Commerce granted Environmental Sampling Technologies (EST), 1717 Commercial Drive, St. Joseph, MO, USA exclusive license to manufacture and sell SPMDs in the USA. The license also covers the organic solvent dialysis procedure. At this time, SPMDs are commercially available from EST or Exposmeter AB, Trehörningen 34, 922 66 Taveljö,

Sweden. However, it is important to examine key aspects of the SPMD preparation process and associated QC issues.

4.3. EVALUATION OF COMPONENTS AND PREPARATION OF SPMDs

Careful attention to pre-cleaning all SPMD components is a critical part of ensuring that potential interferences are at acceptably low levels. To that end, the layflat, low-density polyethylene (LDPE) tubing used for SPMDs contains no antioxidants, blockers, slip additives, plasticizers, etc. Prior to use, it is batch extracted with high purity hexane (see Chapter 5). Typical treatment consists of three, 24 hour extractions at about 26 °C with a minimum of 2.2 mL of hexane per cm of tubing (2.5 cm wide). This step removes most of the lower-molecular-weight polyethylene oligomers (the so-called polyethylene waxes which are present in all LDPE) and other potentially interfering (analytically) compounds present in or sorbed by the LDPE. Following this cleanup or preparation process, representative samples of the LDPE membrane are further extracted, as described for SPMDs (see Chapter 5). These extracts are purified using size exclusion chromatography (SEC) to remove residual LDPE oligomers, then evaluated by gas chromatography (GC). Detection of potential interferences is by means of an electron capture detector (ECD), a flame ionization detector (FID) or a mass spectrometer (MS). Examples of these analytical techniques are presented in more detail in Chapter 5. If the analyses of concentrated LDPE extract ($\leq$1 mL) show only negligible levels of analytical interferences, the cleaned tubing is stored at room temperature (refrigerated if long term storage/preservation is planned) in sealed metal cans under an inert atmosphere (usually argon) until use.

Triolein is also examined for potential analytical interferences and contaminant residues before use in SPMDs. Generally, the triolein used for fabrication of SPMDs is purified and its purity subsequently verified by GC or GC-MS methods. This purification process has been described in detail previously (Lebo et al., 2004) and is summarized in Section 5.4.

Because SPMDs have high sampling rates (R_ss) for vapor phase contaminants, all SPMDs are assembled in an environmentally controlled room equipped with an activated carbon air filtration system for the removal of airborne contaminants. SPMDs of almost any length can be prepared after allowance of space for the molecular welds or heat seals (i.e., $\approx$2.5 cm for each end). However, different lengths of SPMDs should maintain the standard surface-area-to-volume ($A\ V^{-1}$) ratio, which is given below. At room temperature, triolein is viscous and can cling to surfaces. This characteristic can cause errors in the volume of triolein delivered by common pipettors. To ensure accurate volumetric delivery, a pipettor equipped with a total displacement plunger is employed to deliver triolein into the LDPE tubing. Afterwards, the triolein is formed into a thin film throughout the length

of the tubing, using a gloved hand (caution: gloves must be powder-free and pre-rinsed to remove surficial contaminants). Care is used to force any air out when forming the triolein film. Then, the open end of the tubing is heat-sealed. To ensure durability of the closure, three to four seals are normally used at each end. Finally, tether loops of LDPE tubing (no triolein) can be welded to both ends of the SPMD membrane to facilitate deployment. The desirability of tether loops is dependent on the method of deployment.

Standardization of SPMDs is essential to permit a more universal comparability of passive sampler data. Toward this goal, a standard SPMD design has been defined (Huckins et al., 2002). Because commercially available SPMDs are modeled after the original USGS design, are of uniform construction, are used globally, and represent the configuration used in most calibration studies, the specifications of these devices are operationally defined as "standard". Depending on study objectives, the use of non-standard SPMDs or other passive samplers may be advantageous. However, we recommend the inclusion of a few standard SPMDs in these studies as well to aid in data comparability.

4.4. SPECIFICATIONS OF THE STANDARD SPMD

The design of commercially available SPMDs consists of a specified length (e.g., 91.4 cm between the inner-LDPE welds for 1 mL of triolein) of additive free, 2.5 cm wide layflat LDPE tubing. The LDPE wall thickness ranges between 70–95 μm and the triolein used is ≥95% purity. Note that in the USA, all commercially available SPMDs are fabricated with ≥99% purity triolein. The $A\ V^{-1}$ ratio is about 90 $cm^2\ cm^{-3}$ (lipid plus membrane), or about 460 $cm^2\ mL^{-1}$ of triolein. The standard SPMD thereby consists of approximately 20% triolein. For the 1 mL triolein configuration, the whole device typically weighs about 4.4 to 4.6 g.

Any length of SPMD with an $A\ V^{-1}$ ratio of about 460 $cm^2\ mL^{-1}$ of ≥95% triolein, having an approximate 0.25 lipid-to-membrane-mass ratio (i.e., 20% lipid) and a 70–95 μm wall thickness is considered a standard SPMD. However, the aforementioned QC certification requirements for the membrane and triolein must be met. Because most SPMD calibration data and field data are based on the standard configuration, the use of non-standard designs for monitoring must be weighed against the lack of data comparability.

4.5. PRE-EXPOSURE CONSIDERATIONS

Although the goals or endpoints of SPMD studies vary widely, a number of questions should at least be considered prior to initiation of exposures. These questions include the following: 1) are there threshold limit values (air) or water quality criteria for chemicals of concern, and if so, has the lowest environmental concentration of concern (C_c) been established for target compounds; 2) will study

sampling protocols provide adequate masses of target compounds for analysis or toxicity assessment at levels of concern; 3) is there any information available on turbulence and flow rates, temperature, biofouling potential, and turbidity at exposure sites; 4) are SPMD calibration data available for target compounds; 5) do target compounds undergo photolysis (i.e., photodegradation), and if so, will deployment devices and site conditions (e.g., light penetration of site water or turbidity, natural shading and albedo or light reflectance of site surfaces) adequately protect SPMD concentrates from photodegradation; 6) will SPMD deployment devices be secure from vandalism or theft at study sites; and 7) will residues accumulated in SPMDs represent linear (integrative), curvilinear or equilibrium uptake kinetics?

Clearly, question 1 is not applicable when the project is a reconnaissance for unknown toxics. In regard to question 2, investigators can sometimes (assuming key parameters such as R_s values are known or can be approximated and that uptake of the chemicals of interest is linear throughout the exposure) use the following simple relationship for guidance.

$$R_s t n\, C_c P_r E_t > \mathrm{MQL}\, V_i \tag{4.1}$$

Where R_s is the sampling rate given as the volume of sampled matrix extracted of analyte per day, t is days of exposure, n is the number of SPMDs per sample, C_c is defined above, P_r is the overall procedural or method recovery (given as a fraction of one; thus 1 is taken as 100% recovery) for the analyte, E_t is the fraction of the total of sample extract injected into the instrument used for analyte quantitation, MQL is the method quantitation limit and V_i is the volume of the standard injected. For example, if $2,2',5,5'$-tetrachlorobiphenyl's aqueous R_s is 6.4 L d^{-1} at 12 °C and <1 cm s^{-1} flow (Meadows et al., 1998) and the C_c is 0.2 ng L^{-1}, then a single 1 mL-triolein SPMD (standard configuration as defined in Section 4.4) exposed to 0.2 ng L^{-1} of aqueous $2,2',5,5'$-tetrachlorobiphenyl would sample about 38 ng over the course of 30 days. Assuming an instrumental MQL of 1 pg μL^{-1}, a V_i of 1 μL, a P_r of 0.8 and an E_t of 0.001, then 31 pg is >1pg and the relationship given above (Eq. 4.1) holds, assuming uptake remained linear. When the R_s of a compound of concern is not available, for this exercise it is acceptable to use the R_s of another chemical with a similar K_{ow}. Although this approach of forecasting sampling and analytical outcomes is useful for planning, it is clearly only a rough estimation because of the many variables involved. In particular, commonly available laboratory-derived R_s values may not reflect actual *in situ* R_s values, which can only be accurately derived when using performance reference compounds (PRCs; see Chapter 3 for details).

Generally, there is little data available on site conditions with the possible exceptions of seasonal average temperatures and river flow rates at USGS gaging stations (question 3). Thus, reconnaissance of study sites is often needed to assess exposure conditions and potential problems. A reconnaissance of study sites is also an important part of assessing the potential for vandalism and theft (question 6)

and the precautions needed. The available sampling rate data related to question 4 can be found in Appendix A.

Unfortunately, question 5 has received little attention in the passive sampling literature, even though the potential for photolysis of certain compounds accumulated in SPMDs and other passive samplers may be high. For example, Kochany and Maguire (1994) have reviewed the literature on the photolysis of polycyclic aromatic hydrocarbons (PAHs) in water. They found that photolysis of most PAHs occur within the 300–400 nm wavelength range (i.e., both UV-A and UV-B wavelengths) and that photoreaction rates are rapid in clear river water and in clear areas of the upper layer of the ocean (i.e., top 35 m). In clear laboratory water, photolysis half-lives of 11 PAHs ranged from 0.13 hour for 9-methylanthracene to 71 hours for naphthalene. In general, it appears that the alkyl-substituted PAHs are more photolabile than unsubstituted PAHs and that smaller PAHs photolyze less rapidly than larger PAHs (Kochany and Maguire, 1994). However, photolysis is markedly attenuated in turbid water, and Lee et al. (1978) found that in outdoor ecosystem enclosures, only the higher molecular weight PAHs were removed primarily by photolysis. Because LDPE does little to quench UV-A and UV-B wavelengths of solar radiation, photolysis of residues in SPMDs has been used as an activation method for the Mutatox assay (Johnson, 2001).

In view of the potential for photolysis of chemicals in clear water and air, Orazio et al. (2002) exposed SPMDs spiked with the 16 priority pollutant PAHs to sunlight in a 1 m deep pond (relatively clear water) and outdoor air. In both cases, SPMDs were deployed in stainless steel canisters (Figure 4.1), designed by Harry Prest (Long Marine Laboratory, Santa Cruz, CA, USA), and naked, i.e., tethered without any protective covering. The canisters were placed so that the longitudinal axis was perpendicular to the sun at noon (i.e., they were mounted horizontally) and in some cases aluminum foil was used to further shield the canisters or SPMDs inside canisters. Exposure periods were as long as one week for these experiments. During these exposures, significant losses (due to volatilization) of naphthalene, acenaphthylene and acenaphthene from SPMDs were expected. Also, Orazio et al. (2002) investigated the effects of brief ($\leq$2 h), direct sunlight exposure on polybrominated diphenyl ethers (PBDEs) in SPMDs.

The major finding of the Orazio et al. (2002) study included the following. PAHs in SPMDs deployed in Prest-type canisters (both with and without additional aluminum foil shielding) for one week in pond water (1 m deep), showed no photolysis. The PAHs in contiguously deployed naked SPMDs were found to have suffered extensive photolysis. Atmospheric exposures appear to be of even greater concern. For example, certain PAHs in SPMDs exposed to direct sunlight were photolyzed after only two minutes. After one week exposure (air) to direct sunlight, PAHs in SPMDs underwent photolysis even with additional foil shielding over the canisters. In a similar manner, a two minute exposure to direct sunlight (air) resulted in photolysis of a number of higher molecular weight PBDEs. These data suggest that the likelihood for photolysis of compounds in SPMDs is much greater in atmospheric exposures than in aqueous exposures. This suggestion is

FIGURE 4.1 A stainless steel deployment device designed by Harrry Prest, Santa Cruz, CA, which has the capacity for four 1 mL triolein SPMDs. The whole apparatus, loaded with SPMDs, fits in a 3.85 L gas tight steel can (Figure 4.2) for transport to and from the field.

in line with the proposed mechanism of PAH photolysis (Kochany and Maguire, 1994), where oxygen may be rate limiting. Oxygen levels are much lower in water than in air (also see discussion on oxygen permeability of LDPE in Section 3.9.2.). Recently, Bartkow et al. (2004) found that photolysis of deuterated-PAHs (i.e., PRCs) occurred after a 32 day exposure of SPMDs to air inside galvanized iron chambers with louvers on all sides and open bottoms. In view of these findings, we recommend the development of atmospheric deployment devices that exclude all light, yet allow for air exchange. Perhaps, the mounting of Prest-type canisters (see Section 4.7. for description) inside chambers similar to the Bartkow et al. (2004) design but with louvered metal bottoms, would result in deployment devices protective of photosensitive compounds. For exposures in clear, fast water, canisters with double walls and offset holes may be required, whereas canisters as described in Section 4.7. can be used in more quiescent-shallow waters if effective shading structures or chambers can be mounted over the deployment devices. Finally, the use of a photosensitive, high K_{ow} deuterated-PAH spiked into SPMDs will serve as an indicator that photolysis of some classes of target compounds has occurred.

The following equations can be used for predicting times that SPMD sampling will represent linear, curvilinear and equilibrium kinetics (question 7), assuming key parameters such as R_s values are known or can be approximated.

$$t_{1/2} = -\ln 0.5 K_{sa/w} V_s / R_s \approx 0.693 K_{oa/w}\, V_s / R_s \quad (4.2)$$

$$t_{95} = -\ln 0.05 K_{sa/w} V_s / R_s \approx 2.99 K_{oa/w}\, V_s / R_s \quad (4.3)$$

Where $t_{1/2}$ and t_{95} are the times to reach 50% and 95% of the equilibrium concentrations, respectively, $K_{sa/w}$ is the equilibrium SPMD-air (a) or SPMD-water (w) partition coefficient, V_s is the volume of the SPMD, and $K_{oa/w}$ and R_s were defined in Chapter 3. Note that Eq. 4.3 is essentially Eq. 1.2. Sampling can be considered as integrative during the linear uptake phase or about one $t_{1/2}$, and exposure concentrations derived from SPMD levels (see Chapter 3) represent time weighted average concentrations. To confirm the assumption of linear uptake necessary for the use of Eq. 4.1 presented earlier, we use Eq. 4.2 and the example of $2, 2', 5, 5'$-tetrachlorobiphenyl. Again, we assume an R_s of 6.4 L d^{-1} for a 1 mL triolein SPMD ($V_s = 5$ cm^3), and from Huckins et al. (1993), we derived a K_{sw} of 1.19×10^5. Using these data, the computed $t_{1/2}$ for 2,2′,5,5′-tetrachlorobiphenyl is 64 d. Thus, the linear uptake assumption for Eq. 4.1 is likely valid as we assumed only a 30 day exposure. This exercise is unnecessary when using the exponential Eq. 3.21.

When exposure time exceeds slightly more than four-$t_{1/2}$s or $\approx t_{95}$ for a chemical, the SPMD is essentially at equilibrium with the ambient environment. Therefore, the time period in between the $t_{1/2}$ and t_{95} values represents the curvilinear region of uptake. Because it is not possible to accurately predict *in situ* SPMD exchange rates (e.g., R_s) *a priori*, this exercise is for planning only and is no substitute for the use of PRCs as discussed in Chapter 3.

4.6. STORAGE, TRANSPORT AND RETRIEVAL

Sample preservation during storage, transport and retrieval must be considered to maintain QC. Prior to field deployment, SPMDs can be stored under argon at $\leq -15\,°C$, in solvent rinsed, gas-tight sealed metal cans (Figure 4.2.). The cans can be purchased or are provided by the commercial supplier of SPMDs. If PRCs (see Chapters 1 and 3) are used in any of the SPMDs, the PRC-containing SPMDs must be kept separate from the others. The canned samplers should be shipped to the field on ice in efficient coolers that are designated only for SPMD transport. Although it may not be completely essential to transport SPMDs without PRCs to the field at low temperatures (the SPMDs are in an inert atmosphere until the seal on the can is broken), it is always preferable to maintain the samplers frozen or at near-freezing temperatures. In particular, SPMDs with PRCs should be maintained at freezing or near-freezing conditions during transport to and from sampling sites to minimize losses of these QC compounds. A variety of coolants can be used for

FIGURE 4.2 For storage and shipping, SPMDs (shown on a deployment apparatus rack) are placed in a clean metal can, flushed with argon, and sealed with a gas tight lid. This figure reproduced courtesy of the American Petroleum Institute (Huckins et al., 2002).

shipping SPMDs, including ice, blue ice, and dry ice. After SPMD deployment, the lids are resealed on the shipping cans and the cans are stored refrigerated until retrieval of the SPMDs.

Following retrieval from the exposure medium, SPMDs are immediately sealed inside the same labeled metal cans and transported (frozen or near frozen) back to the analytical laboratory in a cooler. If it is necessary to delay the shipping of exposed SPMDs more than a few hours, then they must be stored frozen at $\leq -15\ ^\circ C$ in the sealed metal cans. (Caution: failure to maintain exposed SPMDs under freezing conditions can result in significant losses of analytes with relatively high fugacities [e.g., naphthalene]). However, no measurable losses of 2,4,5-trichlorophenol (high fugacity from SPMDs at room temperature) were observed from SPMDs stored at $-15\ ^\circ C$ for 6 months in sealed cans (Huckins, 1995b).

4.7. DEPLOYMENT DEVICES

SPMDs have been successfully deployed in a variety of deployment devices (Ellis et al., 1995; Lebo et al., 1995; Petty et al., 1995). The commercially available

FIGURE 4.3 A commercially available stainless steel deployment canister (see Section 4.7), which has a capacity of five 1-mL triolein SPMDs. Each SPMD is placed on a separate deployment rack and the five deployment racks are held in place by a threaded center pin.

deployment canister (Environmental Sampling Technologies [EST], St Joseph, MO) shown in Figure 4.3, is the most widely used system. This stainless steel canister holds a maximum of five standard SPMDs mounted on individual racks, but the whole apparatus is too large to fit into a 3.85 L gas-tight steel can (Figure 4.2 shows a 3.85 L can with an SPMD mounted on a rack). Although the Prest stainless steel canister (Figure 4.1) only holds four standard SPMDs, the SPMD-loaded canister easily fits into the 3.85 L cans for transport to the field. Thus, using the Prest system has an advantage of minimizing handling and time required to deploy and recover SPMDs at sampling sites.

Regardless of the choice of SPMD deployment structure, certain generic guidelines should be used in its design and construction. These include the following: 1) metal containment structures must be free of cutting oils or other potential interferences, i.e., they must be decontaminated before each use; 2) use of most plastic components should be minimized (Teflon and perhaps some grades of PVC are exceptions), due to the possible presence of leachable organic residues, and in some cases, competitive sorption of analytes by the plastic; 3) the design of

the structure should minimize abrasion of the LDPE membrane, even in turbulent environments, should reduce site-to-site differences in the effective thickness of the SPMD aqueous or air boundary layers (note that container designs that baffle flow can be used to accomplish these goals), and should maintain adequate exchange rates at the membrane surfaces, i.e., sampling should not cause significant or differential depletion of chemical concentrations at the SPMD-exposure media interface; 4) once the SPMDs are mounted in the deployment device, the lipid-containing portion of the layflat tubes should not make contact with container walls, and any SPMD tether loops should not self-adhere thereby reducing the effective surface area (generally, some tension on SPMD tether loops and/or the use of a Möbius configuration [Lebo et al., 1992] prevents this problem); 5) as discussed in Section 4.5., additional shading structures beyond the deployment canisters or double wall canisters may be required to protect photosensitive target compounds (e.g., PAHs and brominated diphenyl ethers) from sunlight; 6) the structure should be adequately tethered to prevent loss during flood events; 7) because vandalism is always a potential problem in the field, the structure should be amenable to hiding; and 8) designs that minimize "silting in" should be used if deployments are at the sediment-water interface.

As suggested earlier, deployment systems that baffle flow-turbulence and protect SPMDs from sunlight are needed for many exposure scenarios. However, any reduction in flow-turbulence at the membrane-exposure medium interface will result in a reduction in SPMD sampling rates for aqueous solutes with log K_{ow}s > 4.5 or for vapors with log K_{oa}s > 8.5, as postulated in Chapter 3. Louch et al. (2003) measured river flow velocity just outside an EST SPMD deployment apparatus and inside the apparatus loaded with SPMDs and found that inside flow was about a 50% less than outside flow. Figure 3.6, suggests that measurements of bulk-media flow are poor predictors of SPMD sampling rates. Thus, we cannot assume that sampling rates are halved but we can assume that they are reduced. Potential reductions in SPMD sampling rates due to container baffling effects and biofouling should be considered when estimating the number of SPMDs required per sample to achieve satisfactory quantitation limits for a project. Studies have shown that *C.V.*s of hydrophobic contaminant concentrations in replicate SPMDs deployed inside the canisters shown in Figures 4.1 and 4.3 are generally <25% (Huckins, 1998; Louch et al., 2003). Consequently, it seems unlikely that some SPMDs in a canister would experience reduced uptake relative to others.

4.7.1. Precautions and Procedures During Deployments

Because SPMDs sequester a wide variety of organic solutes or vapors of hydrophobic chemicals, care must be used to prevent inadvertent contamination of the devices. Of particular concern for SPMDs destined to be used for environmental sampling is the fact that SPMDs clear large volumes of vapor phase chemicals from air. For example, under low flow conditions (<5 cm s^{-1}) at about 22 °C the R_s

or SPMD sampling rate (1 mL standard device) of vapor phase phenanthrene is 4.3 m^3 d^{-1}, which is about the same rate as that observed for dissolved phase phenanthrene (i.e., 3.6 L d^{-1} at <1 cm s^{-1} flow and 18 °C), after the differences in the density of air and water are taken into account (note that we are not inferring that density adjustments alone can account for volumetric differences in R_s values for air and water). An atmospheric sampling rate of 4.3 m^3 d^{-1} is equivalent to about 3 L min^{-1} (many other vapors are sampled at an even higher rates) of air cleared of vapor. Clearly, SPMD air exposure must be minimized to prevent sample contamination.

Although SPMDs do require special considerations, proper handling of SPMDs generally consists of logical precautions, which can be learned without special training and are related to good laboratory practices. SPMDs are used in a wide variety of environmental systems, ranging from wetlands and lakes to more energetic systems such as rivers, estuaries and ocean environments, as well as a wide range of atmospheric exposure conditions. However, the following practices and considerations apply to all deployments. 1) Before deployment and prior to retrieval, inspect study sites for nearby sources of vapor-phase contaminants, including fumes from engines, oils, tars, gasoline, diesel fuel, paints, solvents, cigarette smoke (i.e., no smoking during deployments and retrievals), asphalt pavement, etc. Record any findings of potential sources of contamination for each site. 2) Atmospheric exposure time during aqueous deployment and retrieval should be minimized, because when the SPMD is exposed to site air, sampling begins immediately. Atmospheric levels of some target compounds may be higher than their concentrations in aquatic systems to be sampled. Also remember that during SPMD recovery, photolysis of some compounds may be rapid. 3) Ensure that cans with SPMD field blanks (the field blank SPMDs provide a record of any chemical accumulated in SPMDs during transport, deployment and retrieval; see Chapter 5 for detailed definitions of QC samples and their suggested use) are open to the air while sample SPMDs are being deployed and retrieved. 4) If waterborne chemicals are visible as surface layers of oils, tars, gasoline, etc., or a biofilm is visible on the surface of the water, where target compounds are potentially elevated (i.e., relative to the water column), precautions may be needed to reduce contamination during placement of the deployment devices into the aquatic system. 5) Hand lotions, perfumes, colognes, powdered gloves (use powder-free gloves), etc, should not be used when handling samplers or deployment devices as they may contain chemicals accumulated by the SPMDs (Petty et al., 2000). 6) The procedure for retrieval of the SPMDs is essentially the reverse of the deployment sequence and the same precautions apply. 7) Following retrieval, immediately place the SPMDs back into the original metal cans, as provided by the supplier, and seal the lids on the cans (Caution: if the lid is not completely sealed on the can, contamination of SPMDs from airborne chemicals during transport back to the analytical laboratory is highly probable). 8) Finally, place the cans containing the SPMDs into a cooler and maintain frozen pending and during shipment to the processing laboratory.

The procedures given above are designed to prevent any contamination of SPMDs, to minimize losses of PRCs and accumulated analytes, and to reduce the possibility of analyte photolysis. These precautionary steps are particularly important when target compounds are at ultra-trace levels, as it may be difficult to delineate handling, storage and shipping-related contamination from analytes concentrated during the exposure.

Because environmental variables affect the uptake of target analytes, regardless of analyte types or sampling approach (i.e., kinetic or equilibrium), a record should be kept on site conditions during exposures. Relevant data include temperature (a minimum of the beginning and end of the deployment), the visual extent of fouling (i.e., light, medium, heavy, none), and an estimation of turbulence-flow rates (i.e., cm s^{-1}) for water deployments. This type of data is helpful even when PRCs are used, because it provides supporting information on the possible causes of significant differences between calibration R_Ss and *in situ* R_Ss and the differences of *in situ* R_Ss among sites. As with any research project, notes should be taken describing the site location and characteristics not discussed above and events occurring during deployment and retrieval that may affect data quality. This information may prove invaluable if QC-related questions arise during sample processing and analytical procedures, and will often be helpful in conducting site assessments.

Successful applications of the SPMD technology under a wide variety of field conditions have been demonstrated by a number of researchers (see Appendix B or CERC, 2004). The common threads among successful applications of SPMDs are a basic understanding of potential sources of sample contamination and losses, the functional aspects of the SPMD technique, and the adherence to sound sampling approaches and good laboratory practices.

4.8. REFERENCES

Bartkow, M.E.; Huckins, J.N.; Müller, J.F. 2004, Field-based evaluation of semipermeable membrane devices (SPMDs) as passive air samplers of polyaromatic hydrocarbons (PAHs). *Atmos. Environ.* **38**: 5983–5900.

CERC 2004, SPMD Home Page. USGS Columbia Environmental Research Center: Columbia, MO; http://wwwaux.cerc.cr. usgs.gov/SPMD/index.htm.; (accessed December, 2004).

Ellis, G.S.; Huckins, J.N.; Rostad, C.E.; Schmitt, C.J.; Petty J.D.; MacCarthy, P. 1995, Evaluation of lipid-containing semipermeable membrane devices (SPMDs) for monitoring organochlorine contaminants in the Upper Mississippi River. *Environ. Toxicol. Chem.* **14**: 1875–1884.

Huckins, J.N.; Lebo, J.A.; Tubergen, M.W.; Manuweera, G.K.; Gibson, V.L.; Petty, J.D. 1992, Binary Concentration and Recovery Process. U. S. Patent 5,098,573, March 24, 1992.

Huckins, J.N.; Manuweera, G.K.; Petty, J.D.; Mackay, D.; Lebo, J.A. 1993, Lipid-containing semipermeable membrane devices for monitoring organic contaminants in water. *Environ. Sci. Technol.* **27**: 2489–2496.

Huckins, J.N.; Petty, J.D.; Zajicek, J.L.; Gibson, V.L. 1995a, Device for the Removal and Concentration of Organic Compounds from the Atmosphere. U. S. Patent 5,395,426, March 7, 1995.

Huckins, J.N. 1995b, Stability and residence times of chemicals in frozen SPMDs. USGS Columbia Environmental Research Center: Columbia, MO; Unpublished work.

Huckins, J.N.; Lebo, J.A.; Tubergen, M.W.; Manuweera, G.K.; Gibson, V.L.; Petty, J.D. 1996, Binary Concentration and Recovery Process. Canadian Patent 2,037,320, December 17, 1996.

Huckins, J.N. 1998, Effect of deployment devices on performance reference compounds (PRCs) loss. USGS Columbia Environmental Research Center: Columbia, MO; Unpublished work.

Huckins, J.N.; Petty, J.D.; Prest, H.F.; Clark, R.C.; Alvarez, D.A.; Orazio, C.E.; Lebo, J.A.; Cranor, W.L.; Johnson, B.T. 2002, *A Guide for the Use of Semipermeable Membrane Devices (SPMDs) as Samplers of Waterborne Hydrophobic Organic Contaminants*; Publication No. 4690; American Petroleum Institute (API): Washington, DC.

Johnson, B.T. 2001, USGS Columbia Environmental Research Center: Columbia, MO. Personal communication.

Kochany, J.; Maguire, R.J. 1994, Abiotic transformations of polynuclear aromatic hydrocarbons and polynuclear aromatic nitrogen hetrocycles in aquatic environments. *Sci. Total Environ*. **144**: 17–31.

Lebo, J.A.; Zajicek, J.L.; Huckins, J.N.; Petty, J.D.; Peterman, P.H. 1992, Use of semipermeable membrane devices for in situ monitoring of polycyclic aromatic hydrocarbons in aquatic environments. *Chemosphere* **25**: 697–718.

Lebo, J.A.; Gale, R.W.; Petty, J.D.; Tillitt, D.E.; Huckins, J.N.; Meadows, J.C.; Orazio, C.E.; Echols, K.R.; Schroeder, D.J.; Inmon, L.E. 1995, Use of the semipermeable membrane device (SPMD) as an in situ sampler of waterborne bioavailable PCDD and PCDF residues at sub-part-per-quadrillion concentrations. *Environ. Sci. Technol.* **29**: 2886–2892.

Lebo, J.A.; Almeida, F.V.; Cranor, W.L.; Petty, J.D.; Huckins, J.N.; Rastall, A.; Alvarez, D.A.; Mogensen, B.B.; Johnson, B.T. 2004, Purification of triolein for use in semipermeable membrane devices (SPMDs). *Chemosphere* **54**: 1217–1224.

Lee, R.F.; Gardner, W.D.; Anderson, J.W.; Blaylock, J.W.; Bardwell-Clarke, J. 1978, Fate of polycyclic aromatic hydrocarbons in controlled ecosystem enclosures. *Environ. Sci. Technol.* **12**: 832–838.

Louch, J.; Allen, G.; Erickson, C.; Wilson, G.; Schmedding, D. 2003, Interpreting results from field deployments of semipermeable membrane devices. *Environ. Sci. Technol.* **37**: 1202–1207.

Meadows, J.C.; Echols, K.R.; Huckins, J.N.; Borsuk, F.A.; Carline, R.F.; Tillitt, D.E. 1998, Estimation of uptake rate constants for PCB congeners accumulated by semipermeable membrane devices and brown trout (Salmo trutta). *Environ. Sci. Technol.* **32**: 1847–1852.

Orazio, C.E.; Haynes, S.A.; Lebo, J.A.; Meadows, J.C.; Huckins, J.N.; Petty, J.D. 2002, Potential for Photodegradation of Contaminants During SPMD Sampling. Presented at the 23rd Annual National Meeting of the Society of Environmental Toxicology and Chemistry; November 16–20, 2002; Salt Lake City; UT; Abstract P192.

Petty, J.D.; Huckins, J.N.; Orazio, C.E, Lebo, J.A.; Poulton, B.C.; Gale, R.W.; Charbonneau, C.S.; Kaiser, E.M. 1995, Determination of bioavailable organochlorine pesticide residues in the Lower Missouri River. *Environ. Sci. Technol.* **29**: 2561–2566.

Petty, J.D.; Gale, R.W.; Huckins, J.N.; Cranor, W.L.; Alvarez, D.A.; Clark, R.C. 2000, *Development and Application of Techniques for Sampling Bioavailable Airborne Contaminants-Tentatively Identified Compounds by Gas Chromatography/Mass Spectrometry*. USGS Columbia Environmental Research Center: Columbia, MO; Unpublished report to U.S. EPA National Exposure Assessment Laboratory: Las Vegas, NV.

Chapter 5

Analytical Chemistry Related to SPMDs

5.1. ANALYTICAL SPEED, SELECTIVITY AND QUANTITATION LIMITS

Based on the results from more than 50 interlaboratory comparisons, Horwitz et al. (1980) showed that, as target compound concentrations in complex matrices decrease, the relative standard deviation or coefficient of variation (*C.V.*) of analytical results increases exponentially. There are a number of potential causes for this problem, but at very low environmental concentrations, method selectivity (i.e., the ability to distinguish the analyte from interferences) is a major factor. Because passive samplers such as the SPMD accumulate a broad range of nonpolar chemicals (including complex mixtures of anthropogenic and biogenic compounds characteristic of the site and sample matrix), sampling must be considered non-selective. Fortunately, passive samplers with nonpolar sequestration phases concentrate potential interferences with low octanol-water partition coefficients (K_{ow}s) less than the nonpolar target compounds. However, this enrichment effect is offset when trace ($<1\ \mu g\ L^{-1}$) or ultra trace ($<1\ ng\ L^{-1}$) detection or quantitation limits are required due to the much higher concentrations of potential interferences (relative to analyte concentrations).

Two approaches are generally used to develop methods with lower detection and quantitation limits for target compounds. One approach involves the use of sample cleanup methods such as size exclusion chromatography (SEC) for the

selective removal of interferences and various fractionation techniques to obtain class separations prior to analysis. The other involves the use of instrumentation capable of high analyte selectivity such as a gas chromatograph (GC) or a liquid chromatograph (LC) interfaced with a mass spectrometer (MS; especially high resolution MS and MS-MS systems). In the first case, the use of multiple cleanup steps must be balanced by the potential for analyte losses during each step and the associated propagation of errors or measurement uncertainty. However, use of good laboratory practices and performance-based methods for multi-step cleanup procedures have increased analyte recoveries and analytical precision, and reduced detection and quantitation limits.

Advancements have also been made in the use of analytical instrumentation for both sample cleanup and quantitation at trace levels. However, a number of problems still remain. For example, matrix effects or interfering compounds can cause ionization-suppression or ionization enhancement (Jones-Lepp, 2004; Meyer, 2004) using MS and poor chromatographic resolution with co-eluting compounds and shifting retention times. These factors combine to reduce the sensitivity of the analysis and the certainty of compound identification. Some progress is being made with innovations such as the ChromatoProbe device for dirty sample injection (Maštovská and Lehotay, 2003), but for extracts with complex mixtures of compounds, it is doubtful that the need for class fractionation can be avoided.

To reduce costs of sample analyses, efforts are often directed toward increasing analytical speed (e.g., Maštovská and Lehotay, 2003). Generally, several trade-offs result from increased speed of analysis, which can be illustrated as follows:

Solid-phase microextraction (SPME) fibers provide a good example of a passive method that can be used for rapid analysis of water samples. After turbulent sample extraction (<1 hr), the fibers can be directly introduced (i.e., the entire sample is analyzed) into a fast GC system (Gorecki and Pawliszyn, 1997). Depending on the analytical instrument used, SPME method quantitation limits (MQL) may approach pg levels. For a particular compound and instrument, this limitation stems from the sorbent-phase volume (<1 μL for most SPMEs), the partition coefficient of the analyte, and the relative concentration and partition coefficient of interferences present in a sample. To obtain lower quantitation limits with passive samplers, the sorbent phase volume must be increased and some sample cleanup is required. From Table 1.1, a 1 mL triolein SPMD has about 5×10^3 times greater sorbent phase volume than an SPME, and during the same time interval, the volume of water or air extracted by the SPMD is hundreds of times greater than the SPME. The large volume of sample matrix extracted allows pg L^{-1} detection and quantitation limits when coupled with selective cleanup and fractionation

procedures. Using composite samples of SPMDs (n = 9 SPMDs per sample) and rigorous cleanup and fractionation, McCarthy and Gale (2001) have quantified the homologous- tetrachlorodibenzo-*p*-dioxins and tetrachlorodibenzofurans in river water at $<$pg L^{-1}.

Procedures used for the analysis of SPMD samples are similar to those typically utilized for the determination of organic contaminant concentrations in environmental matrices such as aquatic organisms. However, extracts from aquatic organisms can vary widely in the quantities and compositions of lipids and other co-extracted biogenic materials, while SPMD extracts (i.e., dialysates) are more uniform, well characterized, and generally contain significantly less lipid. Thus, sample processing procedures and methods for the analysis of SPMD samples are generally more amenable to standardization than those used for aquatic organism tissues, and in some cases, require fewer labor-intensive steps.

Contaminants accumulated by SPMDs include a broad array of waterborne and airborne organic chemicals and comprise most of the bioconcentratable organic chemicals of concern to environmental scientists. In fact, nearly any nonpolar organic chemical with a molecular cross sectional diameter no greater than about 10 Å will be accumulated by the SPMD, given appropriate exposure conditions. Consequently, the SPMD approach provides a convenient means for assessing complex mixtures of organic chemicals present in air, water, sediments and soil. Because of the non-specificity of nonpolar contaminants accumulated by SPMDs, the physicochemical properties of individual compounds (i.e., those relevant to chromatographic separations and instrumental analysis) in extracts containing complex mixtures may overlap. Furthermore, analyte levels for some chemicals may be close to quantitation limits, even though a single 1 mL triolein SPMD may extract $>$100 L of water or 100 m^3 of air during a 30 d exposure. Simply put, these sample characteristics necessitate the use of analytical methods that are performance-based and specific for the analytes of interest. Sample analyses based on dilute-and-shoot or extraction and instrumental desorption generally do not provide satisfactory results.

The use of sophisticated instrumental systems such as high-resolution GC-MS does not guarantee satisfactory quantitation of the hundreds of chemicals sometimes present in SPMDs without some fractionation of sample residues. Thus, the complexity of target residues, as well as interferences from the matrix sampled can be determinants in the cleanup and separation procedures needed for satisfactory analyses. The following discussion presents the salient features of the typical processing and analytical procedures applied to SPMD samples.

5.2. QUALITY CONTROL

The application of appropriate Quality Control (QC) procedures or criteria is a mandatory consideration in the deployment and analysis of SPMDs (e.g., Petty et al., 2000a). Similar to any performance-based methodology or approach,

QC samples must address specific issues of analyte recovery, background in SPMD components, and any contamination incurred during transport, deployment, retrieval, storage, processing, enrichment, and fractionation operations. The exact level of QC required should be determined during the development of a project's experimental design. In general, QC samples represent 20–50% of a "sample set". We operationally define a laboratory sample set as a group of samples (includes both exposed SPMDs and QC samples from the same study) that are processed and analyzed together. The number of samples in a set generally ranges from 6 to 30. The upper size limit of a sample set is often constrained by non-automated analytical procedures (e.g., chromatographic cleanup and fractionation), where the analyst must monitor the performance of one or more steps.

For projects needing stringent QC, control charts are recommended to monitor analyte recoveries throughout an investigation (see Taylor, 1987, for a detailed discussion). Briefly, during each quarter of a project, the last 20 observations of recoveries from QC spikes are used to generate a control chart. Control limits are established for the analytical process as described by Taylor (1987). When control limits are exceeded, sample analyses are suspended until the problem step(s) can be identified and corrected. These actions must follow an appropriate protocol for corrective action. The results of this type of investigation or procedure modification become a part of the permanent record of the sample set and the project.

Herein, we describe the basic QC samples and parameters related to the performance of SPMD studies, and elucidate their role in conducting studies. Also, a general overview of SPMD analytical procedures and data applicability are given.

5.2.1. SPMD-Fabrication Blanks

This type of QC blank consists of a batch or subset of individual SPMDs of the same size and material as those prepared for a specific project. After preparation, SPMD-fabrication blanks are maintained frozen in vapor-tight metal cans under argon at −10 to −20 °C in the laboratory until the analysis of the project SPMDs. Processing and analysis of these blanks is concurrent with and identical to that of environmentally exposed SPMDs. The primary purpose of this type of QC sample is to account for any background contribution due to interferences from SPMD components, and for contamination incurred during laboratory storage, processing, and analytical procedures.

5.2.2. SPMD-Process Blanks

This type of QC blank consists of a subset of SPMDs, made just prior to initiation of the analysis of an SPMD sample set. Operationally, the only difference between SPMD-process blanks and SPMD-fabrication blanks is the time of preparation and that the SPMD-process blanks are not subjected to storage, but are immediately processed and analyzed along with the environmentally exposed

SPMDs. Use of this type of blank is generally limited to laboratories that assemble SPMDs. If the numbers of SPMD-fabrication blanks are inadequate, SPMD-process blanks can be used to determine analyte recovery and the precision of the overall analytical method. Also, this type of QC sample can be used for other purposes, such as determining potential effects of storage or changes in batches or lots of SPMD materials.

5.2.3. Reagent Blanks

These blanks consist of portions of all solvents (volumes identical to those used for SPMD samples) used during the processing, enrichment, and instrumental analysis of an SPMD sample, that are carried along with SPMD samples through the entire analytical procedure. This type of QC sample (at least one for each sample set) provides information on background due to laboratory reagents and procedures. The use of reagent blanks is strongly recommended, because they greatly facilitate diagnosis of any interference problems encountered during SPMD analysis.

5.2.4. Field/Trip-Blank SPMDs

These blanks are a subset of the SPMDs (at least one per sampling site) prepared for a specific field study and are identical to those that will be deployed. Field-blank SPMDs are used to account for contamination during transport (both to and from study sites) and during deployment and retrieval of exposed SPMDs. Field-blank SPMDs can also be spiked with performance reference compounds (PRCs) to provide the "day 0" concentration of the PRC (see Chapter 3) used in the assessment of the effects of environmental conditions on analyte sampling rates (i.e., derivation of an exposure adjustment factor) which facilitates *in situ* calibration (Booij et al., 1998). These blanks are treated the same as deployed devices, with the exception that they are not exposed to the matrix of interest at the study sites and are stored frozen during the exposure period. In the case of air sampling, these QC samples are the trip blank SPMDs, i.e., these blanks accompany the deployment SPMDs during transport to and from the deployment site, but unlike aqueous exposures, the container is not opened during deployment and retrieval.

As suggested earlier, field-blank SPMDs are taken to the field in sealed metal cans and one or more cans are opened to the atmosphere at each site (note that field-blank SPMDs are typically left inside the open cans) during both deployment and retrieval of SPMDs from aquatic systems. The time periods that field-blank SPMDs are exposed to site air should be the same as that required to deploy and retrieve SPMDs. Afterwards, the cans with the field-blank SPMDs are resealed and shipped to the analytical laboratory along with the deployed SPMDs. Non-spiked (i.e., no PRCs) field-blank SPMDs and PRC-containing field-blank SPMDs are processed and analyzed exactly as are deployed SPMDs. However,

when perdeuterated polycyclic aromatic hydrocarbons (PAHs) are used as PRCs, then GC-MS, or GC-FID must be used for separation and quantitation of native PAHs and their perdeuterated counterparts.

5.2.5. PRC Samples

When environmental conditions at an exposure site differ from those used for laboratory calibrations or when calibration data for an analyte are not available, at least one SPMD per site is spiked with PRCs. The type of compounds used for PRCs and their spiking levels were discussed earlier. PRC samples and standard SPMD samples (i.e., field-deployed SPMDs) differ only by the presence of the PRCs. Handling, processing and analysis are also identical. As implied above, the purpose of the PRC sample is to provide data for estimation of *in situ* sampling rates of target compounds.

5.2.6. SPMD Spikes

Spiked SPMDs (at least one per sample set) are used to determine the recoveries of target compounds and to establish "control limits" for the analytical process. The *C.V.* for each analyte is used to set control limits for that compound. SPMD-fabrication or -process blanks are used for this type of QC sample. Sample processing and analysis of SPMD spikes is exactly the same as for deployed samples. The triolein of individual SPMD blanks is directly fortified with target compound mixtures. The amounts of target compounds used for SPMD spikes (note that the carrier solvent volume should not exceed 10% of the lipid volume) vary but are based on achieving an instrumental response that is near the midpoint of the appropriate calibration curves. For example, 2 μg of each priority pollutant PAH is generally spiked into 1 mL of triolein in a standard SPMD. Assuming a 75% recovery, the concentration of each priority pollutant PAH will be 1.5 μg mL^{-1} (final sample volume of 1 mL), and upon analysis with a GC-Mass Specific Detector (MSD), the instrumental response will fall near the midpoint of the PAH calibration curve. In the case of organochlorine pesticides (OCPs), 40 ng of each compound is generally spiked, and based on the same assumptions given above, the concentration of each OCP will be 30 ng mL^{-1}, at a final volume of 1 mL. As in the example above, the GC-electron capture detector (ECD) response will fall at about the midpoint of the OCP calibration curve.

5.2.7. Procedural Spikes

These type of spikes are used when a rapid and independent assessment of individual steps in sample processing and enrichment is desired. The spikes used are radiolabeled (^{14}C- or ^{3}H- labeled) compounds, which typically consist of a high molecular weight PAH or a chlorinated compound. For assessment of the dialytic step of overall analyte recovery from SPMDs a procedural blank is spiked directly

with the radiolabeled compound(s). For assessment of additional processing steps, the radiolabeled compound is injected into an appropriate solvent which is treated the same as sample extracts at the same point in the processing sequence. The fortification levels used for these spikes are about the same as described earlier for the SPMD spikes. These QC samples are used as a troubleshooting aid to rapidly identify abnormalities in specific steps that might contribute to low recoveries of analytes from SPMD spikes. Also, procedural spikes are used to develop control charts and are an integral part of any corrective action assessment.

5.2.8. Expected QC Results

Based on the examination of analytical data from polychlorinated biphenyls (PCBs), OCPs and PAHs spiked into SPMDs, which have subsequently been subjected to the entire SPMD analytical procedure described herein, recoveries are generally $>75\%$ with good precision (i.e., *C.V.*s $\leq \pm 20\%$). Surprisingly, the *C.V.*s for the analysis of contaminants present in replicate SPMDs deployed contiguously at the same sites and treated identically during analysis are often equivalent to *C.V.*s of SPMD spikes. This observation suggests that the variability of analyte sampling rates of replicate SPMDs in the field is small and that the analytical methods used for field-deployed SPMDs are robust.

DeVita and Crunkilton (1998) have examined QC associated with the use of SPMDs. The results of their study demonstrated that quality control measures applied to SPMD analysis met or surpassed conventional guidelines (EPA Method 610 for PAHs in water was used for this comparison) for precision and accuracy. This elevated level of data quality was achieved even though measurements of both overall precision and accuracy of SPMD data encompassed more steps (each with the potential for variability) than the conventional method. In summary, DeVita and Crunkilton (1998) found that QC measures could be used to validate data from the analysis of SPMDs used in the field. In view of the state of SPMD QC, it appears that the SPMD approach for monitoring hydrophobic organic contaminants is equivalent to some EPA-approved methods.

5.3. SAMPLE PREPARATION

The processing, enrichment, and fractionation of SPMDs for instrumental analysis of residues have been described in a number of publications (Ellis et al., 1995; Lebo et al., 1995; Petty et al., 1995, 1998a, 1998b, 2000a; Huckins et al., 1996; Bergqvist et al., 1998a). Preparation of SPMD samples for residue analysis generally involves the following steps: 1) removal of exterior surficial periphyton and debris; 2) organic solvent dialysis (OSD); 3) size exclusion chromatography; and 4) class-specific fractionation using chromatographic techniques. All solvents used in these procedures are of high purity (e.g., chromatography grade, spectroscopy grade, etc.). Although Figure 5.1 illustrates an approach commonly used

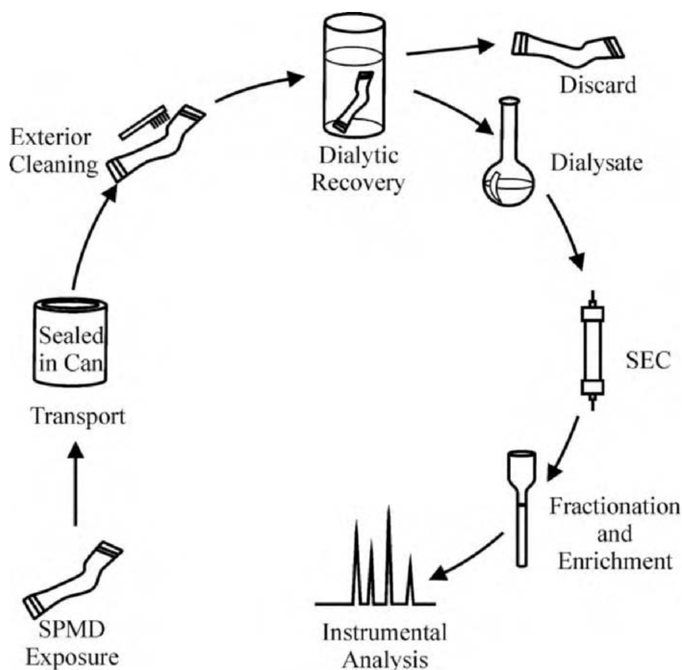

Figure 5.1 Key aspects of the SPMD sampling and residue analysis process. Often class fractionation is required following SEC when extracts contain complex mixtures of chemicals. Reprinted with permission from the American Petroleum Institute (Huckins et al., 2002).

for analytical chemistry of SPMDs, the specific sequence of cleanup and fractionation steps needed for a particular project depends on the goals of the project. These goals dictate the methods used for sample analysis (e.g., residue analysis of complex mixtures of contaminants or bioassay) and the required analytical detection and quantitation limits or assay sensitivity. Furthermore matrix effects or interferences related to the medium sampled and the sampler components, and the selectivity of the instrument or bioassay used must be taken into consideration. Herein, the focus is on the analytical chemistry of SPMDs but some of the same methods are used for bioassays as well.

5.3.1. Cleaning Exposed SPMDs

Before dialytic recovery of concentrated analytes, any periphyton or biofilm, carbonate salts, etc., on the SPMD membrane are removed by the following sequence of steps. First, each individual SPMD is immersed in about 200 mL of hexane in a glass beaker for about 20 to 30 seconds. Afterwards, the hexane is discarded. Then, SPMDs are placed in a stainless steel pan and washed with copious amounts of running water (tap water is generally used but a 1 L sample should

be analyzed for any potential interferences prior to use), while being scrubbed vigorously with a clean toothbrush. At this point the SPMDs are examined for small holes in the membrane. If a hole is found, and other replicate SPMDs are not available, the hole is isolated by heat-sealing. After the integrity of each SPMD has been ensured, they are submerged in a tank of 1M HCl for approximately 30 s to remove any adhering mineral salts. Following the HCl treatment, the SPMDs are again rinsed with running water to remove the acid. All water on the membrane surfaces is removed by brief rinses of high purity acetone, followed by high purity isopropyl alcohol. After cleaning, SPMDs are allowed to air dry for a minimal time period (typically <6 min.) on a piece of solvent-rinsed aluminum foil.

5.3.2. Extraction and Cleanup of SPMDs

Because of the very low levels of interferences observed in SPMDs (Lebo et al., 1995), individual devices can be combined to create a composite sample. This allows for lower detection and quantitation limits and provides increased contaminant mass for use in bioassays or other endpoints. Analytes are recovered from intact SPMDs by OSD (Huckins et al., 1990, 1993; Petty et al., 2000a) in glass jars fitted with solvent-rinsed aluminum foil under screw-type lids. Interestingly, this dialytic technique is also used for the cleanup of extracts from other environmental samples and is the subject of several journal articles (Meadows et al., 1993; Bergqvist et al., 1998b; Strandberg et al., 1998). A minimum of 180 mL of high purity hexane per standard 91.4 cm SPMD per dialytic treatment is used. SPMDs are dialyzed individually. The procedure consists of 18 hours (h) of OSD, followed by 4 to 6 h of OSD with fresh solvent (total of 360 mL of hexane). Dialytic separations are performed at a constant temperature of 18 °C, because this sub-ambient temperature has been shown to minimize the amount of co-dialyzed lipid components and low density polyethylene (LDPE) waxes, while maintaining good-to-excellent recoveries of analytes. (Note that this standardized extraction method contrasts with the wide variety of solvents and solvent mixtures used for the extraction of biomonitoring organism [BMO] tissues. Randall et al. [1991] have shown that extracted lipids vary by about four-fold depending on the extracting solvent used.) The two dialysates for each sample are combined and quantitatively transferred to round bottom flasks. The volumes of the dialysates are reduced to approximately 5 mL using rotary evaporation, quantitatively transferred to test tubes by filtration through a pre-rinsed glass fiber filter, and the volumes subsequently reduced to approximately 1 mL. At this point, carryover of lipids and LDPE waxes for a standard 1 mL triolein ($\geq$95% purity) SPMD should be <30 mg. When using SPMDs with triolein purified by the Lebo et al. (2004) method, SPMD dialysates generally can be used for bioassay-biomarker tests without additional cleanup (see Chapter 6).

The following chromatographic techniques are representative of those used by a number of investigators for the further enrichment and fractionation of analytes. The concentrated dialysate is subjected to SEC to remove co-dialyzed lipid

materials and LDPE waxes. A typical SEC system consists of a high performance liquid chromatograph, equipped with an autosampler, a fraction collector, a UV detector operated at 254 nm and a 300 mm × 21.2 mm i.d. Phenogel column (10 μm particle size, 10 nm pore size). The SEC column is from Phenomenex, Torrance, CA, USA. Equivalent components and columns can be used for the SEC treatment. The mobile phase consists of 2% methanol in 98% dichloromethane. The SEC procedure results in the elimination (discarding) of nearly all lipid materials, LDPE oligomers, and elemental sulfur. The chromatography system must be calibrated on a daily basis. For example, this can be accomplished by injecting a solution containing di-2-ethylhexylphthalate (DEHP), biphenyl, naphthalene, coronene, and elemental sulfur. These compounds elute in the order listed. Following calibration of the SEC system, the fraction collector is adjusted such that two fractions, "dump" and "collect" are produced for each injection. The "dump" fraction begins upon sample injection and stops upon initiation of the "collect" fraction. The "collect" fraction is initiated between the apex of the DEHP peak and the biphenyl peak. The "collect" fraction is terminated at 70% of the time between the apex of the coronene chromatographic peak and the apex of the sulfur chromatographic peak. This SEC procedure removes elemental sulfur (often found in aqueous deployed SPMDs) from the SPMD sample extracts.

Not all laboratories use SEC for the cleanup of SPMD dialysates. For example, Booij et al. (2003) used a 0.6 cm i.d. column containing 2 g of silica gel 60 (deactivated with 6% water [wt/wt]) obtained from Merck, Whitehouse Station, NJ, USA; to purify dialysates from 1 mL triolein SPMDs. The concentrated dialysates were applied to the silica gel columns, and PAHs and PCBs were quantitatively eluted with 40 mL of high purity pentane. Less than 0.01 mg of non-target residues coeluted with analytes in the pentane.

Because different SEC collect-fractions and subsequent enrichment techniques are used for PAHs than for PCBs and OCPs, the sample extracts are split into two portions before SEC. For the PAH portion of the samples, the "collect" fraction is initiated at the point 70% of the time between the apex of the DEHP chromatographic peak and the apex of the biphenyl chromatographic peak. For the OCP and PCB portion of the samples, the "collect" fraction is initiated at the point 50% of the time between the apex of the DEHP chromatographic peak and the apex of the biphenyl chromatographic peak. The "dump" fraction contains the co-extracted lipid components, the LDPE oligomers, etc. and is discarded to waste. The fractions collected are amended with about 2 mL of isooctane, reduced to a volume of about 1 mL on a rotoevaporation system, and quantitatively transferred with hexane into test tubes. Each collect fraction is reduced in volume to approximately 1 mL using rotary evaporation and nitrogen (high purity) blow-down. After transfer to vials or test tubes, the resulting concentrate is typically adjusted to a final volume of about 2 mL.

Chemical enrichment and class fractionation procedures vary from laboratory to laboratory. Thus, no universal method for further enrichment and fractionation exists. However, the following provides some specific examples of commonly used

enrichment and fractionation methods. Following SEC treatment, the SPMD sample extracts are enriched using open column (glass) adsorption chromatography. The portion designated for analysis of PCBs and OCPs (1 mL), is applied to an activated Florisil (heated at 475 °C for 8 hrs and subsequently stored at 130 °C) column (5 g) and target compounds are eluted with 60 mL of 75:25 ($V V^{-1}$) methyl *tert*-butyl ether: hexane. Following volume reduction (1 mL), the eluate is applied to an activated (130 °C) silica gel column (SG-60; 5 g). Two fractions are collected; fraction SG-1 (46 mL of hexane) and SG-2 (55 mL of 40:60 [$V V^{-1}$] methyl *tert*-butyl ether: hexane). The PCB residues and nonpolar OCPs elute in SG-1, and the remaining OCP residues elute in SG-2 (several nonpolar OCPs are split between SG-1 and SG-2). Those portions of the post-SEC sample extracts that are destined for analysis of PAHs are treated as follows. The solutions (1 mL) are applied to tri-adsorbent columns consisting of (top to bottom) 3 g phosphoric acid/silica gel; 3 g potassium silicate (KS); and 3 g of activated silica gel (Petty et al., 2004). The PAHs are eluted from the tri-adsorbent column with 50 mL of 4% methyl *tert*-butyl ether in hexane.

5.4. POTENTIAL INTERFERENCES

While the extracts of SPMDs are generally less difficult to purify than are extracts of tissue or sediment, certain interferences can be problematic for some types of analyses. The most important of these potential interferences are co-dialyzed polyethylene oligomers (i.e., the so-called polyethylene waxes), oleic acid, and methyl oleate. The latter two interferences are residual from the synthesis of the triolein. Also, oxidation products of triolein may be present in dialysates of SPMDs that have been exposed (especially in the presence of light) to air for periods exceeding 30 d. For a standard 1-mL triolein SPMD, the mass of all these interferences in dialysates is generally <30 mg or about 6 mg g^{-1} of SPMD (Huckins et al., 1996). Another potential interference is elemental sulfur, which is often present in sediment pore water and is concentrated by SPMDs. However, both polyethylene waxes and elemental sulfur are readily removed using the previously described SEC procedure.

Unfortunately, small amounts of oleic acid and methyl oleate are generally present in the post-SEC sample extracts. Both of these lipids can be a source of analytical interference when the concentrated SEC eluate is evaluated by GC-MS. However, the interference from oleic acid and methyl oleate is generally greater for SPMD field blanks, fabrication blanks, and process blanks than it is for environmentally exposed SPMDs. The lower level of interfering lipid in environmentally exposed SPMDs is due to the diffusion of much of both methyl oleate and oleic acid to the exterior membrane surface (during exposures), where the residues dissipate, degrade or are removed during membrane cleaning.

Oleic acid can be completely removed by using a tri-adsorbent cleanup procedure or by using a small column of KS (5 g) and eluting with dichloromethane or

any weaker solvent that will successfully elute the targeted compounds. Also, the previously described Florisil cleanup procedure removes any residual oleic acid in the post-SEC extracts. However, methyl oleate is often more problematic. While most of the methyl oleate is eliminated during the aforementioned SEC treatment, a small portion remains in the sample extract. Because the methyl oleate contains a polar functional group, it is found in the SG-2 fraction rather than SG-1. Methyl oleate causes little or no problem when the analysis is performed using GC-ECD or GC-PID. However, it interferes with GC-FID determination of PAHs or full scan GC-MS analyses. If necessary, methyl oleate concentrations can be further reduced ($\approx$99.6% reduction) by another pass through SEC. Also, residual methyl oleate can be completely removed using destructive techniques, such as cleanup with sulfuric acid impregnated silica gel. Unfortunately, this approach is only applicable when targeted compounds (e.g., PCBs, chlorinated dioxins and furans, and selected OCPs) do not degrade in the presence of strong acid.

Gustavson et al. (2000) developed a convenient and novel solid phase extraction (SPE) method for the removal of methyl oleate from SPMD dialysates containing PAHs. A small SPE column (1 g or 0.5 g) containing a dual-zone silica (normal phase)-based restricted-access sorbent (Diazem, Midland, MI, USA) is used for the separation. The capacity of this sorbent to remove methyl oleate is about 1.8% (lipid/sorbent; wt wt^{-1}). The PAHs are eluted with 19 mL of hexane and methylene chloride (97:3; $V V^{-1}$) and recoveries of all PAHs are typically $\geq$72%.

More recently, commercially available SPMDs contain triolein of $\geq$99% purity. Furthermore, Lebo et al. (2004) developed an improved approach to greatly reduce potential interferences caused by methyl oleate, oleic acid, and other interferences, by removing these chemicals from triolein prior to its use in SPMDs. The method is tailored to the purification of kg quantities of triolein, but it can be scaled down to accommodate as little as 1 g of triolein. The following is an example of the purification procedure. One kg of triolein is distributed equally among 40, 250 mL polypropylene centrifuge tubes. The 25 g portions of triolein are each partitioned with 200 mL of high purity methanol, and then the tubes are centrifuged and placed in a freezer ($<-20\,^{\circ}$C) overnight. The next day, the methanol supernatants are decanted and discarded. This partitioning step is repeated six times. Subsequently, the purified triolein is consolidated in a 2 L round bottomed flask. Residual methanol is removed using rotary evaporation and the triolein is distributed among about 20, 50 mL amber bottles (or glass ampoules), blanketed with argon and stored frozen ($<-20\,^{\circ}$C). Throughout the procedure, exposure to light (UV-A and B) and air must be minimized.

The purity of the purified triolein is verified as follows. According to standard procedures, replicate standard SPMDs are made using the purified triolein. The SPMDs are dialyzed and the dialysates are subjected to SEC fractionation. (Prior to SEC, dialysates should have $<$500 µg methyl oleate, and essentially no oleic acid.) The fractions collected from the SEC are evaluated by GC with ECD, FID, and MS. In order to pass the pre-use certification, the dialysate from a standard SPMD, after SEC, should contain less than 5 µg of methyl oleate, GC-ECD chromatograms

should have no coincident peaks (OCPs typically analyzed for in environmental samples) at levels greater than 1 ng $SPMD^{-1}$, and no coincident ions using MS detection at a level greater than 20 ng $SPMD^{-1}$ of the priority pollutant polycyclic aromatic hydrocarbons and other targeted analytes.

When using purified triolein, most samples are amenable to bioassay after dialytic enrichment. For example, Microtox bioassay of dialysates of SPMDs shows that the SPMDs made with the purified triolein have lower acute toxicities than dialysates from SPMDs made from unpurified triolein (Johnson, 2001). Finally, examination of the dialysates using the yeast estrogen screen (YES) assay (Routledge and Sumpter, 1996) demonstrated that the purification procedure removes all background estrogenic activity (Lebo et al., 2004). Use of triolein purified by this process expands the potential applicability of SPMD sample extracts to include numerous bioassay procedures (see Chapter 6) and GC-MS as a standard analysis technique.

5.5. INSTRUMENTAL ANALYSIS

After solvent exchange, the SPMD dialysate can be analyzed directly by using high performance liquid chromatography (HPLC). If GC or GC-MS is the instrument of choice, then SEC cleanup and other cleanup and fractionation steps are generally required for best results (Figure 5.1). Although, almost any analytical technique used for determining the presence and concentrations of chemicals in environmental matrices can be applied to the analysis of chemicals in SPMD extracts, the types and levels of chemicals expected to be present often dictate the choice of instrumental requirements. For example, the need for instrumental specificity is underscored by the work of Petty et al. (2000b), where analysis of a single SG-2 fraction (i.e., the OCP fraction) of SPMDs exposed to indoor air revealed approximately 400 detectable components (see Chapter 8 for more details of this study). In this case, it was essential to employ highly selective, mass specific instrumentation such as GC-MS or HPLC-MS to confirm the presence of the analytes and to identify unknowns. These considerations also apply to the analysis of other environmental matrices. However, for the majority of SPMD projects, investigators have flexibility to choose analytical instrumentation and instrumental methods assuming good laboratory and chromatographic practices are followed (e.g., Meadows et al., 1998; Petty et al., 1998a; McCarthy and Gale, 2001).

5.6. DATA FORMAT AND COMPARABILITY

Care should be taken to supply sufficient background information when results from SPMD deployments are reported. The purpose of this background information is to elucidate how the reported results are related to the raw data, to allow users to compare the reported results to those obtained in other studies, and to provide data of known quality for future reference.

5.6.1. Important Background Information

Historically, the results obtained from SPMD deployments have been reported in a number of different units: ng per gram SPMD, ng per mL of SPMD, ng per SPMD, ng per gram triolein, or ng per L water. The general practice is to analyze whole SPMDs, but some investigators discard the LDPE and only analyze the triolein. In addition, some SPMD designs have significantly deviated from the standard configuration. In order to avoid confusion about the design of SPMDs used in a study, the following characteristics should be specified in reports: LDPE membrane thickness, SPMD length and width, triolein purity, and triolein mass fraction. These characteristics fully define the SPMD design used. Other characteristics, such as SPMD surface area, mass, and volume may be listed as well. The label "standard design" is not sufficient to fully characterize the SPMD design, because the standard design allows for a range of LDPE membrane thicknesses (70–95 μm) and triolein purities (≥95%).

A number of exposure-site characteristics should also be listed in order to document possible effects of flow, temperature, and biofouling on the uptake rates. Flow conditions at the membrane surface are particularly important because of the potentially large impact on SPMD sampling rates. Next to external or bulk flow rates, the design or geometry of the deployment apparatus and mounting devices may affect the flow conditions at the SPMD surface the most (Louch et al., 2003), and therefore, should be briefly described. Although exchange kinetics information may adequately be summarized by listing the release rate constants (k_es) of PRCs, the documentation of exposure conditions is invaluable for a better understanding and interpretation of rate constants, both within and among studies. The necessity of including a brief general description of the exposure sites, their geographical coordinates, the beginning and end of the exposure period and any events that may result in field blank contamination may seem self-evident, but should not be forgotten. Exposure site pH is a relevant parameter when acidic or basic contaminants are targeted. Other useful data include: suspended matter, particulate and dissolved organic carbon (*POC* and *DOC*, respectively) contents of exposure water and the dust content of air. In regard to atmospheric exposures, the predominant wind directions should be noted as it may help to interpret the absorbed amounts in terms of geographical sources.

Raw data from SPMD exposures should include target compound levels in the various blanks, and the amounts found in exposed SPMDs in ng per sample. When the triolein phase is separately analyzed, the raw data should include the amounts in the LDPE phase as well. When PRCs are used, the measured $t = 0$ levels and the calculated spike levels should be included as an additional check on PRC recovery.

Information on whether the average blank levels were subtracted should also be supplied with the processed data. In addition, the method detection limits (MDLs) and MQLs should be listed, as well as the criteria used to determine MDLs and MQLs. The methods or equations used to calculate aqueous or atmospheric

Table 5.1 Important Background Information to be Supplied with SPMD Data

Stage	Required Information
SPMD design	LDPE membrane thickness length and width (excluding mounting loops) triolein mass fraction triolein purity
Exposure	water or air flow rate exposure cage geometry air samplers: wind direction location (coordinates, and preferably a digital picture) start and end date and time physical appearance after exposure (description, and preferably a digital picture) temperature pH (when organic acids or bases are the target analytes) suspended matter, and *POC* and *DOC* levels (water) or particle (air) levels other observations relevant to QC
Raw data	PRC levels in non-exposed SPMDs (experimental and calculated) blank levels (fabrication, process, reagent, field) fraction processed (whole SPMD recommended!) amount of analyte per sampler
Processed data	blank corrections, MDL, MQL concentration in SPMD (when applicable) C_w or C_a calculation method (when applicable)

concentrations should be fully documented. The main reason for recording this information is that calculation methods are subject to continual improvement, as more calibration data become available. Other important information includes the sources of sampling rates and partition coefficients, the methods used to calculate PRC-derived sampling rates, and the schemes applied for estimating the sampling rates of non-PRC analytes. Because there often is some ambiguity in the choice of literature values of log K_{ow} (aqueous exposures) and log octanol-air partition coefficient (K_{oa}) values (atmospheric exposures), a full listing of these parameters is essential.

A summary of essential background information to be supplied with SPMD data is given in Table 5.1. Compliance with this list secures valuable data for the future, with a relatively small investment of time.

5.6.2. The Triolein Phase and Lipid Normalization

Processing of the triolein alone (i.e., without analyzing the LDPE as well) is not encouraged for a number of reasons. First of all, the LDPE constitutes a significant part of the total SPMD sorption capacity, in contrast to biota, where the sorption capacity of the non-lipid phase is often considered to be negligible. Data on membrane-lipid partition coefficients (K_{mL}) is very limited, but the available

information suggests that these partition coefficients are in the range 0.1 to 0.6 g g^{-1} (Huckins et al., 1990, 1993; Hofmans, 1998). Given the fact that the LDPE mass in SPMDs is four times as large as the triolein mass, these values imply that the LDPE membrane contains about 30 to 70% of the analyte amounts that are absorbed by the SPMDs. Discarding the LDPE phase would therefore result in a significant loss of analyte. A second reason why the LDPE phase should not be discarded is that by far the greatest part of the calibration data are based on whole-SPMD data rather than on triolein-only data. Because of the limited numbers of measured K_{mL} values, it is in practice very difficult, if not impossible, to accurately convert calibration data for whole-SPMDs into sampling rate data for the triolein phase alone.

The practice of lipid normalization finds its origin in biomonitoring research and equilibrium partition (EP) theory, where it was observed that biota with larger lipid contents generally had higher levels of bioconcentratable chemicals. The main prerequisite for lipid normalization of contaminant concentrations in BMOs is that thermodynamic equilibrium is attained for the compounds of interest. When concentrations in BMOs are to be compared among different species, lipid normalization is only helpful when this condition is met for all BMO samples. Other assumptions related to lipid normalization are that differences in the composition of organism lipids (Schneider, 1982) and in the physiological state among the BMOs are negligible (Huckins et al., 2004). In regard to biomagnification (see Section 7.8 for definition)-mediated deviations from EP theory, corrections are made by using food chain multipliers. Because SPMDs can be viewed as a lipid pool contained in a non-lipid matrix, it is tempting to apply most of these concepts of lipid normalization to SPMDs as well. Unfortunately, this practice leads to results that are often difficult to interpret and to conclusions that may be plainly wrong. First, the non-lipid phase of SPMDs contains a significant fraction of the analytes. This contribution of the membrane to the total sorption capacity of the device could be accounted for in terms of a "lipid-equivalent mass" (m_{Leq})

$$m_{\mathrm{Leq}} = m_{\mathrm{L}} + K_{\mathrm{mL}}\, m_{\mathrm{m}} \tag{5.1}$$

where m_{L} and m_{m} are the mass of the triolein and the LDPE membrane, respectively. A complicating factor is that the lipid-equivalent mass differs among compounds, and often cannot be calculated because of lack of K_{mL} data. Using the range of K_{mL} values given earlier ($K_{\mathrm{mL}} = 0.1$ to 0.6 g g^{-1}), and the mass fraction of a standard-design SPMD (20% triolein and 80% membrane), m_{Leq} values range from 28 to 68% of the SPMD, depending on the compound. The compound-dependent lipid-equivalent mass of an SPMD is difficult conceptually, and thus may lead to errors in the normalization process.

As suggested earlier, all samples must attain equilibrium before lipid normalization is appropriate. However, SPMDs are not designed to reach equilibrium during typical exposure periods of one month or less. In fact, attainment of equilibrium may take years for some compounds and exposure conditions. Prior to equilibrium, the amount of a contaminant accumulated by an SPMD or BMO is

not limited by the size of the lipid pool, but rather by the contaminant sampling rate, which is proportional to the surface area of the sampler-water interface. In this case, lipid-normalization clearly leads to erroneous results. For example, Meadows et al. (1998) reported that the uptake rate constants (k_us) of SPMDs ($\approx$30–70% effective lipid content) and brown trout (*Salmo trutta*) ($\approx$2–3% lipid content) are similar when expressed on a wet weight (tissue) and whole SPMD basis. If this study was extended and trout had just attained equilibrium concentrations, the levels in SPMDs would represent only about 4–10% of the equilibrium concentrations. At this point in time, lipid normalization of trout and SPMD concentrations would result in an apparent $\geq$10-fold higher concentration in trout than in SPMDs, even though the actual amounts of residues sequestered per gram of whole sampling matrix would be equivalent. Unfortunately, normalization artifacts or errors occur quite often in reports comparing SPMDs and BMOs.

5.7. REFERENCES

Bergqvist, P.-A.; Strandberg, B.; Ekelund, R.; Rappe, C.; Granmo, Å. 1998a, Temporal monitoring of organochlorine compounds in seawater by semipermeable membranes following a flooding episode in Western Europe. *Environ. Sci. Technol.* **32**: 3887–3892.

Bergqvist, P.-A.; Strandberg, B.; Rappe, C. 1998b, Lipid removal using semipermeable membranes in PCDD and PCDF analysis of fat-rich environmental samples. *Chemosphere* **38**: 933–943.

Booij, K.; Sleiderink, H.M.; Smedes, F. 1998, Calibrating the uptake kinetics of semipermeable membrane devices using exposure standards. *Environ. Toxicol. Chem.* **17**: 1236–1245.

Booij, K.; Hofmans, H.E.; Fischer, C.V.; van Weerlee, E.M. 2003, Temperature-dependent uptake rates of nonpolar organic compounds by semipermeable membrane devices and low-density polyethylene membranes.*Environ. Sci. Technol.* **37**: 361–366.

DeVita, W.M. and Crunkilton, R.L. 1998, Quality Control Associated with Use of Semipermeable Membrane Devices. In *Environmental Toxicology & Risk Assessment*, *Seventh Volume;* Little, E.E., Delonay, A.J., Greenberg, B.M., Eds.; ASTM STP 1333; American Society for Testing and Materials: West Conshocken, PA; pp. 237–245.

Ellis, G.S.; Huckins, J.N.; Rostad, C.E.; Schmitt, C.J.; Petty J.D.; MacCarthy, P. 1995, Evaluation of lipid-containing semipermeable membrane devices (SPMDs) for monitoring organochlorine contaminants in the Upper Mississippi River. *Environ. Toxicol. Chem.* **14**: 1875–1884.

Górecki, T. and Pawliszyn, J. 1997, Field-portable solid-phase microextraction/fast GC system for trace analysis. *Field Anal. Chem. Tech.* **1**: 227–284.

Gustavson, K.E.; DeVita, W.; Revis, A.; Harkin, J.M. 2000, A novel use of a dual-zone restricted access sorbent: Normal phase separations of methyl oleate and polynuclear aromatic hydrocarbons stemming from semipermeable membrane devices. *J. Chromatogr. A* **883**: 143–149.

Hofmans, H.E. 1998, Numerical Modeling of the Exchange Kinetics of Semipermeable Membrane Devices. MSc Thesis, Netherlands Institute for Sea Research: Den Burg, The Netherlands.

Horwitz, W.; Kamps, L.R.; Boyer, K.W. 1980, Quality assurance in the analysis of foods for trace constituents. *J. AOAC* **63**: 1344–1354.

Huckins, J.N.; Tubergen, M.W.; Manuweera, G.K. 1990, Semipermeable membrane devices containing model lipid: A new approach to monitoring the availability of lipophilic contaminants and estimating their bioconcentration potential. *Chemosphere* **20**: 533–552.

Huckins, J.N.; Manuweera, G.K.; Petty, J.D.; Mackay, D.; Lebo, J.A. 1993, Lipid-containing semipermeable membrane devices for monitoring organic contaminants in water. *Environ. Sci. Technol.* **27**: 2489–2496.

Huckins, J.N.; Petty, J.D.; Lebo, J.A.; Orazio, C.E.; Prest, H.F.; Tillitt, D.E.; Ellis, G.S.; Johnson, B.T.; Manuweera, G.K. 1996, Semipermeable Membrane Devices (SPMDs) for the Concentration and Assessment of Bioavailable Organic Contaminants in Aquatic Environments. In *Techniques in Aquatic Toxicology*; Ostrander, G.K., Ed.; CRC Press: Boca Raton, FL; pp. 625–655.

Huckins, J.N.; Petty, J.D.; Prest, H.F.; Clark, R.C.; Alvarez, D.A.; Orazio, C.E.; Lebo, J.A.; Cranor, W.L.; Johnson, B.T. 2002, *A Guide for the Use of Semipermeable Membrane Devices (SPMDs) as Samplers of Waterborne Hydrophobic Organic Contaminants;* Publication No. 4690; American Petroleum Institute (API): Washington, DC.

Huckins, J.N.; Prest, H.F.; Petty, J.D.; Lebo, J.A.; Hodgins, M.M.; Clark, R.C.; Alvarez, D.A.; Gala, W.R.; Steen, A.; Gale, R.W.; Ingersoll, C.G. 2004, Overview and comparison of lipid-containing semipermeable membrane devices (SPMDs) and oysters (Crassostrea gigas) for assessing chemical exposure. *Environ. Toxicol. Chem.* **23**: 1617–1628.

Johnson, B.T. 2001, USGS Columbia Environmental Research Center, Columbia, MO. Personal communication.

Jones-Lepp, T. 2004, U.S. EPA, National Exposure Research Laboratory: Las Vegas, NV; Personal communication.

Lebo, J.A.; Gale, R.W.; Petty, J.D.; Tillitt, D.E.; Huckins, J.N.; Meadows, J.C.; Orazio, C.E.; Echols, K.R.; Schroeder, D.J.; Inmon, L.E. 1995, Use of the semipermeable membrane device (SPMD) as an in situ sampler of waterborne bioavailable PCDD and PCDF residues at sub-part-per-quadrillion concentrations. *Environ. Sci. Technol.* **29**: 2886–2892.

Lebo, J.A.; Almeida, F.V.; Cranor, W.L.; Petty, J.D.; Huckins, J.N.; Rastall, A.; Alvarez, D.A.; Mogensen, B.B.; Johnson, B.T. 2004, Purification of triolein for use in semipermeable membrane devices (SPMDs). *Chemosphere* **54**: 1217–1224.

Louch, J.; Allen, G.; Erickson, C.; Wilson, G.; Schmedding, D. 2003, Interpreting results from field deployments of semipermeable membrane devices. *Environ. Sci. Technol.* **37**: 1202–1207.

Maštovská, K. and Lehotay, S.J. 2003, Practical approaches to fast gas chromatography-mass spectrometry. *J. Chromatogr. A* **1000**: 153–180.

McCarthy, K.A. and Gale, R.W. 2001, Evaluation of persistent hydrophobic organic compounds in the Columbia River Basin using semipermeable membrane devices. *Hydrol. Process* **15**: 1271–1283.

Meadows, J.C.; Tillitt, D.E.; Huckins, J.N.; Schroeder, D. 1993, Large-scale dialysis of sample lipids using a semipermeable membrane device. *Chemosphere* **26**: 1993–2006.

Meadows, J.C.; Echols, K.R.; Huckins, J.N.; Borsuk, F.A.; Carline, R.F.; Tillitt, D.E. 1998, Estimation of uptake rate constants for PCB congeners accumulated by semipermeable membrane devices and brown trout (Salmo trutta). *Environ. Sci. Technol.* **32**: 1847–1852.

Meyer, M. 2004, USGS Organic Geochemistry Research Laboratory: Lawrence KS; Personal communication.

Petty, J.D.; Huckins, J.N.; Orazio, C.E, Lebo, J.A.; Poulton, B.C.; Gale, R.W.; Charbonneau, C.S.; Kaiser, E.M. 1995, Determination of bioavailable organochlorine pesticide residues in the Lower Missouri River. *Environ. Sci. Technol.* **29**: 2561–2566.

Petty, J.D.; Poulton, B.C.; Charbonneau, C.S.; Huckins, J.N.; Jones, S.B.; Cameron, J.T.; Prest, H.F. 1998a, Determination of bioavailable contaminants in the Lower Missouri River following the flood of 1993. *Environ. Sci. Technol.* **32**: 837–842.

Petty, J.D.; Huckins, J.N.; Cranor, W.L.; Clark, R.C. 1998b, *Determination of Dieldrin in Ground Water from the George Air Force Base; California*. USGS Columbia Environmental Research Center: Columbia, MO; Unpublished report to U.S. EPA, San Francisco; CA.

Petty, J.D.; Orazio, C.E.; Huckins, J.N.; Gale, R.W.; Lebo, J.A.; Meadows, J.C.; Echols, K.R.; Cranor, W.I. 2000a, Considerations involved with the use of semipermeable membrane devices for monitoring environmental contaminants. *J. Chromatogr. A* **879**: 83–95.

Petty, J.D.; Gale, R.W.; Huckins, J.N.; Cranor, W.L.; Alvarez, D.A.; Clark, R.C. 2000b, *Development and Application of Techniques for Sampling Bioavailable Airborne Contaminants-Tentatively Identified Compounds by Gas Chromatography/Mass Spectrometry*. USGS Columbia

Environmental Research Center : Columbia, MO; Unpublished report to U.S. EPA National Exposure Assessment Laboratory: Las Vegas; NV.

Petty, J.D.; Huckins, J.N.; Alvarez, D.A.; Brumbaugh, W.G.; Cranor, W.L.; Gale, R.W.; Rastall, A.C.; Jones-Lepp, T.L.; Leiker, T.J.; Rostad C.E.; Furlong, E.T. 2004, A holistic passive integrative sampling approach for assessing the presence and potential impacts of waterborne environmental contaminants. *Chemosphere* **54**: 695–705.

Randal, R.C.; Lee, H. II.; Ozretich, R.J.; Lake, J.L.; Pruell, R.J. 1991, Evaluation of selected lipid methods for normalizing pollutant bioaccumulation. *Environ. Toxicol. Chem.* **10**: 1431–1436.

Routledge, E.J. and Sumpter, J.P. 1996, Estrogenic activity of surfactants and some of their degradation products assessed using a recombinant yeast screen. *Environ. Toxicol. Chem.* **15**: 214–248.

Schneider, R. 1982, Polychlorinated biphenyls (PCBs) in cod tissues from the Western Baltic: Significance of equilibrium partitioning and lipid composition in the bioaccumulation of lipophilic pollutants in gill-breathing animals. *Meeresforschung* **29**: 69–79.

Strandberg, B.; Bergqvist, P.-A.; Rappe, C. 1998, Dialysis with semipermeable membranes as an efficient lipid removal method in the analysis of bioaccumulative chemicals. *Anal. Chem.* **70**: 526–533.

Taylor; J.K. 1987, *Quality Assurance of Chemical Measurements*; Lewis Publishers: Boca Ratan, FL.

Chapter 6

Bioassay of SPMD Extracts or Diluents

6.1. OVERVIEW AND RATIONALE OF THE SPMD-TOXICITY SCREENING APPROACH

In addition to instrumental methods of qualitative and quantitative analyses, chemicals sequestered by SPMDs are amenable to examination by a variety of bioassays (Huckins et al., 1996; Zajicek et al., 1996; Parrott and Tillitt, 1997; Johnson, 1998; Johnson et al., 2004; Petty et al., 1998, 2000, 2004; Parrott et al., 1999; Sabaliūnas et al., 1999, 2000; Rastall et al., 2004). These assays include biomarker or bioindicator tests, immunoassays, and classic toxicity tests. In this chapter the words "bioindicator" and "biomarker" are used interchangeably but the tests refer to *in vitro* and *in vivo* indicators of toxicity and exposure. Bioassays used to assess extracts or diluents of SPMDs include but are not limited to the following: Microtox, Mutatox, mixed function oxygenase (MFO) induction-ethoxyresorufin-*O*-deethylase (EROD) activity, sister chromatid exchange, vitellogenin (VGT) induction via interperitoneal injection of test species, enzyme-linked immunosorbent assay (ELISA), Daphtoxkit F, Ames mutagenicity test, and yeast estrogen screen (YES) assay. Some of these assays incorporate metabolic activation systems (e.g., Mutatox and EROD). This approach makes it possible to account for metabolic transformation processes that may enhance or reduce the effects of chemical residues in organism tissues. The marriage of SPMDs and compatible bioassays offers many avenues of investigation, all potentially providing information

concerning the relative toxicological significance of exposure to chemicals present in the environmental matrices sampled.

A major challenge for ecotoxicologists is to obtain relevant samples suitable for testing from environmental systems. Most hydrophobic organic contaminants are present in environmental matrices only at trace- to ultra-trace- levels. However, the sometimes-slow processes of bioconcentration (uptake via respiration-dermal absorption) and bioaccumulation (uptake from both respiration-dermal absorption and diet) can lead to elevated concentrations of contaminants in exposed organisms, which can result in a variety of adverse effects. These chemical uptake processes are especially relevant to the magnitude of adverse environmental effects of persistent hydrophobic organic contaminants. Those contaminants with log octanol-water partition coefficients (K_{ow}s) between 4 and 7 are of particular concern. In many cases, bioassays (especially the more rapid cellular-based assays) do not fully account for the effect of bioaccumulation on tissue concentrations of aquatic organisms. Also, a number of the aforementioned assays have relatively low sensitivities for many common pollutants. For example, the Microtox test often requires high ng to low μg amounts of priority pollutants to elicit a measurable response. Direct testing of environmental waters with this bioassay may lead to false-negative errors in assessing the potential risk of waterborne residues to aquatic life. To avoid this type of error and expand the use of biomarker tests for ranking toxicity potential, a pre-concentration method is needed that mimics the bioconcentration process. SPMDs offer several advantages over other potential pre-concentration methods, including: 1) a biomimetic design; 2) only bioavailable, dissolved-phase (in the case of waterborne chemicals) residues are sampled; 3) sampling is generally integrative, which permits the SPMD sample to reflect contribution from episodic contamination events; and 4) significant statistical advantages, due to high reproducibility, relative to biomonitors (Prest et al., 1997; Huckins et al., 1998). Consequently, the SPMD-bioassay assessment approach enhances an investigator's ability to screen for the relative toxicological significance of environmental hydrophobic organic chemical (HOC) residues.

If an investigator demonstrates that an SPMD extract is toxic or genotoxic when using a specific biomarker test, questions may arise as to the relevance of the finding in regard to risk assessment. Clearly, the SPMD-bioassay combination is useful as a screening tool for ranking the potential toxicities of bioconcentratable residues at multiple sites and for determining sources of pollutants. However, the justification for a specific level of pre-concentration prior to use of bioassay tests to account for the toxicological effects of residue bioconcentration in tissues is less clear. This is, in part, due to the wide variation in bioconcentration factors (*BCF*s) for the same chemical among different species. Also, depending on the specifics of biomarker experimental conditions (e.g., exposure or incubation time) and the type of organisms or cell lines used, chemicals in the incubation medium are also concentrated by the test organisms to some unknown degree. Although the exposure duration is only five minutes for the basic Microtox test, the high surface area to volume ratio of bacteria likely facilitates uptake rates.

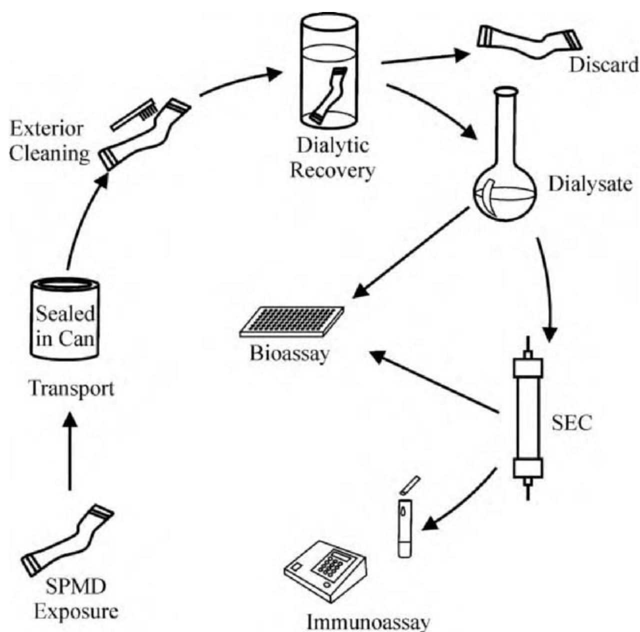

FIGURE 6.1 Illustration of the SPMD *in vitro* bioassay and immunoassay protocol, which includes sampling, different levels of processing and enrichment, and bioassay or immunoassay. Reprinted with permission from the American Petroleum Institute (Huckins et al., 2002).

Regardless of the complexity of predicting an appropriate pre-concentration factor, some level of pre-concentration is often needed to permit application of bioindicator tests and certain other bioassays to the assessment of trace or ultra-trace contaminants. Obviously, the maximum level of pre-concentration, or the time-dependent SPMD concentration factor (*CF;* see definition in Section 7.5) should not exceed the measured or estimated *BCF* of a chemical for the species of concern. However, this may not be true when organisms biotransform compounds of concern. Clearly, metabolic activity differences among species can affect residue body burdens (Connell, 1990). Often, investigators choose SPMD exposure durations on the basis of convenience. Generally, exposure periods seldom exceed 30 days (EROD for ultra-trace levels of dioxins, furans and coplanar PCBs may be an exception). Exposures of 30 days or less generally result in SPMD *CFs* less than the reported *BCFs* of many stable hydrophobic compounds in test organisms.

SPMD dialysates (extracts), rinses of the exterior membrane surface (only SPMDs exposed to air), and aliquots thereof often contain a number of classes of chemicals. Figure 6.1 shows various levels of processing and enrichment used for SPMD derived bioassay samples. We strongly recommend the use of SPMDs with triolein purified by the method of Lebo et al. (2004) for bioassays to reduce the probability of false-positive results or for controls that fail to meet quality control

(QC) criteria. After transferring the enriched SPMD extract to an appropriate carrier solvent such as dimethyl sulfoxide (DMSO), the toxicity of the sample can be assessed with a wide variety of bioassays. If the test endpoint is an effects concentration for 50% of test organisms (EC_{50}), the units are a specific mass or volume (mg or mL) of whole SPMD per volume (mL or L) of carrier solvent. Obviously, investigators must keep track of sample splits, dilutions, etc. When analytical chemistry is also performed and SPMD uptake rate data are available for the detected residues, the measured EC_{50} value can be related to the volume of water (V_{w-tox}) sampled at a site that contained sufficient mass of bioavailable contaminants to elicit the observed toxicological response. If the above conditions are met, the following model can be used to derive V_{w-tox}

$$V_{w-tox} = k_u t \, EC_{50} \, V_c \tag{6.1}$$

where the $k_u t$ represents the volume of water extracted per g of SPMD, and V_c is the volume of carrier solvent (includes correction for any serial dilutions) used in each determination of the EC_{50} value. If k_us are available for the chemicals identified in the SPMDs and for the aquatic organisms of interest (e.g., see Mackay et al., 1992a; 1992b; 1997), then $V_{w-tox}C_w$ (represents the mass of bioavailable contaminants eliciting the bioassay response) can be compared to organism $k_u t$ $M_o C_w$ (mass of bioavailable contaminants exposed to organism of concern during a specified time interval [t]); where M_o is organism mass in g. Obviously, this approach is limited by a general lack of applicable rate constant data, the potential for unidentified contaminants to elicit toxic responses, and the paucity of data on chemical concentrations in biomarker cell lines or organisms (i.e., the *CF* associated with the transfer of chemicals from the test medium to the test cells or organisms).

Kočí et al. (2003) developed the V_{tox} approach for assessing the relative toxicity of SPMD extracts. They defined $V_{tox(50)}$ as the media volume that is needed to reduce the toxicity of the extract of a 1-day exposed standard SPMD to a 50% effect level. The following relationship is used to determine V_{tox}

$$V_{tox(50)} = 1/(s_n \, EC_{50} \, d) \tag{6.2}$$

where V_{tox} has units of mL d^{-1}, s_n is the number of standard SPMDs per mL of carrier solvent used for the assay, the EC_{50} is the 50% effect concentration (mL carrier solvent per mL test solution), and d is days of exposure.

The following sections describe several commonly used bioassay tests that have been successfully used in conjunction with SPMDs. However, no attempt was made to cover all of the *in vitro* assays used for SPMD extracts.

6.2. MICROTOX AND MUTATOX

Several investigators (e.g., Huckins et al., 1996; Cleveland et al., 1997; Johnson, 1998; Johnson et al., 2004; Sabaliūnas et al., 1999, 2000; Petty et al.,

Table 6.1 Toxicological Evaluation of Polycyclic Aromatic Hydrocarbons (PAHs) with Microtox Basic Test and Mutatox[a]. Reprinted with permission from the American Petroleum Institute (Huckins et al., 2002)

	Microtox		Mutatox
Compounds	EC_{50}[b]	CI[c]	genotoxicity[d]
acenaphthylene	0.34	0.25–0.47	positive
phenanthrene	0.48	0.33–0.68	positive
fluorene	0.50	0.35–0.70	positive
anthracene	0.64	0.53–0.78	positive
benz[*a*]anthracene	0.73	0.65–0.81	positive
acenaphthene	0.75	0.69–0.81	positive
2-aminoanthracene	0.75	0.49–1.2	positive
fluoranthene	0.83	0.63–1.08	positive
naphthalene	0.90	0.85–0.99	positive
chrysene	0.92	0.85–0.99	positive
2-aminonaphthalene	1.3	1.1–1.5	positive
2-acetamidofluorene	2.3	1.3–4.1	positive
2-aminofluorene	4.1	2.5–6.4	positive
benzo[*a*]pyrene	10.7	6.4–18.2	positive
3-methylcholanthracene	19.9	18.3–21.5	positive
7,12-dimethylbenzanthracene	33.1	14.6–74.7	positive
pyrene	>500	—	positive
DMSO (control)	ND[e]	—	negative

[a] Data from Johnson (1998).
[b] 5 minute $EC_{50} = \mu g\ mL^{-1}$.
[c] CI = 95% confidence interval.
[d] 1% rat S9 activation.
[e] ND = not detected.

2000) have determined the toxicity and/or genotoxicity (i.e., DNA-damaging potential) of purified SPMD extracts, of SPMD lipid, or of liver homogenates obtained from organisms exposed to SPMD extracts using the Microtox and Mutatox assays (Microbics, 1992). Unfortunately, the Mutatox cell line is currently unavailable from the supplier, but we include information on the test in the hope of future availability. The Microtox *in vitro* test is based on the chemically induced reduction in the level of light generated by bioluminescent bacterium *Vibrio fischeri*, while the Mutatox *in vitro* test is based on a chemically induced increase in light from a dark-mutant strain of *V. fischeri*. The degree of the decrease in light (Microtox) or increase in light (Mutatox), when compared to controls, indicates the relative acute toxicity (i.e., the basic Microtox test) and genotoxicity (Mutatox), respectively of the sample extract. The toxicological endpoint for the Microtox test is an EC_{50} value and 95% confidence interval (i.e., the test is quantitative), whereas the endpoint for the Mutatox test is qualitative, providing a yes or no assessment of the presence of DNA-damaging substances. Johnson (1998) has determined the acute toxicities and genotoxicities of many chemicals, including PAHs (see Table 6.1). Table 6.2 gives an example of using Microtox and Mutatox to determine

Table 6.2 Use of Microtox and Mutatox to Determine the Toxicity of SPMD Concentrates. Reprinted with permission from the American Petroleum Institute (Huckins et al., 2002)

Sample type	Microtox toxicity EC_{50}[a]	Mutatox genotoxicity
SPMDs		
Winter Quarters Bay[b]	3.1 (2.9 – 3.3)[f]	negative
McMurdo Sound[b]	88 (28 – 275)	negative
Flat Branch[c]	NA[g]	positive
Quality control		
procedural blank[d]	ND[h]	negative
laboratory blank SPMD[e]	ND	negative
microtox phenol reference toxicant (μg mL^{-1} H2O)	19 (17 – 21)	NA
mutatox benzo[*a*]pyrene reference toxicant(1 μg /Vial)	NA	positive

[a] Assays were conducted on lipid diluent or dialysates and EC_{50} values represent mg of SPMD lipid mL^{-1} carrier solvent.
[b] SPMDs exposed to Antarctica sediments in microcosms (Huckins et al., 1996).
[c] SPMDs exposed to a small urban stream (Lebo et al., 1992).
[d] Solvents and reagents used in tests.
[e] Freshly prepared blank SPMD, carried through Microtox and Mutatox test.
[f] Microtox values are 5-minute EC50s with 95% confidence intervals (in parentheses).
[g] None analyzed.
[h] None detected.

the potential toxicities of SPMD extracts from two separate studies (Huckins et al., 1996). Note that EC_{50} values given in Table 6.2 are given in units of mg SPMD lipid per mL of carrier solvent. As discussed in Section 5.6.2., SPMD extracts generally represent whole SPMDs, thus, units of mg or mL of whole SPMDs are advised. The positive Mutatox response for the Flat Branch sample (Table 6.2) is not surprising because of the relatively high levels of PAHs detected there by Lebo et al. (1992).

Microtox responds well to a wide array of hydrophobic chemicals (see the work of Johnson [1998] in which a variety of pesticides, industrial chemicals and petroleum products were tested). Apparently, Microtox is highly responsive to compounds with a narcosis mode of toxicity (Johnson, 1998; Sabaliūnas et al., 1998). As shown by Johnson (1998) chemicals that elicit narcosis include multiple chemical classes.

Clearly, the mode(s) of action eliciting a genotoxic response are more chemical-structure specific (Johnson, 1998). As suggested by Johnson (1998), *in vitro* metabolic activation is required to assess the genotoxicity of SPMD residues with Mutatox. Typically, a rat liver S9 fraction is used for the exogenous metabolic activation step (Microbics, 1992). At first glance, Mutatox appears to be well suited for the assessment of SPMD extracts. However, Sabaliūnas et al. (2000) have pointed out several potential difficulties and shortcomings of the test in its present form. These include reduced light intensity due to cytotoxicity or cell death, delays in the genotoxic response of some samples beyond standard

measurement times, and lower sensitivity of measurements based on reverse mutations. Test sensitivity is not an issue when SPMDs are used to pre-concentrate samples. Also, in the Mutatox protocol (Johnson, 1998), a sample is designated as genotoxic only when two positive responses are recorded, each at different concentrations within a single dilution series. Generally, cytotoxic effects should be evident from the shape of the dose-response curve, and increased turbidity in exposed samples relative to controls is also used as a cytotoxicity indicator (Johnson, 1998; Johnson et al., 2004). However, the concerns raised by Sabaliūnas et al. (1999), require further investigation before Mutatox can be used with total confidence.

6.3. MIXED FUNCTION OXIDASE-7-ETHOXYRESORUFIN-*O*-DEETHYLASE (MFO-EROD)

SPMDs are often applied to concentrate trace levels of environmental contaminants that induce mixed function oxidase (MFO) activity (Huckins et al., 1996; Parrott and Tillitt, 1997; Parrott et al., 1999; Petty et al., 2000). MFOs are a category of enzymes that aid in the biotransformation and clearance of many hydrophobic compounds. One of the most widely recognized MFO enzymes is cytochrome P4501A1 (often measured as ethoxyresorufin-*O*-deethylase [EROD] activity). Increased EROD activity indicates exposure to certain types of organic compounds. These include planar polycyclic aromatic compounds, either halogenated (e.g., polychlorinated dioxins and furans and planar PCBs) or PAHs. Because determination of EROD activity is relatively simple (Parrott et al., 1999), this endpoint is often used as a screening tool for the assessment of sites potentially contaminated with these classes of chemicals. Specific cell lines, e.g., H4IIE rat hepatoma cells and the PLHC-1 fish (*Poeciliopsis lucida*) hepatoma cells are most commonly used for the measurement of EROD activity (Tillitt et al., 1991; Lebo et al., 1995; Huckins et al., 1996; Parrott and Tillitt, 1997, Whyte et al., 2004). However, exposed organisms can also be employed in determining EROD activity (e.g., Petty et al., 1998, 2000; Whyte et al., 2000). In this approach, enzymatic activity is standardized to cellular protein content using the method of Lorenzen and Kennedy (1993). This method corrects for the attenuation of EROD due to cytotoxicity.

EROD activity is measured in the H4IIE cells as follows. The cells are seeded at 7,000 cells per well in 250 μL of Dulbecco's modified Eagles culture media (Tillitt et al., 1991). After an initial incubation period of 24 hours, the cells are dosed with 5 μL volumes of enriched SPMD extracts (cleanup of extracts generally includes dialysis and size exclusion chromatography [SEC]) and incubated for an additional 72 hours. Sample dose is typically expressed as g-equivalents triolein or whole SPMD per mg cellular protein. Multiple exposures are performed at each of six (typically) sample concentrations, using a dilution series. Afterwards, the microtiter plates are washed three times with distilled water to lyse the cells. EROD activity (pmol mg^{-1} cellular protein per min) in each sample is measured

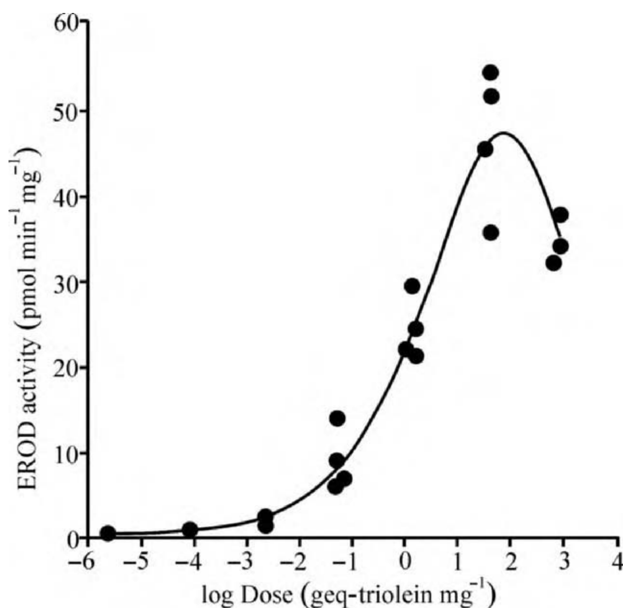

FIGURE 6.2 Ethoxyresorufin-*O*-deethylase (EROD) induction in H4IIE rat hepatoma cells exposed to an SPMD dialysate. Four Standard SPMDs were deployed for a 28 day period in Bayou Meto, Arkansas. Doses of dialysate were normalized to gram-equivalents of triolein per mg of cellular protein. This figure was generated by Don Tillitt, USGS-CERC, Columbia, MO, USA and is reprinted with permission from the American Petroleum Institute (Huckins et al., 2002).

kinetically, and the linear portion of the sample dose-response curve is compared to a 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) standard response (pg TCDD mg^{-1} cellular protein) curve. The standard response curve is generally based on eight concentrations of TCDD, and it is used to quantify the total toxic equivalents (TEQs) of samples (Gale et al., 2000). TEQ values of samples represent the concentrations of TCDD required to give equivalent EROD responses. Ankley et al. (1991) and Whyte et al. (2004) have given details of the procedure for TEQ calculation.

Figure 6.2, shows a specific example of the use of the H4IIE-EROD assay for purified SPMD extracts. After purification of SPMD extracts, Gale et al. (2000) showed that H4IIE-determined TEQs were well correlated with instrumentally-determined TEQs.

6.4. NEUROTOXICITY ENDPOINTS

The use of SPMDs to sequester hydrophobic contaminants for incorporation into bioindicator test-based screening is increasing in both frequency of application and in the array of modes of action. For example, as a focused part of a broader

survey of ecological conditions, species diversity, and habitat quality, SPMDs were deployed in two major water sources of the Santa Cruz River, near Nogales, Arizona, USA. The Santa Cruz River rises in the United States, flows southward into Mexico, turns north and flows back into the United States near Nogales, Arizona. This river is a major source of water in this very arid region and is of critical importance to both the United States and Mexico. Because of the multiple uses of the water of the Santa Cruz River, it is important to determine the presence of waterborne contaminants and the potential for adverse effects on aquatic organisms and ultimately humans. The SPMD samplers were deployed in the effluent of the International Wastewater Treatment Plant (IWWTP) and the Nogales Wash, which are two major water sources of the Santa Cruz River at Nogales, Arizona, USA (Petty et al., 2000).

Following dialysis and treatment by SEC, the sample extracts were solvent exchanged into sterile DMSO. Subsequently, four rainbow trout (*Oncorhynchus mykiss* [RBT]) were placed in each of seven tanks (each tank is considered as a treatment and a replicate is an individual fish within a tank) in 18 °C well water (280 mg L^{-1} hardness as $CaCO_3$) using flow-through conditions. RBT were fed once daily throughout the study. Following a 48 hour acclimation, RBT were injected interperitoneally with 100 μL of a 1:1 mixture of an SPMD extract or appropriate controls in DMSO or corn oil. Controls included non-deployed SPMD extracts, SEC blanks, and DMSO blanks. The same injection procedure was repeated 6 days later. RBT were sacrificed 11 days after initial exposure to the extracts, and the plasma, liver, gills, and brain were immediately removed from each fish and maintained at −80 °C until assayed.

Brain tissue was homogenized and portions were used to determine acetylcholinesterase activity (AChE), and for muscarinic cholinergic receptor (MChR) and β-andrenoceptor (βAR) binding *in vitro* assays. Determination of AChE was performed according to the method of Gard and Hooper (1993) as modified by Beauvais (1997) in which the activity of the enzyme is measured by hydrolysis of acetylcholine and the reaction of the thiocholine product with a colorimetric reagent. The MChR binding assay was performed according to the method of Jones and King (1995) in which crude membrane preparations are incubated with a radioligand specific for MChR. βAR binding was assayed following a standard method (Steevens et al., 1996). After incubation, samples were filtered through GF/B glass fiber filters, with radioactivity being measured using a liquid scintillation counter at an efficiency of 46%. None of the blanks or control samples elicited any measurable response in these assays, indicative of a controlled and interference-free set of samples. The results of these assays are presented in Tables 6.3 and 6.4.

An examination of the data reveals that the average values of plasma cholinesterase were depressed in fish exposed to the SPMD sample extracts from the IWWTP site compared to all controls, although only significantly lower compared to the SEC blanks ($p < 0.05$). A similar trend was observed with the Nogales Wash sample extracts. A number of chemicals determined to be present in the

Table 6.3 Brain MChR Binding and Brain and Plasma Cholinesterase Activities in Rainbow Trout (*Oncorhynchus mykiss*) Exposed to Sample Extracts and Controls. Reprinted from Petty et al. (2000), copyright (2000); reproduced with permission from Elsevier

	Binding MChR		Cholinesterase[c]	
Exposure medium	K_D[a]	B_{MAX}[b]	Brain	Plasma
Controls				
DMSO[d], $n = 3$	62 ± 10	193 ± 23	14.73 ± 0.83	0.051 ± 0.009
reagent blanks, $n = 2$	55 ± 6	205 ± 10	14.38 ± 0.08	0.46 ± 0.014
SPMD blanks, $n = 3$	61 ± 5	203 ± 17	13.95 ± 0.74	0.061 ± 0.004
SEC[e] blanks, $n = 3$	72 ± 9	205 ± 9	15.41 ± 0.38	0.055 ± 0.002
Samples				
IWWTP[f] SPMDs, $n= 4$	83 ± 29	227 ± 17	14.40 ± 0.46	0.034 ± 0.002
Nogales Wash SPMDs, $n = 4$	65 ± 7	227 ± 17	15.46 ± 1.04	0.042 ± 0.003

[a] Picomol
[b] Femtomol mg^{-1} protein.
[c] $\mu mol\ min^{-1} g^{-1}$ tissue.
[d] Dimethyl sulfoxide.
[e] Size exclusion chromatography.
[f] International Waste Water Treatment Plant; Significantly different from blanks, $p = 0.05$.

Table 6.4 Brain and Gill βAR Binding in Rainbow Trout (*Oncorhynchus mykiss*) Exposed to Sample Extracts and Controls. Reprinted from Petty et al. (2000), copyright (2000); reproduced with permission from Elsevier

	Brain		Gill	
Exposure medium	K_D[a]	B_{MAX}[b]	K_D	B_{MAX}
Controls				
DMSO[c], $n = 3$	235 ± 118	18 ± 9	445 ± 66	116 ± 5
reagent blanks, $n = 3$	1,047 ± 139	55 ± 4	943 ± 20	171 ± 22
SPMD blanks, $n= 3$	1,047 ± 139	82 ± 39	589 ± 284	116 ± 19
SEC[d] blanks, $n = 3$	745 ± 348	42 ± 16	471 ± 16	140 ± 20
Samples				
IWWTP[e], $n = 4$	507 ± 294	30 ± 15	449 ± 24	122 ± 12
Nogales Wash[f], $n = 4$	413 ± 270	26 ± 17	532 ± 59	176 ± 18

[a] picomol.
[b] Femtomol mg^{-1} protein.
[c] Dimethyl sulfoxide.
[d] Size exclusion chromatography.
[e] International Waste Water Treatment Plant.
[f] Significantly different from blanks, $p = 0.05$.

SPMD sample extracts, e.g., certain organochlorine pesticides (OCPs), are known to inhibit cholinesterase activity. Therefore, these results were not unexpected. However, it was surprising that a similar response was not observed with brain cholinesterase activity. It is possible that brain cells can more readily metabolize the chemicals, that the chemicals did not pass the brain blood barrier or that the effects occurred earlier in the exposure period, effectively allowing the activity to recover. Considering the numerous neurotoxic chemicals potentially entering aquatic ecosystems or present as airborne vapor phase chemicals, the neurotoxic mode of action related to exposure to contaminants is of increasing interest. Evidence presented in this work demonstrate that SPMDs concentrate members of this class of toxicants.

6.5. ENDOCRINE EFFECTS

Petty et al. (1998, 2000) used a vitellogenin (VGT) assay to assess the endocrine disrupting potential of contaminants in purified SPMD extracts. VGT is an egg yolk phosphoprotein precursor that is synthesized in the liver of female teleosts in response to estrogen from the ovary (Bailey, 1957). A wide variety of environmental contaminants have been shown to have estrogenic activity (Colborn et al., 1993). Equal portions of purified extracts from SPMDs, exposed in the Missouri River after the flood of 1993 and from the IWWTP at the Nogales Wash deployment were individually injected into immature rainbow trout (*Oncorhynchus mykiss*) as described in Section 6.4. The SPMD extracts contained elevated levels of complex mixtures of contaminants, including PAHs and pesticides. The fish injected with these sample extracts exhibited VGT induction, while no induction was observed in fish injected with any of the blank sample extracts.

Another approach for determining potential endocrine disrupting effects is the YES assay (Routledge and Sumpter, 1996). In this assay, recombinant yeast cells stably transfected with the gene for human estrogen receptor (hER) and containing expression plasmids carrying strong promoter sequences and the lac-Z (β-galactosidase) reporter gene are used to assess the estrogenic potential of chemicals or mixtures of chemicals. Using appropriate growth media, the yeast recombinant cells express the hER in a form capable of binding to estrogen response elements (ERE) situated within a promoter sequence on the plasmid. Following the binding of a suitable agonist, the agonist-hER complex interacts with various transcription factors, binds to the ERE and initiates a cascade of events which results in the expression of the lac-Z reporter gene and the secretion of β-galactosidase into the assay medium. By incorporating a chromogenic substrate, chlorophenol-red-β-D-galactopyranoside (CPRG), the estrogenic potential can be determined photometrically at 540 nm following the conversion of the CPRG from yellow to red by the β-galactosidase released into the growth medium in response to the presence of hER in the sample.

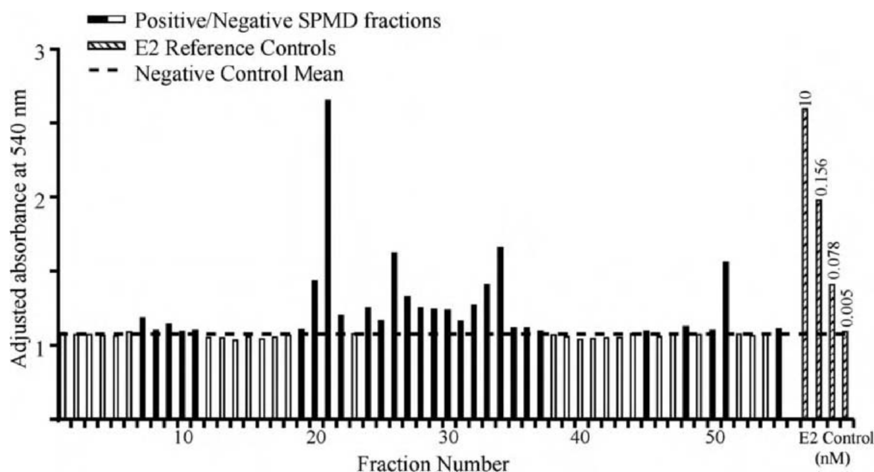

Figure 6.3 YES assay of HPLC fractions of extracts from SPMDs exposed to the Elizabeth River, VA, USA. Reproduced courtesy of Andrew Rastall, University of Heidelberg, Heidelberg, Germany.

Petty et al. (2000) exposed SPMDs to river water (Elizabeth River, VA, USA) and then fractionated extracts of exposed SPMDs using high performance liquid chromatography (HPLC; C_{18} column). Compounds in 55 fractions were separated on the basis of their K_{ow}s and the estrogenic activity of each fraction was assessed using the YES assay. Figure 6.3 shows the results of this test. Fractions 21 (log K_{ow} range = 4.98 to 5.12), 26 (log K_{ow} range = 5.83 to 5.97), 34 (log K_{ow} range = 6.96 to 7.10), and 51 (log K_{ow} range = 9.22 to 9.36) had significant estrogenic activity. This work illustrates the complexity of identifying the causal agents resulting in environmental effects. It also suggests that classic toxicity identification and evaluation procedures (i.e., chromatographic fractionation of toxic extracts with subsequent assay of individual fractions) can be successfully applied to this problem.

6.6. EXPOSURE OF LABORATORY ANIMALS TO SPMD EXTRACTS

In addition to biomarker tests, exposure studies using selected laboratory test animals have recently been conducted to obtain data related to the consequences of the presence of mixtures of chemicals in habitats of concern. For example, amphibian deformities have been widely reported in North America (Souder, 2000), and have resulted in numerous attempts to delineate the causes for the high deformity rates observed (Ouellet et al., 1997). Often, it is very difficult to ascertain the effects of contaminants on natural amphibian populations, due principally to the

variety of environmental variables that may act in concert with the contaminants to cause detrimental effects. Because SPMDs are integrative samplers that accumulate the readily bioavailable lipophilic waterborne-chemicals present in aquatic systems, the chemical mixtures so obtained are time-weighted averages (TWA) of exposure. Thus, the exposure of organisms to the complex mixture of hydrophobic chemicals present at a site can be performed using the purified SPMD sample extract and a physiologically neutral carrier medium.

To ascertain whether waterborne bioavailable contaminants were present in ponds in North-Central Minnesota, Bridges et al. (2004) deployed 16 standard SPMDs at each of two sites for 30 days. At one site, a high rate of amphibian deformities had been documented (ranging from 60 to 75% in the mink frog [*Rana septentrionalis*] and 4 to 20% in the northern leopard frog [*Rana pipiens*], Canfield et al., 2000). The reference site had a stable amphibian population (Helgen, 1999) exhibiting no unusual rates of deformities. Following dialysis and SEC cleanup as described in Chapter 5, the extracts from the deployed SPMD samples within each site were pooled into a single composite sample. Extracts from fabrication, field and process blanks were similarly treated. The composite samples in high purity hexane were solvent-exchanged into sterile DMSO so that each 1-mL extract contained residues equivalent to about one day of exposure (i.e., represents the amount of bioavailable residues sequestered by a standard SPMD in 24 hours). Each of these extracts was added to 1 L of water. The test organisms were exposed to UV radiation, (15.6 $\mu W/cm^2$ UV-B, 914.9 $\mu W/cm^2$ UVA; <1 $\mu W/cm^2$ UV-B, 0.02 $\mu W/cm^2$ UVA; respectively) in the presence and absence of SPMD samples extract, to determine the potential effects of the interaction of contaminants and UV radiation (see Bridges et al., 2004 for a detailed description of the exposure system and statistical design of the experiment).

Following a 45 day exposure (at initiation of the exposure, tadpoles were free-swimming but had not developed hind legs; test solutions were renewed every third day, i.e., static renewal exposure) the *R. pipiens* tadpoles were shipped to the Department of Developmental and Cell Biology at the University of California-Irvine where they were held in culture until metamorphosis at which time deformities were assessed (Gardiner and Hoppe, 1999). At metamorphosis the presence of the following types of deformities were recorded: bony triangles, skin webbing, misoriented limbs, and rigid limbs. Bony triangles were defined as the limb bone being bent back on itself such that the proximal and distal ends of the bone were adjacent to one another (Gardiner and Hoppe, 1999). Individuals with skin webbing displayed continuous bands of skin stretching across a joint, which restricted motion of the limb (Meteyer, 2000). Individuals were classified as having multiple deformities if more than one deformity type was noted on a single individual.

At metamorphosis there was equal mortality in both UV treatments, consequently the UV treatments were pooled within SPMD treatments to increase statistical power when analyzing the deformity data. When analyzed independently of SPMD treatment, no significant deformities were found to occur due to the effects of UV ($p > 0.05$). SPMD extracts from the site exhibiting amphibian

deformities produced significantly more bony triangles ($p = 0.025$) and skin webbing ($p = 0.0183$). The percentage of skin webbings in tadpoles exposed to reference site SPMD extracts and field blanks were not significantly different from water controls. The effects of SPMD treatment on the number of frogs exhibiting multiple deformities was marginally significant ($p = 0.052$). There was no difference among SPMD exposures in the number of misoriented limbs observed ($p = 0.65$). Additional results are described in detail in Bridges et al. (2004).

Based upon these results, it is highly probable that waterborne lipophilic chemicals contribute to the observed deformities in amphibian populations at the impacted site. It is highly improbable that microorganisms or viruses originating from the lake water could have caused the deformities because the transport corridors in the SPMD membrane are no more than 10 Å in cross-sectional diameter (far too small to allow viruses to penetrate the sampler membrane).

Research studies employing exposures of organisms to SPMD extracts in a physiologically neutral medium are increasingly being applied. We envision that this approach will continue to find application in a wide variety of contaminant assessment research studies.

6.7. OVERVIEW OF ADDITIONAL ASSAYS

As suggested earlier, a number of other assays have been successfully used with SPMDs, including an immunoassay for PCBs and the Daphtoxkit F for insecticides. Zajicek et al. (1996) explored the use of a commercial ELISA kit from Ohmicron Corporation (the Ohmicron PCB RaPID Assay) to analyze PCB residues sequestered in SPMDs. He found a positive correlation (i.e., $r^2 = 0.999$, $n = 3$) between the PCB concentrations in SPMDs measured by the ELISA and PCBs measured by GC-ECD. ELISA kits are currently available for a number of types of contaminants, determination of test results is rapid, and the kits are generally inexpensive.

Sabaliūnas et al. (2000) showed that a *Daphnia pulex* immobilization test (Daphtoxkit F) was far more sensitive than Microtox to a mixture of insecticides sequestered in SPMDs. This is not surprising because the OCPs and pyrethroid pesticides present in the enriched SPMD extracts are neurotoxins, and the effect thresholds can be much lower than narcosis-type toxicants. Thus, if insecticides are the contaminants of concern, the Daphtoxkit F approach may have some advantage over Microtox.

6.8. POTENTIAL INTERFERENCES

The use of the above assays to evaluate the toxicity of SPMD extracts is not without potential interferences. Sabaliūnas et al. (1999, 2000) examined the potential role of oleic acid and elemental sulfur as contributors to the toxicity of

extracts from environmentally exposed SPMDs. The toxicity of fatty acids has been attributed to their membrane disturbing properties, which include disruption of the calcium pump by the formation of metal salts (Ewald and Sundin, 1993). As mentioned earlier, oleic acid is an impurity in the triolein used in SPMDs, and may also be produced by biotic or abiotic hydrolysis of methyl oleate and triolein (note that this has not been definitively demonstrated to occur during SPMD exposures). During environmental exposures, a significant portion of this triolein impurity diffuses to the exterior surface of an SPMD, where dissipation and degradation occur. Unfortunately, little or no attenuation occurs to the oleic acid levels in laboratory SPMD-field blanks, -fabrication blanks and -process blanks (i.e., SPMDs not environmentally exposed). Thus, the potential for a differential response exists among field exposed SPMDs and associated QC SPMD samples. Elemental sulfur is taken up by bacterial cells and may be reduced to toxic sulfides (Brouwer and Murphy, 1995). Many types of sediment contain relatively large amounts of elemental sulfur and elemental sulfur is readily accumulated by SPMDs. However, a number of analytical methods can be used to remove these potential interferences from SPMD extracts. These include SEC, as described in the Chapter 5 (both oleic acid and sulfur), acid-treated copper wool (sulfur only, see Petty et al., 1995), and KS (oleic acid). Note that other cleanup techniques are also available for these interferences, especially for oleic acid.

Using a preemptive approach, Lebo et al. (2004) have shown that oleic acid and methyl oleate can be removed from triolein prior to use of the triolein in SPMDs (see Chapters 4 and 5). Dialysates from SPMDs prepared using triolein purified by the Lebo et al. (2004) method exhibited lower acute toxicity (Microtox assay) than SPMDs prepared with unpurified triolein. Also, the YES assay demonstrated that the purification method had removed all background estrogenic activity from SPMD extracts. For these reasons, the use of triolein purified by the method of Lebo et al. (2004) is standard for all SPMD studies conducted at CERC, USGS. Also, SPMDs with triolein purified by the Lebo et al. (2004) method are available from the commercial vendor upon request.

Demonstrating the causal link between a specific chemical or mixture of chemicals and the adverse effects observed in the ecosystem of concern is a Sisyphean task. SPMDs offer an approach to sampling lipophilic chemicals in aquatic and terrestrial ecosystems without having prior knowledge of their identities. Further, inclusion of other abiotic factors, e.g., UV radiation, provides an opportunity to assess the impact of multiple stressors and increases the environmental relevance of the research results. Following the determination of a link between exposure to chemicals and observed effects, investigations to identify the chemical or mixture of chemicals causing the effects can be designed and conducted. In conclusion, combining the power of SPMDs to concentrate the environmentally relevant bioavailable portion of complex mixtures of chemicals present in aquatic and terrestrial environments with selected biomarker tests and exposure studies appears to be a useful screening approach for determining the potential consequences of exposure to bioconcentratable contaminants.

6.9. REFERENCES

Ankley, G.T.; Tillitt, D.E.; Giesy, J.P.; Jones, P.D.; Verbrugge, D.A. 1991, Bioassay-derived 2,3,7,8-tetrahlorodibenzo-*p*-dioxin equivalents in the flesh and eggs of Lake Michigan Chinook Salmon and possible implications for reproduction. *Can. J. Fish. Aquat. Sci.* **48**: 1685–1690.

Bailey, R.E. 1957, The effect of estradiol on serum calcium, phosphorus, and protein of goldfish. *J. Exp. Zool.* **136**: 455–469.

Beauvais, S.J. 1997, Factors Affecting Cholinesterase in Aquatic Animals. Ph.D. Thesis, Iowa State University, Ames Iowa.

Bridges, C.M.; Little, E.E.; Gardiner, D.M.; Petty, J.D.; Huckins, J.N. 2004, Assessing the toxicity of teratogenicity of pond water in North-Central Minnesota to amphibians. *Environ. Sci. Pollut. R.* **11**: 233–239.

Brouwer, H. and Murphy, T. 1995, Volatile sulfides and their toxicity in freshwater sediments. *Environ. Toxicol. Chem.*, **14**: 203–208.

Canfield, J.T., Kerstern, S.M., Vanselow, P. 2000, *1997–1999 Field Season Report*. Unpublished report to Minnesota Pollution Control Agency, Minneapolis, MN.

Cleveland, L.; Little, E.E.; Petty, J.D.; Johnson, B.T.; Lebo, J.A.; Orazio, C.E.; Dionne. J.; Crockett, A. 1997, Toxicological and chemical screening of Antarctica sediments: Use of whole sediment toxicity tests, Microtox, Mutatox, and semipermeable membrane devices (SPMDs). *Mar. Pollut. Bull.* **34**: 194–202.

Colborn, T.; vom Saal, F.S.; Soto, A.M. 1993, Developmental effects of endocrine-disrupting chemicals in wildlife and humans. *Environ. Health Persp.* **101**: 533–553.

Connell, D.W. 1990, *Bioaccumulation of Xenobiotic Compounds*. CRC Press: Boca Raton, FL. p 219.

Ewald, G. and Sundin, P. 1993, ATP Leakage from ELD cells after exposure to steric, monochlorostearic, dichlorostearic, and oleic acids. *Pharmacol. Toxicol.* **73**: 159–162.

Gale, R.W.; Long, E.R.; Schwartz, T.R.; Tillitt, D.E. 2000, Evaluation of planar halogenated and polycyclic aromatic hydrocarbons in estuarine sediments using ethoxyresorufin-o-deethylase induction of H4IIE cells. *Environ. Toxicol. Chem.* **19**: 1348–1359.

Gard, N.W. and Hooper, M.J. 1993, Age dependent changes in plasma and brain cholinesterase activities of Eastern Blue-birds and European Starlings. *J. Wildlife Dis.* **29**: 1–7.

Gardiner, D.M. and Hoppe, D.M. 1999, Environmentally induced limb malformations in mink frogs (Rana septentrionalis). *J. Exp. Zool.* **284**: 207–216.

Helgen, J.C. 1999, Minnesota Pollution Control Agency, Minneapolis, M.N. Personal communication.

Huckins, J.N.; Petty, J.D.; Lebo, J.A.; Orazio, C.E.; Prest, H.F.; Tillitt, D.E.; Ellis, G.S.; Johnson, B.T.; Manuweera, G.K. 1996, Semipermeable Membrane Devices (SPMDs) for the Concentration and Assessment of Bioavailable Organic Contaminants in Aquatic Environments. In *Techniques in Aquatic Toxicology*; Ostrander, G.K., Ed.; CRC Press: Boca Raton, FL; pp. 625–655.

Huckins J.N.; Prest H.F.; Petty J.D.; Røe T.I.; Meadows J.C.; Echols K.R.; Lebo J.A.; Clark R.C. 1998, A Overview of the Results of Several Comparisons of Lipid-containing Semipermeable Membrane Devices (SPMDs) and Biomonitoring Organisms for Assessing Organic Chemical Exposure. *Abstracts of the 19th Annual National Meeting; SETAC*; Charlotte, NC; November 15–19, 1998; p 215.

Huckins, J.N.; Petty, J.D.; Prest, H.F.; Clark, R.C.; Alvarez, D.A.; Orazio, C.E.; Lebo, J.A.; Cranor, W.L.; Johnson, B.T. 2002, *A Guide for the Use of Semipermeable Membrane Devices (SPMDs) as Samplers of Waterborne Hydrophobic Organic Contaminants;* Publication No. 4690; American Petroleum Institute (API): Washington, DC.

Johnson, B.T. 1998, Microtox® Toxicity Test System—New Developments and Applications. In *Microscale Testing in Aquatic Toxicology;* Wells, P.G., Lee, K., Blaise, C., Eds; CRC Press: Washington, D.C.; pp. 201–218.

Johnson, B.T.; Petty, J.D.; Huckins, J.N.; Lee, K. 2004, Hazard assessment of simulated oil spill on intertidal areas of the St. Lawrence River with SPMD-TOX. *Environ. Toxicol.* **19**: 329–335.

Jones, S.B. and King, L.B. 1995, Muscarinic cholinergic receptors in brain and atrial membranes of adult Brook Trout Salvelinus fontinalis measured by radiolignad binding techniques. *Comp. Biochem. Physiol*. **112**: 43–50.

Kočí, V.; Mlejnek, M.; Kochánková, L. 2003, Toxicological evaluation of exposed SPMD membranes. *Cent. Eur. J. Chem.* **1**: 28–34.

Lebo, J.A.; Zajicek, J.L.; Huckins, J.N.; Petty, J.D.; Peterman, P.H. 1992, Use of semipermeable membrane devices for in situ monitoring of polycyclic aromatic hydrocarbons in aquatic environments. *Chemosphere* **25**: 697–718.

Lebo, J.A.; Gale, R.W.; Petty, J.D.; Tillitt, D.E.; Huckins, J.N.; Meadows, J.C.; Orazio, C.E.; Echols, K.R.; Schroeder, D.J.; Inmon, L.E. 1995, Use of the semipermeable membrane device (SPMD) as an in situ sampler of waterborne bioavailable PCDD and PCDF residues at sub-part-per-quadrillion concentrations. *Environ. Sci. Technol.* **29**: 2886–2892.

Lebo, J.A.; Almeida, F.V.; Cranor, W.L.; Petty, J.D.; Huckins, J.N.; Rastall, A.; Alvarez, D.A.; Mogensen, B.B.; Johnson, B.T. 2004, Purification of triolein for use in semipermeable membrane devices (SPMDs). *Chemosphere* **54**: 1217–1224.

Lorenzen, A. and Kennedy, S.W. 1993, A fluorescence-based protein assay for use with a microplate reader. *Anal. Biochem*. **214**: 346–348.

Mackay, D.; Shiu, W.Y.; Ma, K.C. 1992a, *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals: Monoaromatic Hydrocarbons, Chlorobenzenes, and PCBs*; Lewis Publishers: Chelsea, MI.; Vol. I.

Mackay, D.; Shiu, W.Y.; Ma, K.C. 1992b, *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals: Polynuclear Aromatic Hydrocarbons, Polychlorinated Dioxins, and Dibenzofurans*; Lewis Publishers: Chelsea, MI.; Vol. II.

Mackay, D.; Shiu, W.Y.; Ma, K.C. 1997, *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals: Pesticide Chemicals*; Lewis Publishers: Boca Raton, FL; Vol. V.

Meteyer, C.U. 2000, *Field Guide to Malformations of Frogs and Toads with Radiographic Interpretations*. USGS National Wildlife Health Center, Madison, WI; Biological Science Report No. USGS/BRD/BSR-2000-0005.

Microbics Corporation 1992, Condensed Protocol for Basic Test, Using Organic Solvent Sample Solubilization. *Microtox Manual, Vol. III; Condensed Protocols*; Carlsbad, CA; 13, 226–232.

Ouellet, M.; Bonin, J.; Rodrigue, J.; DesGranges, J.L.; Lair, S. 1997, Hindlimb deformities (ectromelia, ectrodactyly) in free-living anurans from agricultural habitats. *J. Wildlife Dis*. **33**: 95–104.

Parrott, J.L. and Tillitt, D.E. 1997, The use of Semipermeable Membrane Devices (SPMDs) to Concentrate Inducers of Fish Hepatic Mixed Function Oxygenase (MFO). In *Ecotoxicology: Responses, Biomarkers, and Risk Assessment. An OECD Workshop;* Zelikoff, J.T., Ed.; SOS Publications: Fair Haven, NJ.; pp. 185–196.

Parrott, J.L.; Backus, S.M.; Borgmann, A.I.; Swyripa, M. 1999, The use of semipermeable membrane devices to concentrate chemicals in oil refinery effluent on the Mackenzie River. *Arctic* **52**: 125–138.

Petty, J.D.; Huckins, J.N.; Orazio, C.E, Lebo, J.A.; Poulton, B.C.; Gale, R.W.; Charbonneau, C.S.; Kaiser, E.M. 1995, Determination of bioavailable organochlorine pesticide residues in the Lower Missouri River. *Environ. Sci. Technol.* **29**: 2561–2566.

Petty, J.D.; Poulton, B.C.; Charbonneau, C.S.; Huckins, J.N.; Jones, S.B.; Cameron, J.T.; Prest, H.F. 1998, Determination of bioavailable contaminants in the Lower Missouri River following the flood of 1993. *Environ. Sci. Technol.* **32**: 837–842.

Petty, J.D.; Jones, S.B.; Huckins, J.N.; Cranor, W.L.; Parris , J.T.; McTague, T.B.; Boyle, T.P. 2000, An approach for assessment of water quality using semipermeable membrane devices (SPMDs) and bioindicator tests. *Chemosphere* **41**: 311–321.

Petty, J.D.; Huckins, J.N.; Alvarez, D.A.; Brumbaugh, W.G.; Cranor, W.L.; Gale, R.W.; Rastall, A.C.; Jones-Lepp, T.L.; Leiker, T.J.; Rostad C.E.; Furlong, E.T. 2004, A holistic passive integrative

sampling approach for assessing the presence and potential impacts of waterborne environmental contaminants. *Chemosphere* **54**: 695–705.

Prest, H.F.; Hodgins, M.M.; Petty, J.D.; Huckins, J.N.; Lebo, J.A.; Orazio, C.E.; Gibson, V. 1997, *Laboratory Comparisons of Oysters and Semipermeable Membrane Devices (SPMDs)*. USGS Midwest Science Center, Columbia, MO; Report to the American Petroleum Institute (API): Washington; DC; API Report No. DR 360; p. 105.

Rastall, A.C.; Neziri, A.; Vukovic, Z.; Jung, C.; Mijovic, S.; Hollert, H.; Nikcevic, S.; Erdinger, L. 2004, The identification of readily bioavailable pollutants in Lake Shkodra/Skadar using semipermeable membrane devices (SPMDs), bioassays and chemical analysis. *Environ. Sci. Pollut. R.* **11**: 240–253.

Routledge, E.J. and Sumpter, J.P. 1996, Estrogenic activity of surfactants and some of their degradation products assessed using a recombinant yeast screen. *Environ. Toxicol. Chem.* **15**: 214–248.

Sabaliūnas, D.; Lazutka, J.; Sabaliūniene, I.; Sodergren, A. 1998, Use of semipermeable membrane devices for studying effects of organic pollutants: Comparison of pesticide uptake by semipermeable membrane devices and mussels. *Environ. Toxicol. Chem.* **17**: 1815–1824.

Sabaliūnas, D.; Ellington, J.; Sabaliūniene, I. 1999, Screening bioavailable hydrophobic toxicants in surface waters with semipermeable membrane devices: Role of inherent oleic acid in toxicity evaluations. *Ecotox. Environ. Safe.* **44**: 160–167.

Sabaliūnas, D.; Lazutka, J.R.; Sabaliūniene, I. 2000, Acute toxicity and genotoxicity of aquatic hydrophobic pollutants sampled with semipermeable membrane devices. *Environ. Pollut.* **109**: 251–265. (was 2000b)

Souder, W. 2000, *A Plague of Frogs: The Horrifying True Story*. Hyperion Press: New York.

Steevens, J.A.; Bauman, P.C.; Jones, S.B. 1996, A comparison of β-adrenoceptors and muscarinic cholinergic receptors in tissues of brown bullhead catfish Ameiurus nebulosus from the Black River and Old Woman Creek Ohio. *Environ. Toxciol. Chem.* **15**: 1551–1554.

Tillitt, D.E.; Giesy, J.P.; Ankley, G.T. 1991, Characterization of the H4IIE rat hepatoma cell bioassay as a tool for assessing toxic potency of planar halogenated hydrocarbons in environmental samples. *Environ. Sci. Technol.* **25**: 87–92.

Whyte, J.J.; Jung, R.E.; Schmitt, C.J.; Tillitt, D.E. 2000, Ethoxyresorufin-O-deethylase (EROD) activity in fish as a biomarker of chemical exposure. *Crit. Rev. Toxicol.* **30**: 347–570.

Whyte, J.J.; Schmitt, C.J.; Tillitt, D.E. 2004, The H4IIE cell bioassay as an indicator of dioxin-like chemicals in wildlife and the environment. *Crit. Rev. Toxicol.* **34**: 1–83.

Zajicek, J.L.; Tillitt, D.E.; Huckins, J.N.; Petty, J.D.; Potts, M.E.; Nardone, D.A. 1996, Application of Enzyme-Linked Immunosorbent Assay (ELISA) for Measurement of Polychlorinated Biphenyls (PCBs) from Hydrophobic Solutions: Extracts of Fish and Dialysates of Semipermeable Membrane Devices (SPMDs). In *Environmental Immunochemical Methods*; ACS Symposium Series 646; American Chemical Society: Washington, D.C.; Chapter 26, pp 307–325.

Chapter 7

COMPARISONS TO BIOMONITORING ORGANISMS

7.1. BACKGROUND

Numerous side-by-side comparisons of the accumulation of hydrophobic organic chemicals (HOCs) by lipid-containing semipermeable membrane devices (SPMDs) and a variety of biomonitoring organisms (BMOs) have been conducted (Prest et al., 1992, 1995a, 1995b, 1997; Ellis et al., 1995; Herve et al., 1995; Huckins et al., 1996, 1998a, 2004; Kolok et al., 1996; Peven et al., 1996; Gale et al., 1997; Hofelt and Shea, 1997; Moring and Rose, 1997; Meadows et al., 1998; Sabaliūnas et al., 1998; Wang et al., 1998; Axelman et al., 1999; Utvik et al., 1999; Utvik and Johnsen, 1999; Echols et al., 2000; Granmo et al., 2000; Leppanen and Kukkonen, 2000; Baussant et al., 2001; Booij et al., 2002; Følsvik et al., 2002; Gatermann et al., 2002; Lu et al. 2002; Wang et al., 2002; Richardson et al., 2003; Verweij et al., 2004). The primary goal of these comparisons was to determine the commonality in the types and concentrations of HOCs accumulated by the two monitoring matrices. Both similarities and differences have been observed in the accumulation patterns of SPMDs and BMOs. The inconsistencies of these findings are not surprising in view of the differences between inanimate SPMDs and living organisms. Species of BMOs used for field assessments vary depending on the environmental characteristics of deployment sites and project goals. Significant

physiological, anatomical, and behavioral differences exist across BMO species that may affect the accumulation of HOCs. In contrast, the accumulation of HOCs by SPMDs is solely mediated by passive diffusional and partitioning processes, which are the basis of equilibrium partition (EP) theory. Thus, good correlations between analyte concentrations in side-by-side exposures of BMOs and SPMDs (Hofelt and Shea, 1997; Meadows et al., 1998; Sabaliūnas et al., 1998; Utvik and Johnsen, 1999; Wang et al., 2002) suggest that passive partitioning and diffusional processes ultimately control the residue accumulation patterns in the BMOs, while poor correlations (e.g., Gale et al., 1997; Moring and Rose, 1997) suggest that more complex biological processes largely control residue accumulation patterns in BMOs (Huckins et al., 2004).

For a standard SPMD (see Section 4.4.) of set size, the variables potentially affecting HOC accumulation are limited to physicochemical properties of the analyte, exposure site conditions, and exposure scenario factors such as the constancy of chemical concentrations during the exposure period (Huckins et al., 1993, 2002a, 2002b; Booij et al., 1998). A number of SPMD calibration studies (see Appendix A) have been conducted to determine the effects of analyte physicochemical properties and site conditions such as temperature and flow dynamics on SPMD accumulation rates and equilibrium partition coefficients. Beyond this, PRCs (i.e., performance reference compounds) can be added to SPMD lipid prior to exposures to account for the effects of site-specific conditions on SPMD sampling (Huckins et al., 2002a; also see Chapters 1 and 3 for more information). This ability to generate chemical-specific calibration data and then adjust these values to site-specific conditions means that analyte concentrations obtained using SPMDs are directly comparable across sample sites. Thus, SPMDs are well suited for reliable determinations of HOC sources, concentration gradients and concentration estimates, but their utility for the estimation of bioaccumulation factors (*BAF*s; see Chapter 1 for definition) in species of concern is not as well defined.

The physicochemical properties of chemicals, site-specific exposure conditions, and the exposure scenario, also affect the bioconcentration or bioaccumulation of HOCs (Mackay et al., 1992a, 1992b; Goudreau et al., 1993; Baumard et al., 1998a, 1998b). As suggested earlier, certain behavioral, physiological, and anatomical characteristics of BMO species affect bioaccumulation (Huebner and Pynnönen, 1992; Gilek et al., 1996; Björk and Gilek, 1997; Moring and Rose, 1997; Baumard et al., 1998a; Axelman et al., 1999; Baussant et al., 2001). For example, Björk and Gilek (1997) found that laboratory *BAF*s of selected polychlorinated biphenyl (PCB) congeners in blue mussels (*Mytilus edulis*) varied up to two orders of magnitude due to differences in food ration. Surprisingly, the largest *BAF* was observed at a relatively low food ration of about 0.08 mg L^{-1} particulate organic carbon (*POC*) or 1900 cells mL^{-1}, and higher rations resulted in an exponential decline in *BAF*s. In regard to finfish, Jimenez et al. (1987) found that benzo[*a*]pyrene *BAF*s in bluegill sunfish (*Lepomis macrochirus*) were at least five times higher in unfed fish than in fed fish. Gilek et al. (1996) showed that equilibrium *BAF*s of PCB congeners fell significantly with increases in the size

and mass of blue mussels. In the presence of toxic chemicals, juvenile and adult bivalve mollusks can close their valves for extended periods (Goudreau et al., 1993; ASTM, 1996), which greatly impacts bioaccumulation. Also, xenobiotic metabolism can greatly affect steady-state concentrations of some HOCs in BMO tissues. Some variables known to affect bioaccumulation are difficult to quantify *a priori*, such as intra- and interspecies variability, condition factors, and the role of developmental stages (Franke et al., 1994). Finally, the potential impacts of many of the aforementioned variables and others on equilibrium bioconcentration factors (*BCF*s; see definition in Chapter 1) and *BAF*s are discussed in three ASTM Standard Guides (ASTM, 1984, 1996, 2001), and a review of data from Mackay et al. (1992a, 1992b, 1997) shows orders of magnitude variations in BMO *BCF*s, and uptake (k_us) and depuration (k_es) rate constants for the same chemical (Huckins et al., 2004).

To reduce the effects of differences in uptake kinetics and lipid contents on residue concentrations in BMOs, exposures are typically designed to attain equilibrium concentrations, and the concentrations are lipid normalized. When using the EP approach to assess exposure concentrations, sources, concentration gradients, etc., investigators assume that *BAF*s are independent of exposure concentration while concentrations in tissues or lipids are proportional to exposure concentrations, and that lipid normalization reduces the variability of whole body tissue concentrations. However, these assumptions are not always borne out in studies reported in the peer-reviewed literature. For example, Axelman et al. (1999) found that *BAF*s of individual polycyclic aromatic hydrocarbons (PAHs) in blue mussels deployed in marine water near a smelter were about one order of magnitude greater than the equilibrium *BAF*s of simultaneously deployed blue mussels at a nearby marine reference site that had similar levels of PAHs. Furthermore, the reference-site *BAF*s were about one order of magnitude greater than the *BAF*s of blue mussels reported in the literature. Also, there is debate in the literature about the appropriateness of normalizing tissue concentrations to extractable lipid contents (e.g., Schneider, 1982; Randall et al., 1991; Hebert and Keenleyside, 1995; Stow, 1995; Gray, 2002). As discussed in Section 5.6.2., lipid-normalization of SPMD concentrations is inappropriate in most cases.

Regardless of the marked differences between SPMDs and BMOs, there are some fundamental similarities in the characteristics and processes affecting the accumulation of HOCs in the two matrices. For example, diffusion of non-polar compounds through nonporous organic polymers such as used in the SPMD has been shown to be similar to diffusion across biomembranes (Lieb and Stein, 1969). Furthermore, the processes of solute diffusion across the water boundary layer (WBL) and the lipid-like or lipid-containing membranes of SPMDs and aquatic organisms, and the partitioning between the lipids and the exposure water, are important factors in the accumulation of HOC residues in both matrices. The triolein used in SPMDs is a major lipid in fishes (Huckins et al., 1990) and is representative of fats or the neutral lipid class (Chiou, 1985), which is the largest storage site of persistent HOCs in many organisms.

7.2. IMPLICATIONS OF SELECTED MODELS USED FOR SPMDs AND BMOs

Herein, we examine several equations which are used to determine *BCF*s and *BAFs,* SPMD-water partition coefficients (K_{sw}s), and the more complex exchange processes of some BMOs. Hopefully, the formulation and the assumptions behind these equations further clarify some of commonalities and differences between residue accumulation in BMOs and SPMDs.

Phillips (1980) and Phillips and Rainbow (1993) have stated that each species of aquatic BMO exhibits unique uptake and elimination kinetics for a particular HOC. The ramification of this statement is revealed in the following simple one-compartment model, which is often used for the determination of steady-state *BCF*s and K_{sw}s.

$$BCF = k_u/k_e \tag{7.1}$$

where *BCF*s are generally based on whole body residue concentrations, k_u represents the linear portion of the uptake curve and k_e represents the first-order depuration curve. The following equation provides a more detailed formulation of k_e:

$$k_e = k_o A/(M_{wb} BCF) \tag{7.2}$$

where k_o is the overall mass transfer coefficient, A is the surface area of the membrane where solute or vapor exchange occurs, M_{wb} is the whole body tissue mass and in this case *BCF* has units of mL g^{-1}. The group $k_o A$ can be viewed as the apparent water sampling rate (R_s), with units of L d^{-1}. When the sorption capacity of non-lipid phases can be neglected, the *BCF* can be written in terms of the lipid-water partition coefficient (K_{Lw}, in mL mL^{-1}) and the lipid volume (V_L).

$$BCF \approx K_{Lw} V_L/M_{wb} \tag{7.3}$$

Inspection of Eqs. 7.2 and 7.3 shows that k_e is inversely proportional to the lipid content of the biota (V_L/M_{wb}), whereas k_u is independent of the lipid content. Thus, the generally much lower neutral lipid contents of BMOs result in much higher values of BMO k_es. Also, the BMO *BCF*s are generally much smaller than the SPMD K_{sw}s.

Equation 7.1 utilizes exchange coefficients to predict steady-state *BCF*s and K_{sw}s, and the model assumptions include a uniform lipid phase enclosed in a non-interactive membrane. The model shows that the magnitude of a BMO's *BCF* or an SPMD's K_{sw} is affected by variations in k_u and/or k_e, unless both constants rise or fall proportionally. In the case of SPMDs, Huckins et al. (1993, 2002a) have shown that the uptake and release process is essentially isotropic for HOCs. When residue exchange is isotropic, K_{sw}s will remain relatively constant even when exposure conditions affect SPMD k_u and k_e values. This is not always the case for BMOs, yet isotropic exchange is a fundamental assumption of EP theory.

Metabolism of PAHs by the cytochrome P-450-dependent enzymes in fish is a classic deviation from EP theory. When PAH biotransformation product data are available (e.g., concentrations of PAH conjugates or other metabolites in bile),

two depuration rate constants can be used as follows

$$BCF = k_u/(k_e + k_{em}) \tag{7.4}$$

where k_{em} is the first-order rate constant for HOC metabolism and egestion of metabolites via the bile, feces, and urine, and the rate constant k_e represents outward diffusion of HOCs across the gills or skin. Deviations of loss rates from first-order kinetics invalidate the model for the determination of *BCF*s and result in anisotropic exchange kinetics. Even when the overall depuration of PAHs by fish follows first order kinetics, the resulting tissue concentrations are not always proportional to ambient environmental concentrations. A study reported by Gale et al. (1997) supports the contention that tissue residues are often not proportional to ambient water concentrations (see Chapter 8).

In cases where the depuration of HOCs from BMOs involves enzyme-mediated biotransformations (Eq. 7.4) or active transport mechanisms, and environmental concentrations are high (e.g. near a point source), depuration rates have been shown to follow Michaelis-Menten kinetics (Spacie and Hamelink, 1985). Michaelis-Menten kinetics is elicited when an enzyme or active transport system is saturated with a chemical. This type of kinetics is characterized by lower values of k_es at sites with high HOC concentrations. If k_us are unchanged at high concentration sites, Michaelis-Menten kinetics will result in elevated *BAF*s. However, if chemical concentrations become toxic, finfish likely avoid the area and sessile organisms such as mussels may close their valves for extended periods (Huckins et al., 2004).

A number of models have been developed that include physiologically controlled bioaccumulation parameters (Bruggeman et al., 1981; Rand and Petrocelli, 1985; Gobas et al., 1993; Björk and Gilek, 1997). Following the work of Bruggemann et al. (1981), the relative roles of respiratory and dietary uptake, and residue metabolism can be examined for BMOs using

$$\mathrm{d}C_B/\mathrm{d}t = SFC_f + (E_x R_v/M_{wb})C_w - k_e C_B - k_{em} C_B \tag{7.5}$$

where C_B is the HOC concentration in whole body BMO tissue, S is the fractional assimilation or absorption efficiency of HOCs across the gut, F is the feeding or ingestion rate per unit mass of organism (i.e., g^{-1} d^{-1}), C_f is the HOC concentration in the food, E_x is the fractional extraction efficiency of HOCs from water ventilated through the gills, R_v is the ventilation or filtration rate (bivalves or other filter feeders) of water through the respiratory lamellae (gills) in L d^{-1}, M_{wb} is the mass of whole body tissues, and C_w is given in units of g L^{-1}. A major assumption underlying Eq. 7.5 is that uptake processes and removal processes are additive. The group $k_e C_B$ can be changed to $(k_e + G_p)C_B$, where G is the relative growth rate (g g^{-1} d^{-1}), which can be positive or negative (note: changes in lipid content must be considered as well). Both gill-extraction efficiencies (E_x) and gut-assimilation efficiencies (S) vary considerably (e.g., E_x ranges from about 7 to 60% (McKim et al., 1985) and S ranges from about 1 to 90% (Wang and Fisher, 1999; Thomann, et al., 1992), depending on HOC K_{ow} and molecular structure (Huckins et al., 1998b; Bucheli and Gustafsson, 2000), type of organism (Gobas et al., 1993; Wang

and Fisher, 1999), and the quality of ingested material (Wang and Fisher, 1999; Bucheli and Gustafsson, 2000). Also, behavioral factors such as the avoidance of toxics and differential flow of blood to tissues are not modeled even though they may affect tissue concentration. Equations such as 7.5 are not commonly used in field studies because data to determine the associated rate constants are seldom available. Furthermore, the expansion of models to include additional processes must always be justified in light of the potential increase in error propagation.

Factors other than organism physiology contribute to the variability of *BAF*s and related parameters (i.e., k_us and k_es) reported in the literature. Differences in analytical chemistry conventions used for tissue weighting can be a source of errors and may be problematic when comparing SPMD and BMO concentrations (see Chapter 5). Briefly, tissue weighting approaches include wet weights, dry weights and lipid weighting or normalization. To determine *BAF*s, k_us and k_es, wet tissue concentrations are generally used for fish, while dry tissue weights are generally used for bivalve concentrations. Unlike BMOs, SPMD weighting is standardized to the weight of a whole SPMD. Lipid normalized data are generally derived from dividing tissue concentrations by total lipid concentrations. Hebert and Keenleyside (1995) have pointed out that lipid normalization can reduce precision and the power of statistical tests to detect differences in the data. The lipid normalization approach is based on the assumption that a significant relationship exist between contaminant concentration in tissues and their total lipid concentration. However, Schneider (1982) found poor correlations between HOC concentrations in a marine fish and the total extractable lipid concentration of the tissues. Only when using the neutral triglyceride fraction (i.e., storage fats such as triolein) of the total lipid extracts did correlations improve to an acceptable level. Unfortunately, many bivalves and invertebrates do not have significant levels of triglycerides.

Using PCB levels in five species of freshwater finfish, collected over a course of 20 years, Stow (1995) failed to find a significant relationship between residue concentrations and percent lipid. The finding of Randall et al. (1991) may explain part of the problem. They found that using different extraction solvents for tissues, lipid concentrations can vary by 3.5 fold and that laboratories vary widely in the type of solvents used for the extraction of HOC residues in tissues. Whole body lipid levels across BMO species typically vary from about 1 to 15% (based on wet tissue weights). Thus, the lipid mediated differences in BMO tissue concentrations may be as high as 15 fold. Unlike BMOs, Standard SPMDs have a uniform lipid content, which precludes any need for lipid normalization, and the extraction or dialysis solvent is standardized.

7.3. COMPARISON OF SPMDs AND BMOs

The series of steps involved in the accumulation of HOCs in BMOs is more complex than those associated with residue accumulation in SPMDs. For example,

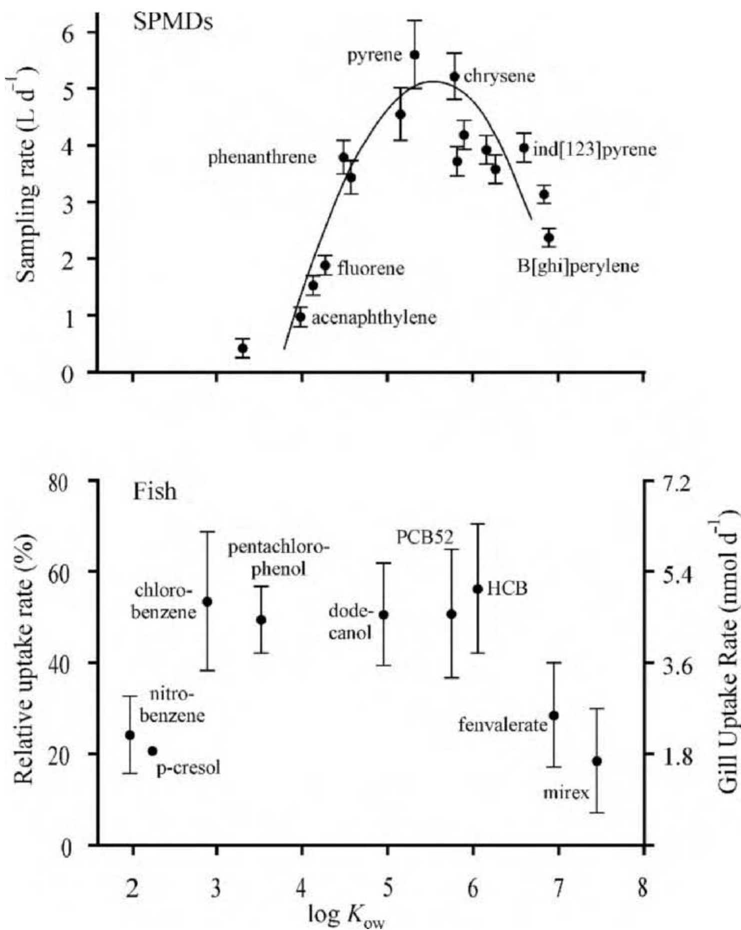

Figure 7.1 Comparison of the patterns of organic contaminant uptake rates (as related to log K_{ow}s) by SPMDs and across fish gills (McKim et al., 1985). Reprinted with permission from the American Petroleum Institute (Huckins et al., 2002).

the rate of residue transport from the gill epithelium via the blood to lipid storage compartments is complicated by differences in blood flows to various tissue groups (Barron, 1990). Thus, comparisons of the relative flux of chemicals across the barriers associated with the water-blood interface (i.e., gills or skin) of organisms and across the barriers to SPMD uptake should provide the best correlations between BMOs and SPMDs, because of the lack of confounding factors such as differential blood flow to tissues, *in vivo* biotransformation of residues, and marked variations in the amounts and types of lipids. Using this approach, Figure 7.1 shows that a plot of organic chemical uptake efficiencies across trout gills (McKim et al., 1985), relative to their log K_{ow}s, has the same parabolic shape as a plot of SPMD

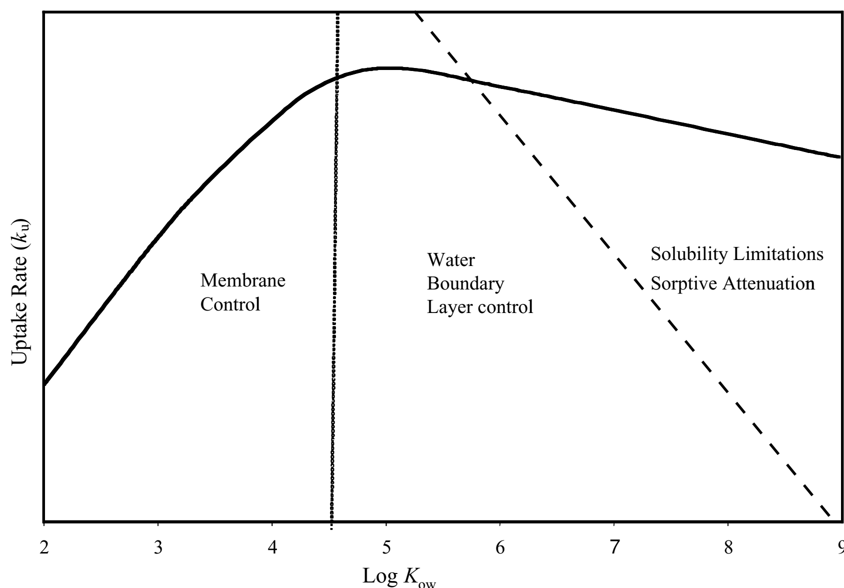

Figure 7.2 Plot of rate constants for the uptake of HOCs by SPMDs and fish, relative to compound hydrophobicity. Also, potential rate-limiting steps/factors are illustrated as related to compound hydrophobicity. Low to moderate flow and turbulence were assumed.

sampling rates of priority pollutant PAHs versus log K_{ow}s. This illustration suggests that similar rate limiting steps govern the uptake of organic chemicals across the water-blood barriers of fish and across the barriers to solute flux into SPMDs.

The parabolic shape of the curves in Figure 7.1 can be partly explained by the following discussion on mass-transfer phenomena (also, see Figure 7.2 and the related discussions in Chapter 3). For chemicals with log K_{ow}s < 4, the rate limiting step in chemical uptake appears to be permeation across the fish respiratory lamellae (gills) and the SPMD membrane (McKim et al., 1985; Huckins et al., 1999 and 2002b). In this case, uptake rate constants and extraction efficiencies rise with increasing membrane-water partition coefficients (K_{mw}s) of chemicals. The region of uptake rate constants and extraction efficiencies represented by compounds with log K_{ow}s ≥ 4 but ≤ 5 is characteristic of the transition from membrane rate control to external WBL rate control. During this transition, resistance in the membrane decreases (due to rising values of K_{mw}; see Eqs. 3.8 and 3.9) to the point where it is similar in magnitude to the resistance of the WBL. Uptake rate constants and extraction efficiencies are often highest for chemicals with log K_{ow}s > 5 but ≤ 6, where membrane resistance becomes insignificant. Finally, when log K_{ow}s of HOCs increase beyond 6, uptake rate constants and extraction efficiencies are expected to slowly fall due to the decreasing molecular diffusion coefficients of compounds with increasingly large molar volumes (see solid line in Figure 7.2). However, plots of uptake rate constants and extraction efficiencies of SPMDs and

BMOs often show greater declines in the sampling of high K_{ow} compounds than can be accounted for by molecular size related decreases in diffusion coefficients (Figure 7.1 and dashed line in Figure 7.2). This phenomenon may be due to a combination of factors described in Chapter 3 such as attenuation of very hydrophobic solute concentrations by sorption to particulate and dissolved organic carbon (i.e., an artifactual overestimation of freely dissolved chemicals), solubility limitations, a switch back to membrane control due to steric impedance (Barron, 1990), ventilation volume limitations of very hydrophobic chemicals, and the reduced solubility of high molecular weight HOCs in high molecular weight storage fats or neutral triglycerides (Chiou, 1985; Schüürman and Klein, 1988). Much of this discussion as well as Figure 7.2 is based on the assumption that the flow and turbulence is low to moderate. When flow and turbulence are high, the switching point between membrane control and WBL control (see vertical dotted line in Figure 7.2) would be shifted to higher K_{ow}s in the case of SPMDs. The effects of flow dynamics on turbulence around BMO gill structures are unknown.

Table 7.1 provides a comparison of selected physical characteristics of a standard SPMD membrane and the gills of fish. The surface area per unit mass of SPMD is at least 9-fold larger than the surface area of fish gills per unit mass of organism. Earlier, Eq. 3.15 showed the direct relationship between surface area of the membrane and uptake rates. The SPMD membrane is at least 8 times thicker than the gill integument of fishes. Equation 3.50 showed the inverse relationship of membrane or barrier thickness (δ) in the mass transfer of solutes. Table 7.1 also shows that the estimated diameters of transient cavities in the low density polyethylene membrane used for SPMDs ranges up to about 10 Å (Hwang and Kammermeyer, 1984), and larger at elevated temperatures. Opperhuizen et al. (1985) postulated that the size of transient cavities in lipoidal regions of biomembranes is $\leq$9.8 Å based on the lack of octachloronaphthalene (log K_{ow} = 8.4, molecular cross-sectional diameter = 9.8 Å) accumulation in fish. More recently, Booij et al. (2002) found that the polybromonated diphenyl ether (PBDE) 209 (decabromodiphenyl ether)

TABLE 7.1 Comparison of Selected Properties of Standard SPMDs and Fish Gills

	Standard SPMD	Fish[a]
Membrane:		
composition	low density polyethylene	complex lipoprotein bilayer
molecular size cutoff	≈10 Å	≈9.5 Å[b]
surface area	≈100 cm^2 g^{-1}	1 – 9 cm^2 g^{-1} tissue
thickness	≈86 μm	0.5 – 11 μm blood-water barrier
Exchange kinetics:		
rate control	membrane if log K_{ow} < 4.5 diffusion layer if log K_{ow} ≥ 4.5	membrane if log K_{ow} < 3 diffusion layer if log K_{ow} ≥ 3

[a] Data obtained from Hayton and Barron (1990) and Gobas et al. (1986).
[b] Hypothesized molecular size cutoff by Opperhuizen et al. (1985).

was not accumulated by blue mussels but was accumulated by SPMDs. The effective molecular cross-sectional diameter of all PBDEs with 2,5-Br substitution on at least one ring is 9.6 Å. These results indicate that steric impedance is not a likely explanation for the lack of PBDE 209 accumulation in mussels. Residues of PBDE 209 were present in the gut of mussels but after a 24 hour depuration period, these residues were essentially eliminated, indicating no assimilation and tissue incorporation.

Not shown in Table 7.1 is the effective thickness of the WBLs (see Figure 3.1), which varies with flow velocity and turbulence and often is the rate limiting step in solute mass transfer. Under quiescent or stagnant conditions, the effective thickness of a WBL can be as much as 1 mm and as much as several mm for an air boundary layer (ABL). Under highly turbulent conditions, the effective thickness of the WBL and the ABL can be thinned to only a few μm. Note that compound hydrophobicity plays an important role in which barrier (e.g., membrane or water) has the greatest resistance to mass transfer as shown by Eq. 3.9. Thus, Table 7.1 gives an estimate of the log K_{ow} values, where the rate-limiting step in mass transfer changes from membrane to WBL control.

Except under turbulent exposure conditions, the effective thickness and related resistance to mass transfer of the SPMD WBL is expected to be greater than that associated with the gills of an aquatic organism. This is due to the active pumping action or ventilation required for respiration, which can be a little more than 1 L d^{-1} g^{-1} for fish under demanding conditions. When bivalves are filter feeding, ventilation rates may be much higher and can be as high as 20 L d^{-1} g^{-1} (e.g., zebra mussel *Dreissena polymorpha*). A review of Eq. 7.5 shows the importance of ventilation rate (R_v), in combination with extraction efficiency, in the clearance or uptake rates of HOCs. Figure 7.1 indicates that gill extraction efficiencies are as high as about 60%. Unfortunately, there is little data on the effects of ventilation volume or flow velocity through the gills on solute extraction efficiencies. Because high flow and turbulence thins the WBL and reduces resistance to mass transfer, extraction efficiencies would be expected to increase. However, high flows also increase the probability of channeling (i.e., insufficient time for solute molecules in the center of interlamellar channels to make random contact with membrane surfaces) through interlamellar spaces, reducing extraction efficiencies. Lower rates of oxygen uptake have been shown for high flow rates (i.e., perfusion) through the gills (Bayne et al., 1976) of rainbow trout (*Oncorhynchus mykiss*).

7.3.1. Similarity of Uptake Rate Constants

Meadows et al. (1998) conducted a 28 d exposure of brown trout (*Salmo trutta*), standard SPMDs and hexane filled dialysis bags (Södergren, 1987) to spring water (total organic carbon <1 mg L^{-1}) contaminated with PCBs. Trout were not fed during the exposure, and temperature and flow conditions remained constant throughout the exposure. A good correlation ($r^2 = 0.89$) was found between the uptake rate constants ($k_{u,F}$s) for whole body trout and the uptake rate constants

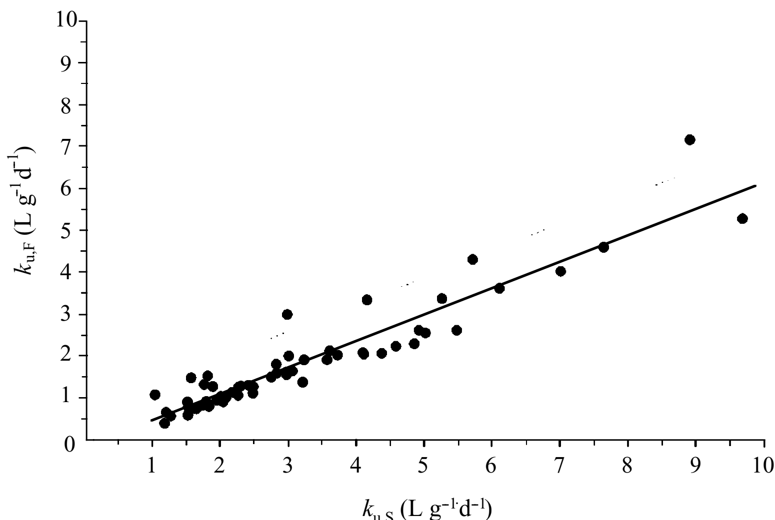

FIGURE 7.3 Comparison of brown trout (*Salmo trutta*) and whole SPMD uptake rate constants ($k_{u,F}$s and $k_{u,S}$s, respectively) for PCB congeners. Reprinted from Meadows et al. (1998), copyright (1998); reproduced with permission from American Chemical Society.

($k_{u,s}$s) for whole SPMDs (Figure 7.3). Congener uptake rate constants for SPMDs averaged about 2-fold higher than those for trout over a 500-fold range in K_{ow}s. The uptake rates of congeners by both trout and SPMDs slowly declined with increasing K_{ow}s. This is consistent with WBL controlled uptake, where diffusion coefficients in the WBL slowly decline with increasing molar volume or molecular weight of solute or vapors. The least hydrophobic congener accumulated by fish and SPMDs had a log K_{ow} of 5.06, which is greater than the log K_{ow} values estimated for the switch from membrane control to WBL control of SPMD and fish uptake rates (Table 7.1).

Even for less persistent HOCs, such as a diverse mixture of PAHs, reasonable correlations have been found between the uptake rate constants for Pacific oysters (*Crassostrea gigas*) and standard SPMDs in controlled side-by-side laboratory exposures (Huckins et al., 2004). In this study, oysters and SPMDs were exposed to three concentrations of PAHs (10 ng L^{-1}, 100 ng L^{-1} and 250 ng L^{-1}; nominal values) in a flow-through system for 20 d and samples were collected every five days. Uptake rate constants were derived from residue concentrations of whole tissue wet weights and whole SPMDs. Figure 7.4 shows that SPMD and oyster k_us correlated well ($r^2 = 0.81$) for the high treatment level, where feeding activity was not observed. Note that the open circles represent data points not included in the regression analysis, because there was a systematic bias (likely an analytical artifact) of values for PAHs with log K_{ow}s within the range of 5.6 to 6.4. Overall, SPMD k_us averaged 1.4 fold higher than the oyster k_us and the *C.V.*s associated with mean SPMD and oyster k_us were 17% and 39%, respectively. Eastern oyster

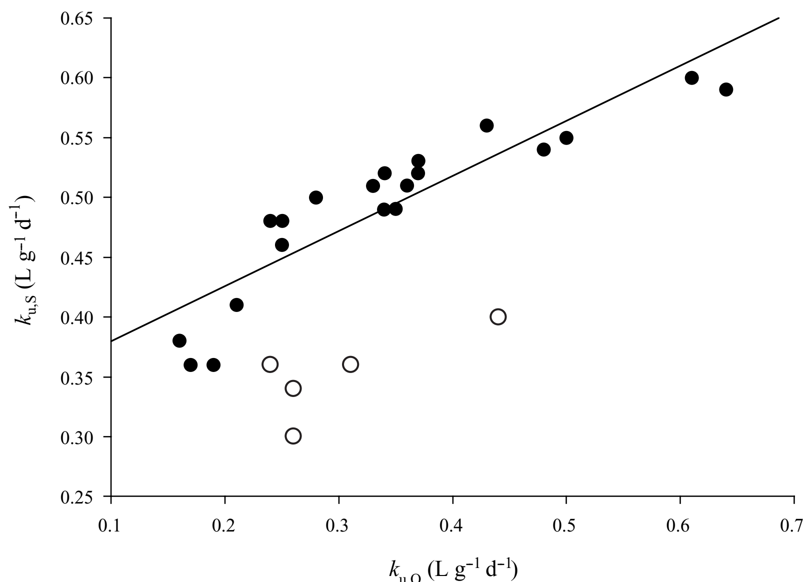

Figure 7.4 Relationship between Pacific oyster (*Crassostrea gigas*) and SPMD uptake-rate constants ($k_{u,O}$ and $k_{u,S}$ respectively), for test chemicals covering the range of test chemical log K_{OW}s (250-ng L^{-1} treatment). Test chemicals within the range of log K_{OW} 5.6 to 6.4 are shown as open symbols but are not used in the regression (see text for explanation). Reprinted from Huckins et al. (2004), copyright (2004); reproduced with permission from Alliance Communication Group.

(*Crassostrea virginica*) k_us for a number of PAHs have been reported by Bender et al. (1988). The mean of the ratios obtained by dividing the SPMD k_us of Huckins et al. (2004) into the eastern oyster k_us of Bender et al. (1988) for the same PAHs is 2.6 ± 1.4 ($n = 10$). This is a relatively small difference considering that exposure conditions can affect both organism and SPMD k_us (e.g., Björk and Gilek, 1997; Booij et al., 1998).

The correlation shown in Figure 7.4 would not be expected to hold for PAHs, when using finfish as a test species. This observation is based on the much higher levels of cytochrome P-450 dependent enzymes in finfish than in shellfish (Buhler and Williams, 1989). The P-450 system mediates Phase I metabolism of PAHs, which in this case consists of enzyme-catalyzed oxidation of the non-polar parent PAH molecule.

7.4. RELATIVE AMOUNTS ACCUMULATED

In another controlled study, Sabaliūnas et al. (1998) exposed SPMDs and lake mussels (*Anodonta piscinalis*) to four pesticides in a laboratory flow-through

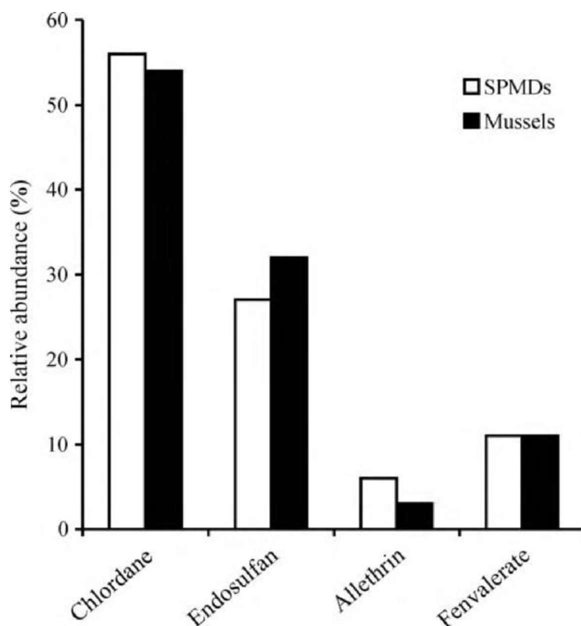

Figure 7.5 Ratios of test chemicals in SPMDs and mussels given as percentages of the total residues. Reprinted from Sabaliūnas et al. (1998), copyright (1998); reproduced with permission from Alliance Communication Group.

system, equipped with a 105 L test chamber. The exposure period was 20 d and samples were collected on d 3, 8, 14 and 20. The pesticides used were chlordane, endosulfan, allethrin, and fenvalerate. The mussels were not fed during the experiment. Based on wet tissue weights and whole SPMDs, SPMD k_us were 3.5 to 5.5 times greater than those for the same pesticides in mussels. However, the pattern of accumulated residues was very similar as shown by Figure 7.5.

Data from the Meadows et al. (1998) study was further analyzed (Echols et al., 1996) by using principle component analysis (PCA) to compare PCB congener concentrations in technical Aroclor mixtures, contaminated spring water, caged brown trout, SPMDs and hexane filled dialysis bags (Södergren, 1987; also, see description in Chapter 1). As stated earlier, caged fish were not fed and exposure conditions were quite stable during the 28 d exposure. Figure 7.6 shows the results of the PCA. The clustering of fish and SPMDs together indicates the close similarity of the concentration profiles of major congeners. This PCA plot further supports the good correlation between SPMD and brown trout rate constants shown in Figure 7.3. However, in vitro bioassay of the SPMD and trout extracts using the PLHC-1 (fish [*Poeciliopsis lucida*] hepatoma cells) ethoxyresorufin-*O*-deethylase (EROD) test indicated that the toxicity of the two types of extracts differ substantially (Meadows, 2005). When the EROD response was normalized to the mass of the total extracted PCBs, EROD induction was thirty times greater

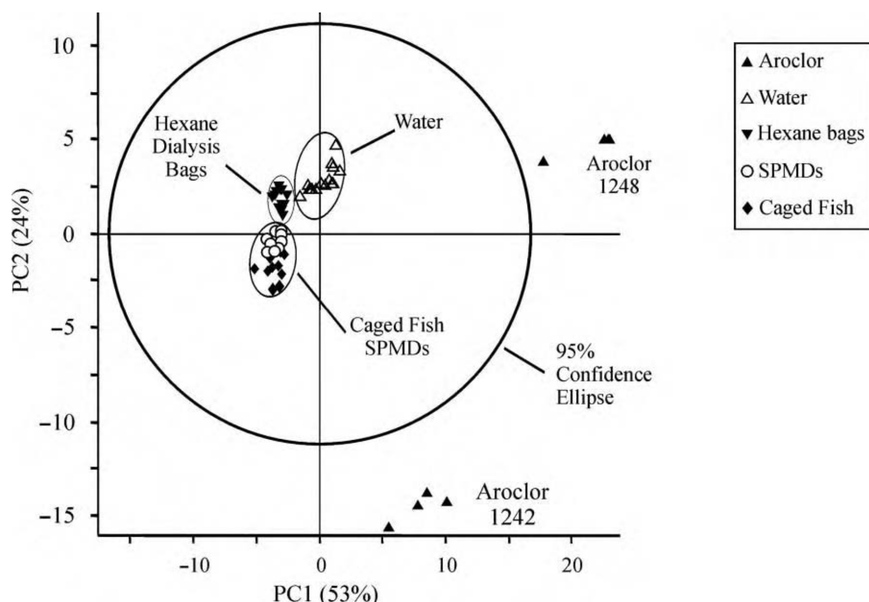

FIGURE 7.6 Principle components analysis (PCA) of PCB congener concentrations in technical Aroclor mixtures, contaminated water, caged brown trout, SPMDs, and hexane filled dialysis bags. The plot shows that 77% of the variance of samples within the 95% confidence ellipse is explained by PC1 and PC2 and that caged fish and SPMDs are clustered together (PCA plot courtesy of Kathy Echols, USGS-CERC, Columbia, MO, USA).

for SPMD extracts than for fish extracts. This assay is highly sensitive to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) and dioxin-like compounds, which include non-*ortho* Cl substituted PCB congeners with four or more chlorines. Therefore, it is likely that difference in the toxicity of SPMD and trout extracts stems from relatively higher levels of non-*ortho* Cl PCBs in the SPMD extracts. To explain this finding, Meadows (2005) hypothesized that non-*ortho* Cl PCBs were selectively metabolized by the fish. The work of Gale et al. (1997) and Peterman (2005) indicate that levels of congener 77 (a non-*ortho* Cl tetrachlorobiphenyl) in channel catfish (*Ictalurus punctatus*) are lower than expected based on EP theory, which supports the selective metabolism hypothesis of Meadows (2005). Finally, because non-*ortho* Cl PCBs represent $<1\%$ of the mass of commercial PCB mixtures, they are not principle components of the PCA shown in Figure 7.6.

These studies show that when the accumulation of HOCs occurs solely by respiration or dermal absorption, BMO and SPMD rate constants correlated very well, but that concentrations in SPMDs are often higher than those in BMOs. However, good correlations between the "fingerprints" or patterns of HOC residues in BMO tissues and SPMDs would not be expected to hold, when diet plays a major role in the uptake of compounds with high K_{ow}s (see Eq. 7.5). For example, Peven et al. (1996) compared the accumulation of organic contaminants by transplanted

blue mussels and standard SPMDs at a known contaminated site in Dorchester Bay, MA, USA. The exposure duration was 95 d and mussels likely fed during the study. Mussel and SPMD concentrations were based on dry weights and whole SPMDs, respectively, and the analytes measured were PAHs, PCBs and total DDT. Mussels were not depurated; thus residue concentrations represented gut contents as well as tissues. Overall, concentrations of total PAHs, PCBs and DDTs were 2 to 7 times higher in SPMDs than in mussels, indicating that differences would have been even greater on a wet-weight basis. Also, Peven et al. (1996) found that when PCB and PAH concentrations in the two sampling matrices were normalized to the highest peak in each mixture, high K_{ow} congeners or components represented a larger fraction in mussels than the corresponding fraction in the SPMDs. Conversely, moderate to low K_{ow} compounds were higher in SPMDs than in mussels. However, the total amounts (e.g., ng) of these high K_{ow} compounds accumulated in an SPMD sample was about the same as that found in a similar sized BMO sample. Furthermore, Booij et al. (2002) and McCarthy and Gale (2001) have shown that SPMDs accumulate sufficient residue mass for the quantitation of ultra-trace levels of extremely hydrophobic contaminants such as decabromodiphenyl ether and 2,3,7,8-tetrachlorodibenzo-*p*-dioxin.

7.5. INDEPENDENCE OF CONCENTRATION FACTORS RELATIVE TO EXPOSURE CONCENTRATION

Few reports are available on the potential effect of chemical concentration on the *BAF* in an aquatic organism (e.g., Mayer, 1976). Yet, a key assumption of EP theory is the independency of *BAF*s relative to exposure concentration. To our knowledge, there is only one report (Huckins et al., 2004) in the peer-reviewed literature, where the effect of chemical exposure level on concentration factors (*CF*s) or *BAF*s has been tested in side-by-side BMO and passive sampler exposures. Huckins et al. (2004) defined *CF* as the ratio of the concentration in a sample matrix (whole body [soft tissues in the case of bivalves] or whole SPMDs) relative to the concentration in the ambient exposure medium at any moment in time, whereas the K_{sw} and *BAF* (includes biomagnification) represent the maximal *CF*. Similar to K_{sw}s and *BAF*s, *CF*s are expected to be independent of exposure concentrations, when residue exchange follows first-order kinetics.

Figure 7.7 shows the *CF*s of 10, 100 and 250 ng L^{-1} (nominal treatment levels; actual concentrations were less than nominal and were inversely proportional to hydrophobicity) of PAHs in SPMDs and oysters (*Crassostrea gigas*) after a 20 d exposure period (Huckins et al., 2004). Oyster *CF*s were generally independent of test chemical concentrations for PAHs having low to moderate log K_{ow}s (i.e., log K_{ow}s of 3.4 to $\leq$5.3). Because oysters in the 10-ng L^{-1} treatment appeared to feed while no evidence of feeding was observed in the 250-ng L^{-1} treatment, feeding seemed to have little effect on the *CF*s of these chemicals. This observation corresponds well with the pioneering work of Bruggeman et al. (1981). They

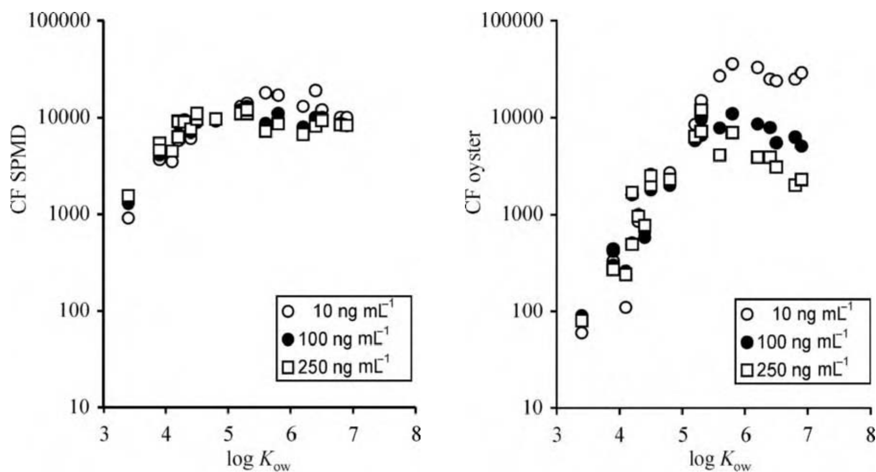

FIGURE 7.7 20-d concentration factors (*CF*s) in whole SPMDs and Pacific oysters (Crassostrea gigas) exposed to 10, 100, and 250 ng L^{-1} of PAHs.

found that food chain or dietary uptake of chemicals exceeded respiratory uptake by fish only when chemicals were quite hydrophobic, i.e., log K_{ow}s >5. Based on Bruggeman et al. (1981) and Connell (1990), the apparent feeding activity of oysters in the 10 ng L^{-1} treatment would not be expected to affect *CF*s of compounds with low to moderate K_{ow}s. For compounds with log K_{ow} values between 3.4 and 5.3, residue accumulation in oyster tissues followed first-order kinetics and EP theory (Figure 7.7). Only the five PAHs with the lowest K_{ow}s attained steady state concentrations in oyster tissues at the end of the 20-d exposure, while other PAHs tested were in the curvilinear phase of uptake.

As expected, the magnitude of PAH *CF*s in SPMDs is generally independent of exposure concentrations (Figure 7.7). The possible exception was the 2-fold higher *CF*s of PAHs (log K_{ow}s $\geq$ 5.6 and $\leq$6.4) in the 10 ng L^{-1} treatment versus the same PAHs in the 250 ng L^{-1} treatment. However, the authors concluded that this difference was artifactual in nature (Huckins et al., 2004). SPMD *CF*s for PAHs within the log K_{ow} range of 3.4 to $\leq$5.3 were generally more than an order of magnitude higher than the corresponding *CF*s for oysters (Figure 7.7). A plausible explanation for the differences in SPMD and oyster *CF*s for low to moderate K_{ow} compounds is the much higher percentage of lipid in SPMDs (effectively >20%; see Section 5.6.2.) than in oysters ($\approx$1.6%; wet weight). Although the lipid contents of BMOs and SPMDs do not directly affect the linear uptake rate constants (Section 7.2.), a higher percentage of lipid does result in a smaller k_e and a longer duration of the integrative or linear uptake phase. Assuming that metabolism of these test chemicals is insignificant, that the lipid in oysters and SPMDs is of similar quality, and that equilibrium was attained in oyster tissues, it seems reasonable to assume that the approximately 12-fold higher lipid content of

SPMDs compared to oysters explains much of the difference in *CF*s between the two sampling matrices. Nevertheless, metabolism of these PAHs cannot be ruled out as a causative factor in the observed differences between SPMD and oyster *CF*s, because cytochrome P-450 levels in some mollusks are fairly high (Buhler and Williams, 1989).

For PAHs with log K_{ow}s ranging from 3.4 to 5.3, differences between the *CF*s in SPMDs and in oysters decreased with increasing K_{ow} (Figure 7.7). In the case of PAHs with log K_{ow}s $\geq$5.6, oyster *CF*s were much higher in the low treatment (10 ng L^{-1}), where feeding appeared to occur, than in the high treatment (250 ng L^{-1}), where feeding activity appeared to be minimal. The ability of juvenile and adult bivalve mollusks to close their valves for extended periods to avoid toxicants is well documented (Huebner and Pynnönen, 1992; Goudreau et al.; 1993; ASTM, 1996, 2001; Moring and Rose, 1997). Furthermore, Toro et al. (2003) have shown an inverse relationship between the k_us of PAHs in the marine giant mussel *Choromytilus chorus* and PAH concentrations at field sites. Oyster *CF*s for high-K_{ow} HOCs were consistent with the valve closure or reduced feeding scenario, because *CF*s were inversely dependent on exposure concentration (Figure 7.7). The differences in oyster *CF*s or *BAF*s across exposure concentrations increased with HOC K_{ow}, and culminated in a 13-fold difference for benzo[g, h, i]perylene. Oyster *CF*s are also 1.3- to 2.9-fold higher than the corresponding SPMD *CF*s for PAHs with log K_{ow}s $\geq$5.6 (10 ng L^{-1} SPMD and oyster treatments), apparently as a result of their somewhat higher uptake rate constants.

7.6. SIMILARITY OF ELIMINATION OR EQUILIBRATION RATE CONSTANTS

Although the relative magnitudes of SPMD and oyster k_us were similar under the conditions of the Huckins et al. (2004) exposure, the k_es and the associated half-lives ($t_{1/2}$s) of residues in the two sampling matrices were markedly different. Table 7.2 summarizes selected bivalve and SPMD first-order k_es and $t_{1/2}$s for PAHs. The $t_{1/2}$ is related to k_e by

$$t_{1/2} = \ln 2/(k_u/K_{sw}) \tag{7.6}$$

In all cases, bivalve k_es are much greater than those of SPMDs, resulting in much shorter $t_{1/2}$s of test compounds. These data are generally consistent with the hypothesis that the fractional lipid content (effectively >20% for SPMDs, versus about 1 to 3% for bivalves [wet weight]) controls the magnitude of k_es and $t_{1/2}$s. However, closer inspection of Table 7.2 and k_e and $t_{1/2}$ values from several other studies (e.g., Pruell et al., 1986; Sericano et al., 1996) suggest that bivalves depurate PAHs with log K_{ow}s >5.8 at greater rates than PAHs with log K_{ow}s ranging from 5 to 5.8. These data do not follow a hydrophobicity model (Barron, 1990). Thus, it appears that active physiological processes such as metabolism may play a role in PAH clearance from bivalve tissues, especially for high K_{ow} test chemicals.

Table 7.2 Comparison of Elimination Rate Constants (k_es; d^{-1}) and Halflives ($t_{1/2}$s; d) Determined in SPMDs and Bivalves

	Huckins et al. (2004)[a]		Huckins et al. (1999)	Bender et al. (1988)	Tse et al. (2000)	
Compound	Oysters k_e ($t_{1/2}$)	SPMDs k_e ($t_{1/2}$)	SPMDs k_e ($t_{1/2}$)	Oysters k_e ($t_{1/2}$)	Mussels k_e ($t_{1/2}$)	SPMDs k_e ($t_{1/2}$)
naphthalene	—[b]	0.18 (3.8)	0.074 (9.6)	—	—	—
biphenyl	—	0.05 (14)		—	—	—
1-methylnaphthalene	—	0.07 (9.9)		—	—	—
acenaphthylene	—	0.06 (11)	0.06 (11)	—	—	—
acenaphthene	—	0.04 (17)	0.04 (17)	—	—	—
1-ethylnaphthalene	0.31 (2.2)	0.02 (35)	—	—	—	—
1,3-dimethylnaphthalene	0.28 (2.5)	0.01 (69)	—	—	—	—
fluorene	0.31 (2.2)	0.02 (35)	0.02 (35)	—	—	—
phenanthrene	0.17 (4.1)	<MQL[c]	0.02 (35)	0.21 (3.3)	—	—
anthracene	0.13 (5.3)	<MQL	0.01 (69)	—	0.22 (3.1)	0.07 (9.9)
2,3,5-trimethylnaphthalene	0.14 (4.9)	—	—	—	—	—
fluoranthene	0.05 (14)	<MQL	0.02 (35)	0.12 (5.8)	0.31 (2.2)	0.01 (69)
pyrene	0.04 (17)	<MQL	0.01 (69)	0.10 (6.9)	0.30 (2.3)	0.01 (69)
benz[*a*]anthracene	0.01 (69)	NML[c]	<0.01 (173)	0.04 (17)	—	—
2-methylfluoranthene	0.01 (69)	—	—	—	—	—
chrysene	0.03 (23)	NML	—	0.05 (14)	—	—
benzo[*b*]fluoranthene	0.03 (23)	NML	—	0.01 (69)	—	—
benzo[*k*]fluoranthene	0.04 (17)	NML	—	—	—	—
benzo[*a*]pyrene	0.03 (23)	NML	—	0.03 (23)	—	—
perylene	0.03 (23)	NML	—	0.07 (9.9)	—	—
indeno[1,2,3-*cd*]pyrene	0.05 (14)	NML	—	—	—	—
dibenz[*a*, *h*]antracene	0.07 (10)	NML	—	—	—	—
benzo[*g*, *h*, *i*]perylene	0.06 (11)	NML	—	0.06 (11)	—	—

[a] 250 ng L^{-1} treatment, k_e values are means ($n = 4$), and C.V.s (in parenthesis) for oysters ranged from 16 to 192%, whereas C.V.s for SPMDs ranged from 11 to 75%.
[b] Not measured or achieved equilibrium.
[c] Method quantitation limit (MDL) or no measurable loss (NML).

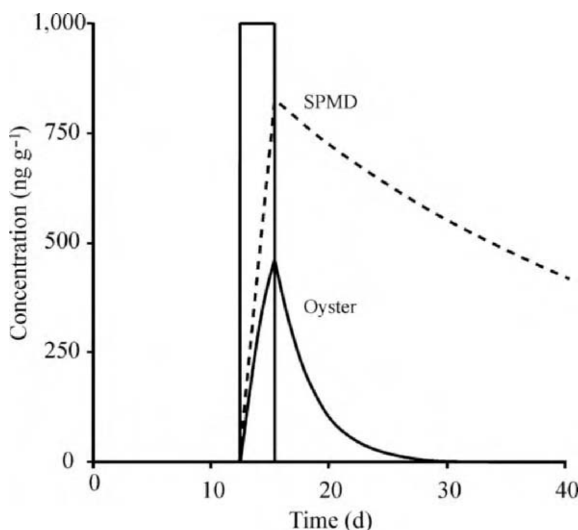

FIGURE 7.8 Model simulation (Gale, 1998) of the response of oysters and SPMDs to a 3-d pulse of fluorene. Reprinted from Huckins et al. (2004), copyright (2004); reproduced with permission from Alliance Communication Group.

Clearly, SPMD k_es follow a hydrophobicity model, where k_es fall with increasing K_{ow}s (Table 7.2).

The lower k_e values in SPMDs compared to BMOs have a major effect on the retention of contaminants that are absorbed during episodic exposure events. Figure 7.8 shows the results of a model simulation (Gale, 1998) of fluorene uptake by oysters and SPMDs, following an episodic fluorene release into water, using the exchange kinetics data reported by Huckins et al., (2004). According to the model, readily detectable levels of fluorene were retained by the SPMDs 25 d after the exposure event, whereas fluorene was completely cleared from oysters in 15 d following the exposure (Fig. 7.8). The first-order residence time (t_m or $1/k_e$; the mean length of time that a molecule remains in a sampling matrix subject to first-order exchange kinetics) of fluorene in oysters and SPMDs was 3 and 50 d, respectively. This simulation highlights a major difference between bivalves and SPMDs. Phillips and Rainbow (1993) have suggested that the implications of short residence times of many chemicals in bivalves exposed to variable or episodic exposure conditions has not been fully recognized by many investigators employing BMOs in monitoring studies. To minimize this problem a "time bulking" approach has been recommended (Phillips and Rainbow, 1993), which consists of matching the end of the linear phase of BMO uptake kinetics to sampling times. Unfortunately, BMO exchange kinetics are not known *a priori*, and sampling through time is labor intensive and costly. However, differences between the clearance rates of persistent HOCs from SPMDs and high lipid content BMOs, such as carp, are not expected to be great.

7.7. COMPARABILITY OF ESTIMATED AND MEASURED *BCF*s OR *BAF*s

Burkhard et al. (2003) have stated that *BAF*s can only be measured using field data, because bioaccumulation is the net result of chemical uptake from all sources and processes. Also, a number of investigators have reported that very long exposures (e.g., $\geq$100 d) are required to reach equilibrium with BMOs (Booij et al., 2002; Verweij et al., 2004) for some high K_{ow} compounds, which may be a source of errors for some regression models. Although we agree with Burkhard et al. (2003) that *BAF*s are unique to a particular environment and BMO species, there is still a need for screening models and methods to estimate *BAF*s. Non-physiological or EP based models assume that the log *BCF* (i.e., the *BAF* in the case where diffusional exchange via the gills and skin is the only uptake and loss mechanism) is linearly related to the K_{ow}. The classic Veith et al. (1979) model is an example of this approach.

$$\log BCF = 0.76 \log K_{ow} - 0.23 \quad (7.7)$$

This regression equation was derived using four species of fish and 84 organic compounds with a wide range of hydrophobicities and generally provides reasonable predictions for compounds with log K_{ow}s < 6. However, some investigators (e.g., Connell and Hawker, 1988) suggested that when compounds covering a very wide range of K_{ow}s (includes very high to super hydrophobic compounds) are considered, biological responses and *BCF*s deviate substantially from a linear relationship. For example, Connell and Hawker (1988) successfully used the following polynomial equation to model *BCF*s of fish for compounds with log K_{ow}s ranging from about 3 to 9.5.

$$\text{Log}\, BCF = 0.0069(\log K_{ow})^4 - 0.185(\log K_{ow})^3 + 1.55(\log K_{ow})^2 - 4.18 \log K_{ow} + 4.79 \quad (7.8)$$

The maximum *BCF* of 4.6 is achieved at a log K_{ow} of 6.7. Connell (1990) pointed out that if only compounds with log K_{ow}s within the range of 3 to 6 are considered Eq. 7.8 reduces to

$$\text{Log}\, BCF = 0.94 \log K_{ow} - 1.0 \quad (7.9)$$

which is similar to Eq. 7.7. Steady state K_{sw}s correlate well to K_{ow}s using the following non-linear relationship (Eq. 3.28)

$$\log K_{sw} = a_0 + 2.321 \log K_{ow} - 0.1618(\log K_{ow})^2 \quad (7.10)$$

where the intercept a_0 is equal to -2.61 for the chemicals examined in this section.

Table 7.3 gives SPMD K_{sw}s (Eq. 7.10), lipid-normalized *BCF*s (Eqs. 7.7 and 7.8), and BCF/K_{sw} ratios for model compounds with log K_{ow} values ranging from 3.0 to 6.0. In this comparison, a lipid content of 5% was adopted for lipid normalization of whole body fish concentrations (note that the whole body lipid content

Table 7.3 Comparison of Regression Model Estimates of K_{sw}s and Lipid-Normalized *BCF*s[a]

log K_{ow}	log K_{sw} Eq. 7.10	log *BCF* Eq. 7.7	log *BCF* Eq. 7.8	BCF/K_{sw} Eq. 7.7	BCF/K_{sw} Eq. 7.8
3	2.9	3.4	3.1	3.2	1.6
4	4.1	4.1	4.1	1.0	1.0
5	5.0	4.9	5.1	0.8	1.3
6	5.5	5.6	5.8	1.3	2.0

[a]A 5% lipid content was assumed for fish.

in fishes typically range from about 2 to 10%). The BCF/K_{sw} ratios produced when using Eqs. 7.7 and 7.8 (Table 7.3) show that SPMD K_{sw}s are within about three-fold of *BCF*s over 3-orders of magnitude and that the mean of BCF/K_{sw} ratios for Eqs. 7.7 and 7.8 is about 1.5. The BCF/K_{sw} ratios (1.6 ± 1.1) produced from Eq. 7.7 *BCF*s are more variable than the BCF/K_{sw} ratios (1.5 ± 0.4) produced from Eq. 7.8 *BCF*s. Overall, the computed K_{sw}s are generally lower than lipid-normalized *BCF*s.

The work of Wang et al. (2002) appears to be a rare case where lipid normalization of SPMD and feral fish concentrations may have been partly justified. This observation is based on the facts that the flow during the exposure was about 100 cm s^{-1} (Huaihe River, China) and that the deployment device did little to buffer the flow at the membrane surface. Flows of this magnitude are known to greatly enhance sampling rates and thus reduce times to attain equilibrium concentrations in SPMDs (see 90 cm s^{-1} sampling rate data in Table A.7 of Appendix A, and discussions in Sections 3.6.2. and 3.6.5.). For example, examination of PCB congener 52 (2,5,2′,5′-tetrachlorobiphenyl) calibration data in Tables A.2 and A.7 of Appendix A show that the log K_{sw} is about 5.6 and that at a flow rate of 90 cm s^{-1} across the membrane surface, the SPMD $k_u = 26$ L g^{-1} d^{-1}. With this data, the $t_{1/2}$ for attainment of equilibrium can be estimated from Eq. 7.6. Using this approach gives a $t_{1/2}$ of about 10 d, which means that during the 28-day exposure period about 3 $t_{1/2}$s elapsed and that SPMDs should have reached about 88% of the equilibrium concentrations of congener 52. Wang et al. (2002) reported lipid normalized PCB concentrations in SPMDs and fish for 21 congeners bracketed by congeners 5 and 101. The discussion of this data is limited to 12 congeners bracketed by congeners 5 and 52 to increase the likelihood that equilibrium was attained. In all cases within the designated congener range, lipid normalized SPMD concentrations were higher than or equal to fish concentrations. The mean of individual values ($n = 12$) obtained by dividing SPMD concentrations by fish concentrations (i.e., K_{sw}/BAF) was 2.3 ± 1.1, which may be due to the fact that the sorption capacity of the membrane was not taken into account. Furthermore, this analysis did not take into account that the effective lipid content of the whole SPMD varies with analyte partition coefficients between the membrane and lipid (see Section

5.6.2.). Also the study did not employ performance reference compounds, which are required to validate attainment of equilibrium. We include this exercise to show that lipid normalization is problematic even when both matrices attain equilibrium and do not recommend the procedure without further proof of concept.

7.8. DIETARY UPTAKE AND BIOMAGNIFICATION

A major criticism of the use of SPMDs and other passive samplers for estimating screening level *BAF*s is that dietary uptake is not modeled and thus the potential for biomagnification is not taken into account. Biomagnification is the sequential increase in chemical concentration going up the trophic levels of a food chain. The biomagnification factor *BMF* is determined by dividing the concentration in the consumer by the concentration in the diet. However, Connell (1990), has observed that the first step in most aquatic food chains is bioconcentration (i.e., the uptake of dissolved-phase residues by autotrophic organisms such as phytoplankton). It is also likely that the dominant route of chemical uptake is water even for food chains based on hetrotrophs and fungi (Schmidt, 2004). Passive samplers, such as SPMDs, provide the best available technology for determining dissolved phase water concentrations of trace to ultra-trace bioaccumulative organics and thus enable *in situ* determination of HOC exposure to organisms at the lowest trophic level in nearly all food chains. Furthermore, the contribution of dietary uptake is generally very small for compounds with log K_{ow}s < 5.5 (e.g., Connell, 1990; Huckins et al., 2004).

Connell (1990) also proposed that, irrespective of whether food or water is the primary source of accumulated chemical, *BMF* values are near unity in aquatic food chains when differences in lipid content are taken into account. More recently, there has been a general acceptance that even after taking differences in lipid contents into account, *BMF*s >1 do occur in some aquatic food chains (Macdonald, et al., 2002). Typically, *BMF*s in finfishes are small (e.g., 3.0-fold) when compared to mammals or birds (e.g., 30-fold) fed similar diets. Finally, until the advent of passive samplers such as the SPMDs, *BMF* multipliers have been easier to estimate than the dissolved phase exposure concentrations. Knowledge of dissolved phase chemical concentrations is a critical part of understanding how aqueous exposure levels relate to the concentrations of residues measured in organisms in various trophic levels of aquatic ecosystems.

7.9. DO SPMDs QUALIFY AS BIOMIMETIC SAMPLERS?

In the context of this chapter, biomimetic is defined as “the use of simple synthetic media to mimic a complex biological process”. Earlier Fendler (1984) defined membrane biomimetic chemistry as “processes in simple media that mimic aspects of biomembranes”. Thus, classical biomimetic approaches target specific

sites and/or modes of action characteristic of a particular species, and are rarely applied to a whole organism or a group of organisms. However, the processes of diffusion and partitioning mediate biouptake at the base of aquatic food chains and are fundamental to homeostasis of all organisms. Also, the bioavailability of HOCs is largely controlled by diffusion and partitioning processes, which in turn affect the accumulation of HOCs by both SPMDs and BMOs. In the case of SPMDs, the rate-limiting step in chemical uptake and release kinetics is always diffusion, and the maximum achievable concentration for a particular exposure level is determined by the chemical's partition coefficient (K_{sw}). Although diffusion may not always be the rate-limiting step in chemical uptake by biota, it is always a key mechanism in the overall uptake process. Likewise, partitioning generally plays an important role in HOC concentrations in BMOs, but the maximum tissue level during a specified interval of time or an organism's life cycle may not correspond to a chemical's partition coefficient because of variations in environmental exposure concentrations, kinetic limitations, biotransformation, and biomagnification.

In this chapter we have shown that the relative fluxes of a wide range of solutes across the gill membrane and the SPMD membrane appear to fit the same pattern (Figure 7.1), suggesting that similar processes are involved. Also, uptake rate constants (i.e., k_us) of SPMDs and BMOs generally appear to be of similar magnitude, and in some cases are reasonably well correlated (Figures 7.3 and 7.4), but this finding may be limited to organism exposure scenarios where water represents the major route of HOC uptake. A major difference between some BMOs and standard SPMDs is in the much higher values of k_es found for BMOs relative to SPMDs. This observation applies to those organisms with low levels of total lipids (especially neutral triglycerides or storage fats) such as bivalves, and those with enzymatic systems capable of metabolizing HOCs, but may not apply to persistent HOCs accumulated in organisms with high fat contents (i.e., $>10\%$). Because the magnitude of the overall k_e largely controls equilibration time, most BMOs are expected to reach equilibrium more rapidly than SPMDs. Regardless of kinetic differences, regression model predictions (Eqs. 7.7, 7.8 and 7.10) of steady-state values of K_{sw}s and *BCF*s in fish appear to agree within about 2-fold after differences in lipid contents are taken into account (Table 7.3).

In summary, the large number of variables which potentially affect the accumulation of HOC in BMOs, suggest that it is unrealistic to expect any single passive sampler to be biomimetic of all BMOs. Also, it is similarly unrealistic to expect that one or two species of BMOs mimic bioaccumulation in all organisms of concern. Literature values of *BCF*s or *BAF*s vary by several orders of magnitude for the same chemical across test species and exposure scenarios (e.g. Mackay et al., 1992a, 1992b, 1997), which underscores the problem of selecting representative sampler designs or BMOs. Thus, SPMDs are biomimetic only when diffusional-partitioning processes mediate HOC concentrations in organisms of concern (i.e., when residue accumulation in organism tissues follows EP theory). The similarity of SPMDs and BMOs is reflected in the proportionality of their uptake rate

constants (whole-weight basis) and partition coefficients (Table 7.3; ratio of lipid-normalized *BCF* to whole-weight $K_{sw} \approx 1.4$) across a range of K_{ow}s. Again, we stress that assessment of the similarity of partition-coefficients can only be made when both SPMDs and BMOs have attained equilibrium. Because SPMDs are designed to remain in the linear uptake mode for compounds with log $K_{ow}s > 4.5$ during typical 4-week exposure periods, the attainment of equilibrium by SPMDs is an exception rather than a rule.

The primary role of SPMDs and other passive samplers is to provide convenient, powerful analytical tools for determining dissolved and vapor phase HOC concentrations in environmental systems. This chapter has shown that they are also useful as biomimetic screening tools for estimating exposure of organisms to bioconcentratable compounds and for deriving *BCF*s based on EP theory. Even for those chemicals that are present at vanishingly small amounts in the dissolved phase and are primarily accumulated via the dietary uptake, SPMDs generally extract sufficient amounts of residues for analysis.

7.10. REFERENCES

American Society for Testing and Materials (ASTM) 1984, Standard Practice for Conducting Bioconcentration Tests with Fishes and Saltwater Bivalve Mollusks. *Annual Book of ASTM Standards No. E 1022-84*; Vol 11.05; Philadelphia; PA; pp. 286–303.

American Society for Testing and Materials (ASTM) 1996, Standard Guide for Conducting Acute Toxicity Tests on Test Materials with Fishes, Macroinvertebrates, and Amphibians. *Annual Book of ASTM Standards, No. E 729-96*; Vol 11.05; Philadelphia, PA; pp. 178–199.

American Society for Testing and Materials (ASTM) 2001, Standard Guide for Conducting In-situ Field Bioassays with Marine, Estuarine, and Freshwater Bivalves. *Annual Book of ASTM Standards; No. E 2122-01*; Vol 11.05; Philadelphia, PA; pp. 1562–1591.

Axelman, J.; Næs, K.; Näf, C.; Broman, D. 1999, Accumulation of polycyclic aromatic hydrocarbons in semipermeable membrane devices and caged mussels (Mytilus edulis) in relation to water column phase distribution. *Environ. Toxicol. Chem.* **18**: 2454–2461.

Baumard, P.; Budzindki, H.; Garrigues, P. 1998a, PAHs in Arcachon Bay, France: Origin and biomonitoring with caged organisms. *Mar. Pollut. Bull.* **36**: 577–586.

Baumard, P.; Budzinski, H.; Garrigues, P.; Sorbe, J.C.; Burgeot, T.; Bellocq, J. 1998b, Concentrations of PAHs (polycyclic aromatic hydrocarbons) in various marine organisms in relation to those in sediments and to trophic level. *Mar. Pollut. Bull.* **36**: 951–960.

Baussant, T.; Sanni, S.; Jonsson, G.; Skadsheim, A.; Børseth, J.F. 2001, Bioaccumulation of polycyclic aromatic compounds: 1. Bioconcentration in two marine species and in semipermeable membrane devices during chronic exposure to dispersed crude oil. *Environ. Toxicol. Chem.* **20**: 1175–1184.

Barron, M.G. 1990, Bioconcentration: Will water-borne organic chemicals accumulate in aquatic organisms. *Environ. Sci. Technol.* **24**: 1612–1618.

Bayne, B.L.; Thompson, R.J.; Widdows, J. 1976, Physiology: I. In *Marine Mussels: Their Ecology and Physiology*; Bayne, B.L., Ed.; Cambridge University Press: London; pp. 121–206.

Bender, M.E.; Hargis, W.J. Jr; Huggett, J.R.; Roberts, M.H. Jr. 1988, Effects of polynuclear aromatic hydrocarbons on fishes and shellfishes: An overview of research in Virginia. *Mar. Environ. Res.* **24**: 237–241.

Björk, M. and Gilek, M. 1997, Bioaccumulation kinetics of PCB 31, 49, and 153 in the blue mussel, Mytilus edulis L. as a function of algal food concentration. *Aquat. Toxicol.* **38**: 101–123.

Booij, K.; Sleiderink, H.M.; Smedes, F. 1998, Calibrating the uptake kinetics of semipermeable membrane devices using exposure standards. *Environ. Toxicol. Chem.* **17**: 1236–1245.

Booij, K.; Zegers, B.N.; Boon, J.P. 2002, Levels of some polybrominated diphenyl ether (PBDE) flame retardants along the Dutch coast as derived from their accumulation in SPMDs and blue mussels (Mytilus edulis). *Chemosphere* **46**: 683–688.

Bruggeman, W.A.; Martron, L.B.J.M.; Kooiman, D.; Hutizinger, O. 1981, Accumulation and elimination kinetics of di-; tri- and tetrachlorobiphenyls in goldfish after dietary and aqueous exposure. *Chemosphere* **10**: 811–832.

Bucheli, T. and Gustafsson, Ö. 2000, Quantification of the soot-water distribution coefficient of PAHs provides mechanistic basis for enhanced sorption observations. *Environ. Sci. Technol.* **34**: 5144–5151.

Buhler, D.R. and Williams, D.E. 1989, Enzymes involved in metabolism of PAHs by fishes and other aquatic animals: Oxidative enzymes (or Phase I enzymes). In *Metabolism of Polycyclic Aromatic Hydrocarbons in the Aquatic Environment*; Varanasi, U., Ed.; CRC Press: Boca Raton, Fl; pp. 151–184.

Burkhard, L.P.; Cook, P.M.; Mount, D.R. 2003, The relationship of bioaccumulative chemicals in water and sediment to residues in fish: A visualization approach. *Environ. Toxicol. Chem.* **22**: 2822–2830.

Chiou, C.T. 1985, Partition coefficients of organic compounds in lipid-water systems and correlations with fish bioconcentration factors. *Environ. Sci. Technol*. **19**: 57–62.

Connell, D.W. and Hawker, D.W. 1988, Use of polynomial expressions to describe the bioconcentrations of hydrophobic chemicals by fish. *Ecotox. Environ. Safe.* **16**: 242–251.

Connell, D.W. 1990, *Bioaccumulation of Xenobiotic Compounds*. CRC Press: Boca Raton, FL; p. 219.

Echols, K.R.; Meadows, J.; Schwartz, T.; Borsuk, F.; Carline, R.; Tillitt, D. 1996, Comparison of SPMDs, Caged Fish, and Hexane Filled Dialysis Bags for Sampling PCBs in Groundwater from a Spring at Sherman's Dale, PA. Presented at the 4th Annual SPMD International Workshop: Kansas City, MO. June 11–13, 1996.

Echols, K.R.; Gale, R.W.; Schwartz, T.R.; Huckins, J.N.; Williams, L.L.; Meadows, J.C.; Morse, D.; Petty, J.D.; Orazio, C.E.; Tillitt, D.E. 2000, Comparing polychlorinated biphenyl concentrations and patterns in the Saginaw River using sediment, caged fish, and semipermeable membrane devices. *Environ. Sci. Technol.* **34**: 4095–4102.

Ellis, G.S.; Huckins, J.N.; Rostad, C.E.; Schmitt, C.J.; Petty J.D.; MacCarthy, P. 1995, Evaluation of lipid-containing semipermeable membrane devices (SPMDs) for monitoring organochlorine contaminants in the Upper Mississippi River. *Environ. Toxicol. Chem.* **14**: 1875–1884.

Fendler, J.H. 1984, Membrane mimetic chemistry. *C&E News*; January 2; 1984; p. 25–39.

Følsvik, N.; Brevik, E.M.; Berge, J.A. 2002, Organotin compounds in a Norwegian fjord. A comparison of concentration levels in semipermeable membrane devices (SPMDs), blue mussels (Mytilus edulis) and water samples. *J. Environ. Monitor.* **4**: 280–283.

Franke, C.; Studinger; G., Berger, G.; Böhling, S.; Bruckmann, U.; Cohors-Fresenborg, D.; Jöhncke, U. 1994, The assessment of bioaccumulation. *Chemosphere* **29**: 1501–1514.

Gale, R.W.; Huckins, J.N.; Petty, J.D.; Peterman, P.H.; Williams, L.L.; Morse, D.; Schwartz, T.R.; Tillitt, D.E. 1997, Comparison of the uptake of dioxin-like compounds by caged channel catfish and semipermeable membrane devices in the Saginaw River, Michigan. *Environ. Sci. Technol.* **32**: 178–187.

Gale, R.W. 1998, Three-compartment model for contaminant accumulation by semipermeable membrane devices. *Environ. Sci. Technol.* **32**: 2292–2300.

Gatermann, R.; Siselli, S.; Hühnerfuss, H.; Rimkus, G. G.; Hecker, M.; Karbe, L. 2002, Synthetic musks in the environment. Part 1: Species-dependent bioaccumulation of polycyclic and nitro musk fragrances in freshwater fish and mussels. *Arch. Environ. Con. Tox.* **42**: 437–446.

Gilek, M.; Björk, M.; NäF, C. 1996, Influence of body size on the uptake, depuration, and bioaccumulation of polychlorinated biphenyl congeners by Baltic Sea blue mussels, Mytilus edulis. *Mar. Biol*. **125**: 499–510.

Gobas, F.A.P.C.; Opperhuizen, A.; Hutzinger, O. 1986, Bioconcentration of hydrophobic chemicals in fish: Relationship with membrane permeation. *Environ. Toxicol. Chem.* **5**: 637–646.

Gobas, F.A.P.C.; Zhang, X.; Wells, R. 1993, Gastrointestional magnification: the mechanism of biomagnification and food chain accumulation of organic chemicals. *Environ. Sci. Technol*. **27**: 2855–2863.

Goudreau, S.E.; Neves, R.J.; Sheehan, R. 1993, Effects of wastewater treatment plant effluents of freshwater mollusks in the upper Clinch River, Virginia, USA. *Hydrobiologia* **252**: 211–230.

Granmo, Å.; Ekelund, R.; Berggren, M.; Brorström-Lunden, E.; Bergqvist, P.-A. 2000, Temporal trend of organochlorine marine pollution indicated by concentrations in mussels, semipermeable membrane devices, and sediment. *Environ. Sci. Technol.* **34**: 3323–3329.

Gray, J.S. 2002, Perceived and real risks: Produced water from oil extraction. *Mar. Pollut. Bull.* **44**: 1171–1172.

Hayton, W.L. and Barron, M.G. 1990, Rate-limiting barriers to xenobiotic uptake by the gill. *Environ. Toxicol. Chem.* **9**: 151–157.

Hebert, C.E. and Keenleyside, K.A. 1995, To normalize or not to normalize? Fat is the question. *Environ. Toxicol. Chem.* **14**: 801–807.

Herve, S.; Prest, H.F.; Heinonen, P.; Hyötyläinen, T.; Koistinen, J.; Paasivirta, J. 1995, Lipid-filled semipermeable membrane devices and mussels as samplers of organochlorine compounds in lake water. *Envrion. Sci. Pollut. R.* **2**: 24–30.

Hofelt, C.S. and Shea, D. 1997, Accumulation of organochlorine pesticides and PCBs by semipermeable membrane devices and Mytilus edulis in New Bedford Harbor. *Environ. Sci. Technol.* **31**: 154–159.

Huckins, J.N.; Tubergen, M.W.; Manuweera, G.K. 1990, Semipermeable membrane devices containing model lipid: A new approach to monitoring the availability of lipophilic contaminants and estimating their bioconcentration potential. *Chemosphere* **20**: 533–552.

Huckins, J.N.; Manuweera, G.K.; Petty, J.D.; Mackay, D.; Lebo, J.A. 1993, Lipid-containing semipermeable membrane devices for monitoring organic contaminants in water. *Environ. Sci. Technol.* **27**: 2489–2496.

Huckins, J.N.; Petty, J.D.; Lebo, J.A.; Orazio, C.E.; Prest, H.F.; Tillitt, D.E.; Ellis, G.S.; Johnson, B.T.; Manuweera, G.K. 1996, Semipermeable Membrane Devices (SPMDs) for the Concentration and Assessment of Bioavailable Organic Contaminants in Aquatic Environments. In *Techniques in Aquatic Toxicology*; Ostrander, G.K., Ed.; CRC Press: Boca Raton, FL; pp. 625–655.

Huckins, J.N.; Prest, H.F.; Petty, J.D.; Røe, T.I.; Meadows, J.C.; Echols, K.R.; Lebo, J.A.; Clark, R.C. 1998a, A Overview of the Results of Several Comparisons of Lipid-containing Semipermeable Membrane Devices (SPMDs) and Biomonitoring Organisms for Assessing Organic Chemical Exposure. *Abstracts of the 19th Annual National Meeting; SETAC*; Charlotte, NC; November 15–19, 1998; p. 215.

Huckins, J.N.; Petty, J.D.; Gale, R.W.; Booij, K.; Prest, H.F.; Clark, R.C. 1998b, Observations on declining SPMD sampling rates for high K_{ow} compounds: *Abstracts of the 19th Annual National Meeting; SETAC*; Charlotte, NC; November 15–19, 1998; pp. 241.

Huckins, J.N.; Petty, J.D.; Orazio, C.E.; Lebo, J.A.; Clark, R.C.; Gibson, V.L.; Gala, W.R.; Echols, K.R. 1999, Determination of uptake kinetics (sampling rates) by lipid-containing semipermeable membrane devices (SPMDs) for polycyclic aromatic hydrocarbons (PAHs) in water. *Environ. Sci. Technol.* **33**: 3918–3923.

Huckins, J.N.; Petty, J.D.; Lebo, J.A.; Almeida, F.V.; Booij, K.; Alvarez, D.A.; Cranor, W.L.; Clark, R.C.; Mogensen, B.B. 2002a, Development of the permeability/performance reference compound (PRC) approach for in situ calibration of semipermeable membrane devices (SPMDs). *Environ. Sci. Technol.* **36**: 85–91.

Huckins, J.N.; Petty, J.D.; Prest, H.F.; Clark, R.C.; Alvarez, D.A.; Orazio, C.E.; Lebo, J.A.; Cranor, W.L.; Johnson, B.T. 2002b, *A Guide for the Use of Semipermeable Membrane Devices (SPMDs) as Samplers of Waterborne Hydrophobic Organic Contaminants*; Publication No. 4690; American Petroleum Institute (API): Washington, DC.

Huckins, J.N.; Prest, H.F.; Petty, J.D.; Lebo, J.A.; Hodgins, M.M.; Clark, R.C.; Alvarez, D.A.; Gala, W.R.; Steen, A.; Gale, R.W.; Ingersoll, C.G. 2004, Overview and comparison of lipid-containing semipermeable membrane devices (SPMDs) and oysters (Crassostrea gigas) for assessing chemical exposure. *Environ. Toxicol. Chem.* **23**: 1617–1628.

Huebner, J.D. and Pynnönen, K.S. 1992, Viability of glochida of two species of Anodonta exposed to low pH and selected metals. *Can. J. Zool.* **70**: 2348–2354.

Hwang, S-T. and Kammermeyer, K. 1984, *Membranes in Separations*. Krieger Publishing: Malabar, FL; pp. 559.

Jimenez, B.D.; Cirmo, C.P.; McCarthy, J. F. 1987, Effects of feeding and temperature on uptake, elimination and metabolism of benzo[*a*]pyrene in the bluegill sunfish (Lepomis macrochirus). *Aquat. Toxicol.* **10**: 41–57.

Kolok, A.S.; Huckins, J.N.; Petty, J.D.; Oris, J.T. 1996, The role of water ventilation and sediment ingestion in the uptake of benzo[*a*]pyrene in gizzard shad (Dorosoma cepedianum). *Environ. Toxicol. Chem.* **10**: 1752–1759.

Leppanen, H. and Kukkonen, V.K. 2000, Effect of sediment-chemical contact time on availability of sediment-associated pyrene and benzo[*a*]pyrene to oligochaete worms and semipermeable membrane devices. *Aquat. Toxicol.* **49**: 227–241.

Lieb, W.R. and Stein, W.D. 1969, Biological membranes behave as non-porous polymeric sheets with respect to the diffusion of non-electrolytes. *Nature* **224**: 240–243.

Lu, Y.; Wang, Z.; Huckins, J.N. 2002, Review of the background of triolein-containing semipermeable membrane devices in aquatic environmental study. *Aquat. Toxicol.* **60**: 139–153.

Macdonald, R.; Mackay, D.; Hickie, B. 2002, Contaminant amplification in the environment. *Environ. Sci. Technol.* **36**: 456A–462A.

Mackay, D.; Shiu, W.Y.; Ma, K.C. 1992a, *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals: Monoaromatic Hydrocarbons, Chlorobenzenes, and PCBs*; Lewis Publishers: Chelsea, MI.; Vol. I.

Mackay, D.; Shiu, W.Y.; Ma, K.C. 1992b, *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals: Polynuclear Aromatic Hydrocarbons, Polychlorinated Dioxins, and Dibenzofurans*; Lewis Publishers: Chelsea, MI.; Vol. II.

Mackay, D.; Shiu, W.Y.; Ma, K.C. 1997, *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals: Pesticide Chemicals*; Lewis Publishers: Boca Raton, FL; Vol. V.

Mayer, F.L. 1976, Residue dynamics of di-2-ethylhexylphthalate in fathead minnows (Pimephales promelas). *J. Fish. Res. Board Can.* **33**: 2610–2613.

McCarthy, K.A. and Gale, R.W. 2001, Evaluation of persistent hydrophobic organic compounds in the Columbia River Basin using semipermeable membrane devices. *Hydrol. Process.* **15**: 1271–1283.

McKim, J.; Schmieder, P.; Veith, G. 1985, Absorption dynamics of organic chemical transport across trout gills as related to octanol-water partition coefficient. *Toxicol. Appl. Pharm.* **77**: 1–10.

Meadows, J.C.; Echols, K.R.; Huckins, J.N.; Borsuk, F.A.; Carline, R.F.; Tillitt, D.E. 1998, Estimation of uptake rate constants for PCB congeners accumulated by semipermeable membrane devices and brown trout (Salmo trutta). *Environ. Sci. Technol.* **32**: 1847–1852.

Meadows, J.C. 2005, USGS Columbia Environmental Research Center, Columbia, MO. USA. Personal communication.

Moring, J.B. and Rose, D.R. 1997, Occurrence and concentration of polycyclic aromatic hydrocarbons in semipermeable membrane devices and clams in three urban streams of the Dallas-Fort Worth Metropolitan Area, Texas. *Chemosphere* **34**: 551–566.

Opperhuizen, A.; van de Velde, E.W.; Gobas, F.A.P.C.; Liem, A.K.D.; van de Steen, J.M.D.; Hutzinger, O.; 1985, Relationship between bioconcentration in fish and steric factors of hydrophobic chemicals. *Chemosphere* **14**: 1871–1896.

Peterman, P.H. 2005, USGS Columbia Environmental Research Center, Columbia, MO. USA. Personal communication.

Peven, C.S.; Uhler, A.D.; Querzoli, F.J. 1996, Caged mussels and semipermeable membrane devices as indicators of organic contaminant uptake in Dorchester and Duxbury Bays, Massachusetts. *Environ. Toxicol. Chem.* **15**: 144–149.

Phillips, D.J.H. 1980, *Quantitative Aquatic Biological Indicators*. Applied Science Publishers: London, UK.

Phillips, D.J.H. and Rainbow, P.S. 1993, *Biomonitoring of Trace Aquatic Contaminants*. Elsevier Applied Science: New York; p. 371.

Prest, H.F.; Jarman, W.M.; Burns, S.A.; Weismuller, T.; Martin, M.; Huckins, J.N. 1992, Passive water sampling via semipermeable membrane devices (SPMDs) in concert with bivalves in the Sacramento/San Joachin river delta. *Chemosphere* **25**: 1811–1824.

Prest, H.F.; Huckins, J.N.; Petty, J.D.; Herve, S.; Paasivirta, J.; Heinonen, P. 1995a, A survey of recent results in passive sampling of water and air by semipermeable membrane devices. *Mar. Pollut. Bull.* **31**: 306–312.

Prest, H.F.; Richardson, B.J.; Jacobson, L.A.; Vedder, J.; Martin, M. 1995b, Monitoring organochlorines with semipermeable membrane devices (SPMDs) and mussels (Mytilus edulis) in Corio Bay, Victoria, Australia. *Mar. Pollut. Bull.* **30**: 543–554.

Prest, H.F.; Hodgins, M.M.; Petty, J.D.; Huckins, J.N.; Lebo, J.A.; Orazio, C.E.; Gibson, V. 1997, *Laboratory Comparisons of Oysters and Semipermeable Membrane Devices (SPMDs).* USGS Midwest Science Center, Columbia, MO; Report to the American Petroleum Institute (API): Washington; DC; API Report No. DR 360.

Pruell, R.J.; Lake, J.L.; Davis, W.R.; Quinn, J.G. 1986, Uptake and depuration of organic contaminants by blue mussel (Mytilus edulis) exposed to environmentally contaminated sediment. *Mar. Biol.* **91**: 497–507.

Rand, G.M. and Petrocelli, S.R., Eds. 1985, *Fundamentals of Aquatic Toxicology, Methods and Applications*; Hemisphere Publishing: Washington, DC.

Randall, R.C.; Lee, H. II; Ozretich, R.J.; Lake, J.L.; Pruell, J. 1991, Evaluation of selected lipid methods for normalizing pollutant bioaccumation. *Environ. Toxicol. Chem.* **10**: 1431–1436.

Richardson, B.J.; Zheng, G.J.; Tse, E.S.C.; De Luca-Abbott, S.B.; Siu, S.Y.M, Lam, P.K.S. 2003, A comparison of polycyclic aromatic hydrocarbon and petroleum hydrocarbon uptake by mussels (Perna viridis) and semi-permeable membrane devices (SPMDs) in Hong Kong Coastal Waters. *Environ. Pollut.* **122**: 223–227.

Sabaliūnas, D.; Lazutka, J.; Sabaliūniene, I.; Södergren, A. 1998, Use of semipermeable membrane devices for studying effects of organic pollutants: Comparison of pesticide uptake by semipermeable membrane devices and mussels. *Environ. Toxicol. Chem.* **17**: 1815–1824.

Schmidt, C. 2004, USGS Columbia Environmental Research Center, Columbia, MO. USA. Personal communication.

Schneider, R. 1982, Polychlorinated biphenyls (PCBs) in cod tissues from the Western Baltic: Significance of equilibrium partitioning and lipid composition in the bioaccumulation of lipophilic pollutants in gill-breathing animals. *Meeresforschung* **29**: 69–79.

Schüürmann, G. and Klein, W. 1988, Advances in bioconcentration prediction. *Chemosphere* **17**: 1551–1574.

Sericano, J.L.; Wade, T.L.; Brooks, J.M. 1996, Accumulation and depuration of organic contaminants by the American oyster (Crassostrea virginica). *Sci. Total Environ.* **179**: 149–160.

Södergren, A. 1987, Solvent filled dialysis membranes simulate uptake of pollutants by aquatic organisms. *Environ. Sci. Technol.* **21**: 855–859.

Spacie, A. and Hamelink, J.L. 1985, Bioaccumulation. In *Fundamentals of Aquatic Toxicology*. Rand, G.M. and Petrocelli, S.R., Eds.; Hemisphere Publishing: Washington; pp. 495–525.

Stow, C.A. 1995, Factors associated with PCB concentrations in Lake Michigan salmonids. *Environ. Sci. Technol.* **29**: 522–527.

Thomann, R.V.; Connolly, J.P.; Parkerton, T.F. 1992, Modeling Accumulation of Organic Chemicals in Aquatic Food Webs. In *Chemical Dynamics in Freshwater Ecosystems.* Gobas F.A.P.C., McCorquodale, J.A., Eds.; Lewis Publishers: Boca Raton; FL.; pp. 153–185.

Toro, B.; Navarro, J.M.; Palma-Fleming, H. 2003, Relationship between bioenergetics responses and organic pollutants in the giant mussel; Chormytilus chorus (Mollusca: Mytilidae). *Aquat. Toxicol.* **63**: 257–269.

Tse, E.; Richardson, B.; Lam, P. 2000, Uptake and release kinetics of selected organochlorines and PAHs by mussels and SPMDs. Presented at the *6th International SPMD Workshop and Symposium*; July 25-27th, 2000; USGS Columbia Environmental Research Center, Columbia, MO.

Utvik, T.I.R.; Durell, G.S.; Johnsen, S. 1999, Determining produced water originating polycyclic aromatic hydrocarbons in North Sea waters: Comparison of sampling techniques. *Mar. Pollut. Bull.* **38**: 977–989.

Utvik, T.I.R. and Johnsen, S. 1999, Bioavailability of polycyclic aromatic hydrocarbons in the North Sea. *Environ. Sci. Technol.* **33**: 1963–1969.

Veith, G.D.; Macek, K.J.; Petrocelli, S.R.; Carroll, J. 1979, An evaluation of using partition coefficients and water solubility to estimate bioconcentration factors for organic chemicals in fish. *Fed. Regist.* **44**: 15926–15981.

Verweij, F.; Booij, K.; Satumalay, K.; van der Molen, N.; van der Oost, R. 2004, Assessment of bioavailable PAH, PCB, and OCP concentrations in water using semipermeable membrane devices (SPMDs), sediments and caged carp. *Chemosphere* **11**: 1675–1689.

Wang, W-X. and Fisher, N.S. 1999, Assimilation efficiencies of chemical contaminants in aquatic invertebrates: A synthesis. *Environ. Toxicol. Chem.* **18**: 2034–2045.

Wang, Y.; Wang, C.; Wang, Z. 1998, Uptake of moderately hydrophobic chlorophenols from water by semipermeable membrane devices (SPMDs) and by goldfish (Crassius auratus). *Chemosphere* **37**: 327–339.

Wang, Z.; Wang, Y.; Ma, M.; Lu, Y.; Huckins, J.N. 2002, Use of triolein-SPMD to assess the bioconcentration processes of hydrophobic organic contaminants in the Huaihe River, China. *Environ. Toxicol. Chem.* **21**: 2378–2384.

Chapter 8

Selected Case Studies

8.1. REVIEW OF SPMD APPLICATIONS

In the previous chapters, we have shown that SPMD technology is useful for a variety of applications in surface water, groundwater, sediments, and air. More specifically, documented applications of SPMD technology include: 1) determination of the presence, sources, and the transport and fate of hydrophobic organic chemicals (HOCs); 2) estimation of ambient time-weighted average (TWA) concentrations of HOC solutes or vapors; 3) determination of the fluxes of bioavailable (i.e., dissolved phase) residues in aquatic systems; 4) *in situ* biomimetic concentration of bioavailable chemicals for screening with bioindicator tests, other bioassays, and immunoassays, and for toxicity identification evaluation investigations; 5) estimation of waterborne chemical exposure to aquatic organisms and the bioconcentration potential of residues; and 6) the enrichment of HOCs in lipid extracts. In this chapter we highlight a number of case studies. These studies do not encompass all of the applications listed above but are intended to provide the reader with a view of several unique attributes of SPMDs as well as to show how they complement existing technology.

8.2. AIR-WATER-MICROLAYER EQUILIBRIUM

SPMDs are powerful tools to assess the degree of equilibrium between environmental compartments. Booij and van Drooge (2001) exposed SPMDs to water

and air at a coastal site during winter. In addition, SPMDs were exposed to the sea surface microlayer (SSM) using an exposure device that caused the SPMDs to intermittently emerge from the water and submerge to a depth of 0.5 cm below the surface.

The SSM conventionally is sampled using rotating drums, glass plates, or metal mesh screens (Hardy et al., 1988; Hardy and Cleary, 1992; Garabetian et al., 1993) which sample the water surface in the sub-millimeter range. With these samplers, a comparison of concentrations in the SSM and in deeper water is often difficult, because substantial corrections for dissolved organic carbon (*DOC*)-bound contaminants have to be applied, particularly for the SSM, where *DOC* concentrations are often elevated. The application of SPMDs for sampling the SSM circumvents the *DOC* correction problem, although at the cost of reduced depth resolution. For the coastal site studied by Booij and van Drooge (2001), the ratios of dissolved polychlorinated biphenyls (PCBs) concentrations between SSM and deeper water layers were 0.8 to 0.9 on average during two time periods, indicating a minimal departure from equilibrium between bulk water and SSM.

The authors also assessed the degree of equilibrium between atmospheric and aqueous PCBs and hexachlorobenzene (HCB). The ratio of absorbed amounts for SPMDs exposed to air (N_a) and water (N_w) is given by

$$\frac{N_a}{N_w} = \frac{C_a}{C_w K_{aw}} \frac{\left[1 - \exp\left(-k_{ea}t\right)\right]}{\left[1 - \exp\left(-k_{ew}t\right)\right]} \tag{8.1}$$

where C_a, C_w are the contaminant concentrations in air and water, k_{ea}, k_{ew} are the exchange rate constants for SPMD-air and SPMD-water, and K_{aw} is the air-water partition coefficient (volume per volume units). This equation has an interesting feature that is worth noting. Because $K_{aw}C_w$ equals the equilibrium atmospheric concentration, the first term at the right-hand side of Eq. 8.1 represents the relative departure from equilibrium. When this term is larger than 1, the air is supersaturated relative to the water phase. Using the dissipation of three PRCs, Booij and Van Drooge (2001) showed that there was reason to believe that k_{ea} and k_{ew} were about the same in their study. The authors concluded that the ratio of the amounts in air-exposed and water-exposed SPMDs was equal to the term $C_a/(C_w K_{aw})$, i.e. equal to the relative departure of equilibrium. Their results indicated that a fair degree of air-water equilibrium existed for PCBs, and that the atmosphere was oversaturated with HCB by a factor of 6 to 9, relative to the water phase (Figure 8.1). In this work, the use of SPMDs allowed the authors to ignore the correction for *DOC*-bound chemicals and permitted the determination of the relative departure (if any) from equilibrium of target compound concentrations in the aqueous and atmospheric boundary layers. This type of data is very useful for modeling the flux of chemicals between the aqueous and atmospheric phases.

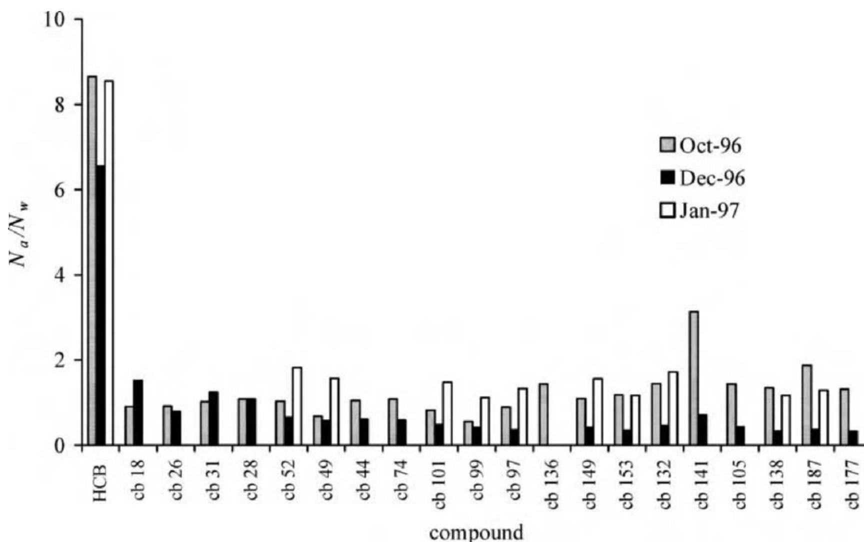

FIGURE 8.1 Ratio of amounts absorbed by air-exposed and water-exposed SPMDs at a Dutch coastal site. Reprinted from Booij and van Drooge (2001), copyright (2001); reproduced with permission from Elsevier.

8.3. SAMPLING INDOOR AIR

In a joint project between the US Environmental Protection Agency (EPA) and the US Geological Survey (USGS), SPMDs were deployed at 57 sites indoors along the border between Arizona (USA) and Mexico (Petty et al., 2002). The exposure period was 30 d and each sample represented a composite of four 1-mL triolein SPMDs. Numerous HOC vapors of historic concern were found in exposed SPMDs, including organochlorine pesticides (OCPs), PCBs, and polycyclic aromatic hydrocarbons (PAHs). In addition, a variety of contaminants of emerging concern, e.g., diazinon, chlorpyrifos, permethrin, etc., were present at many sites. Figure 8.2 illustrates the very high amounts of some of these "current use" pesticides accumulated in SPMD samples.

Also, Petty et al. (2002) performed an in depth analysis of the OCP fraction of SPMD extracts by gas chromatography-mass spectrometry (GC-MS) resulting in the tentative identification of about 400 airborne organic chemicals, which were not present in SPMD field blanks. The OCP fraction represents only one of several enriched fractions from SPMD samples. Table 8.1 summarizes the various classes of compounds tentatively identified in SPMDs exposed to indoor air.

The estimated ambient vapor-phase concentrations of chemicals in indoor air were, in general, below the NIOSH time-weighted average exposure limits for a 40 hr workweek. However, the authors of this study concluded that the consequences of long term human exposure to these complex mixtures of airborne

Table 8.1 Classes of Compounds Tentatively Identified in SPMD Samples Exposed to Indoor Air

Polycyclic aromatic compounds (PAHs)	(28)[a]	Phthalate esters	(5)
benzofluoranthene		diethylhexyl phthalate	
chrysene		dibutyl phthalate	
benz[*a*]anthracene		benzylbutyl phthalate	
fluoranthene		Organochlorine pesticides	(27)
phenanthrene		chlordanes	
fluorene		chlordenes	
pyrene		chlorpyrifos	
		p,p′-DDT	
Alkylated PAHs	(19)		
C1–C5 naphthalenes		Fragrance components	(20)
C1–C4 phenanthrenes		galoxolide	
		polycyclic musk	
C1–C2 pyrenes	(9)	hexyl cinnamaldehyde	
Alkyl biphenyls		manoyl oxide	
C1–C4 biphenyls		menthol	
		musk xylene	
Alkyl benzenes	(5)	jasmal	
		lilial	
Alkyl terphenyls	(3)		
Hydrocarbons	(10)	Terpenoids	(30)
C8–C22 alkanes		calamenene	
		terpineol	
Cyclic non-aromatic hydrocarbons	(9)	cedrol	
C2–C3 tetrahydronaphthalenes		isomethyl ionone	
propyl cyclopentane		xanthene	
Alkyl aldehydes	(10)	Phenolics	(6)
C9–C13 alkyl and alkenyl aldehydes		bis(dimethylbenzyl) phenol	
		bis(dimethylbenzyl)tertiarybutyl phenol	
Alkyl ketones	(9)		
C8–C16 alkyl and alkenyl ketones		Phosphates	
		triphenyl phosphate	
Alkyl alcohols	(15)	cresyl diphenyl phosphate	
C8–C22 alkyl and alkenyl alcohols			
		Unidentified compounds	(120)
Alkyl acids and esters	(16)	possible terpenoid isomers and	
alkyl propanoates		fragrance-related components	
Sterols	(5)		
cholesterol			
sitosterol			
stigmasterol, fucosterol, campesterol			

[a] Parenthetical values correspond to the number of compounds identified in a chemical class.

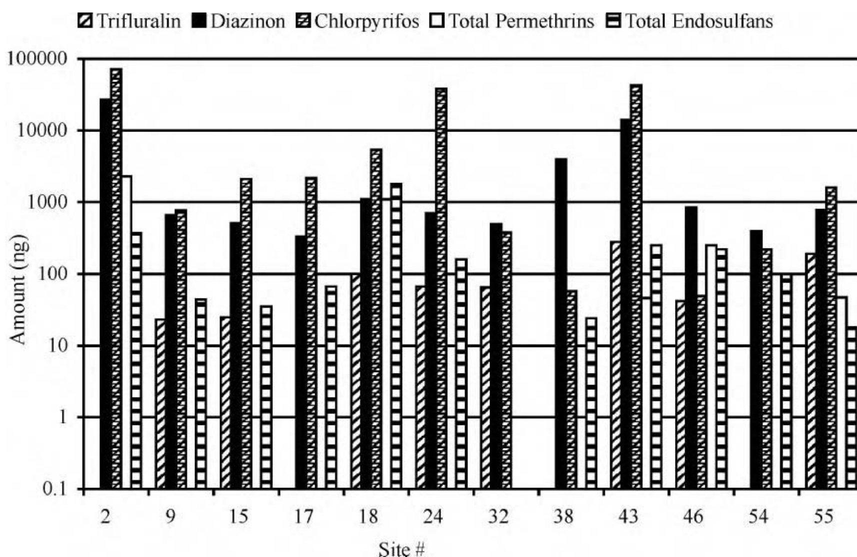

FIGURE 8.2 Amounts of current use pesticides in SPMD samples at selected sites.

chemicals are unknown, especially with respect to gender and age related variables. A major concern is the possibility of additive effects arising from prolonged respiratory exposure. In this study, SPMDs provided a convenient approach for determining the presence of several recognized vapor-phase contaminants and a means of defining the presence of a large number of previously unidentified airborne chemicals.

8.4. FURTHER COMPARISONS OF BIVALVES AND SPMDs

Bivalves are widely used in monitoring programs to assess the waterborne contaminant exposure. These organisms are used because they are immobile, widely available, have very low levels of certain enzyme systems known to mediate the metabolism of many contaminants, and ventilate large volumes of water when feeding (see Chapter 7). However, mounting evidence suggests that the levels of some residues in bivalve tissues often are not proportional to ambient chemical concentrations. This lack of proportionality may result in the inability to reliably extrapolate ambient exposure concentrations, insufficient residue concentration factors for the detection or quantification of target compounds, and higher concentrations of high K_{ow} compounds than predicted by equilibrium partition theory. In combination, these difficulties can lead to the inability to detect the presence of target compounds and to discern concentration gradients or chemical sources.

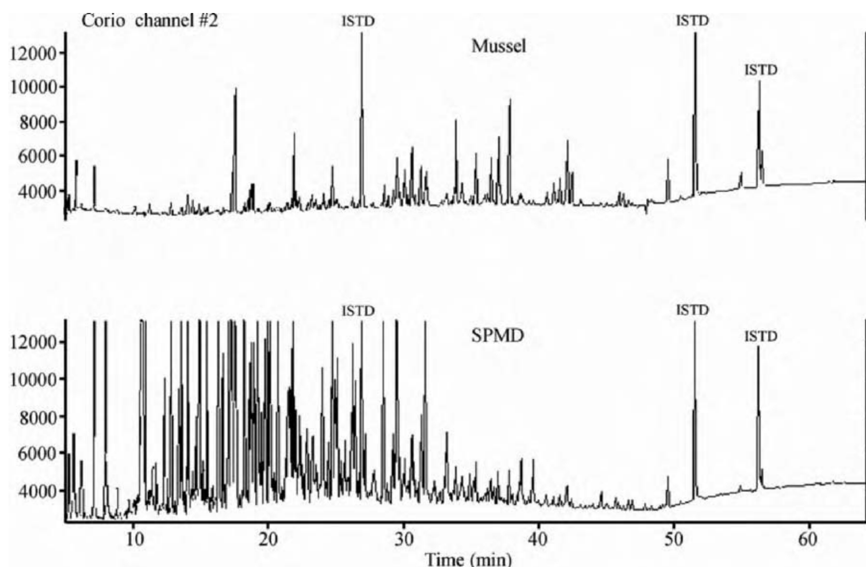

FIGURE 8.3 GC-MS comparison of ion chromatograms of extracts from mussels (*Mytilus edulis*) and SPMDs, Corio Bay Australia. Peaks labeled ISTD are internal standards. Reprinted with permission from the American Petroleum Institute, copyright 2002 (Huckins et al., 2002).

The following example illustrates one aspect of this potential problem. Prest et al. (1995) deployed blue mussels (*Mytilus edulis*) and SPMDs contiguously at several sites, including sites near a refinery effluent, in Corio Bay, Victoria, Australia. This 60 d exposure study was designed to examine the relative abilities of BMOs and SPMDs to monitor a known gradient of chlorinated contaminants. Overall, the levels of chlorinated organic chemicals were about the same in both sample types. However, the GC-MS ion chromatograms from the two matrices differed markedly, as shown in Figure 8.3.

Analysis of these SPMD samples suggested that lower chlorinated PCBs and a complex mixture of unknowns (early eluting, relatively low K_{ow} components) were present at high concentrations in the water column, while data from the mussel samples implied essentially the reverse. These results are not surprising for several reasons. Unlike SPMDs, concentrations of some hydrophobic organic contaminants in bivalves are not necessarily proportional to ambient water concentrations (Huckins et al., 2004). Also, early eluting (GC) chlorinated organics are much more soluble in water than late eluting compounds and would be expected to be present at higher concentrations in aquatic environments than the higher molecular weight (later eluting), very hydrophobic components. However, models successfully used for estimating bioconcentration in aquatic organisms exhibit an inverse relationship between the lipid content of tissues and the related elimination rate constant (k_e). Large k_es mean that time to equilibrium is short and thus the volume of water cleared of chemicals is relatively small. The lipid content of SPMDs is at least an

order-of-magnitude greater than bivalves, while the uptake rates for low K_{ow} compounds are similar (Huckins et al., 2004). Thus, bivalves are expected to accumulate much lower amounts of these compounds than SPMDs. In fact, *BCF*s of organisms with low lipid contents may be inadequate for the detection or quantification of trace amounts of these early eluting compounds. The Prest et al. (1995) study illustrates one other significant difference between BMOs and SPMDs. One of the study sites was in a refinery effluent stream where bivalves could not survive due to elevated temperature and turbidity. However, Prest et al. (1995) concluded that overall bivalves and SPMDs provide complimentary information, such as the ability to better determine the relative roles of respiratory and dietary routes of uptake.

In another bivalve study, SPMDs and Asian clams, *Corbicula fluminea* were deployed at stream sites in the Dallas-Fort Worth Metropolitan Area (Moring and Rose, 1997) to assess the presence and concentrations of bioavailable, dissolved PAHs. Deployment sites were White Rock Creek, West Fork Trinity River and Trinity River below Dallas, and the exposure periods ranged between 30 and 35 d. Bivalves were depurated for 1 d before being processed for analysis. Twenty-four PAHs were measured in SPMDs, 20 of which occurred at all sites and only three PAHs were detected in the co-deployed clams (Figure 8.4). Throughout all sites, non-alkylated PAHs were found at greater levels in SPMDs than the alkylated forms. Nine out of the 16 EPA priority pollutant PAHs were detected in SPMDs. In several cases (i.e., benz[*a*]anthracene, benzo[*a*]pyrene, and chrysene), estimated concentrations in water exceeded the EPA's human health criteria. This example illustrates that the occurrence of potentially toxicologically significant residues of PAHs may not be detected when using BMOs in some environments. It seems unlikely that the depuration of gut contents prior to analysis would have been responsible for the small number of PAHs detected in these samples. A much more likely explanation is chemical stressor induced valve closure, limiting water exchange only to that necessary for survival (e.g., Goudreau et al., 1993; Hellou et al., 2004; Huckins et al., 2004).

8.5. ESTIMATION OF EXPOSURE TO DIOXIN-LIKE COMPOUNDS USING SEDIMENTS, CAGED FISH, AND SPMDs

Gale et al. (1997) conducted a study in the Saginaw River, MI, USA to compare the SPMD method of water sampling with sediment-based and caged fish based methods for assessing exposure to dioxin-like compounds. More specifically, the targeted compounds were planar halogenated hydrocarbons (PHHs), which consisted of planar PCBs, polychlorinated dibenzo-*p*-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs). The list of target compounds was expanded to include polychlorinated dibenzothiophenes (PCDTs) after finding PCDT residues at all sites. The log K_{ow}s of target compounds ranged from 6.1 to 8.2. Fish and SPMDs were exposed for 28 d at five sites and sediment samples (0–10 cm depth) were collected at each site. SPMDs used were of standard design

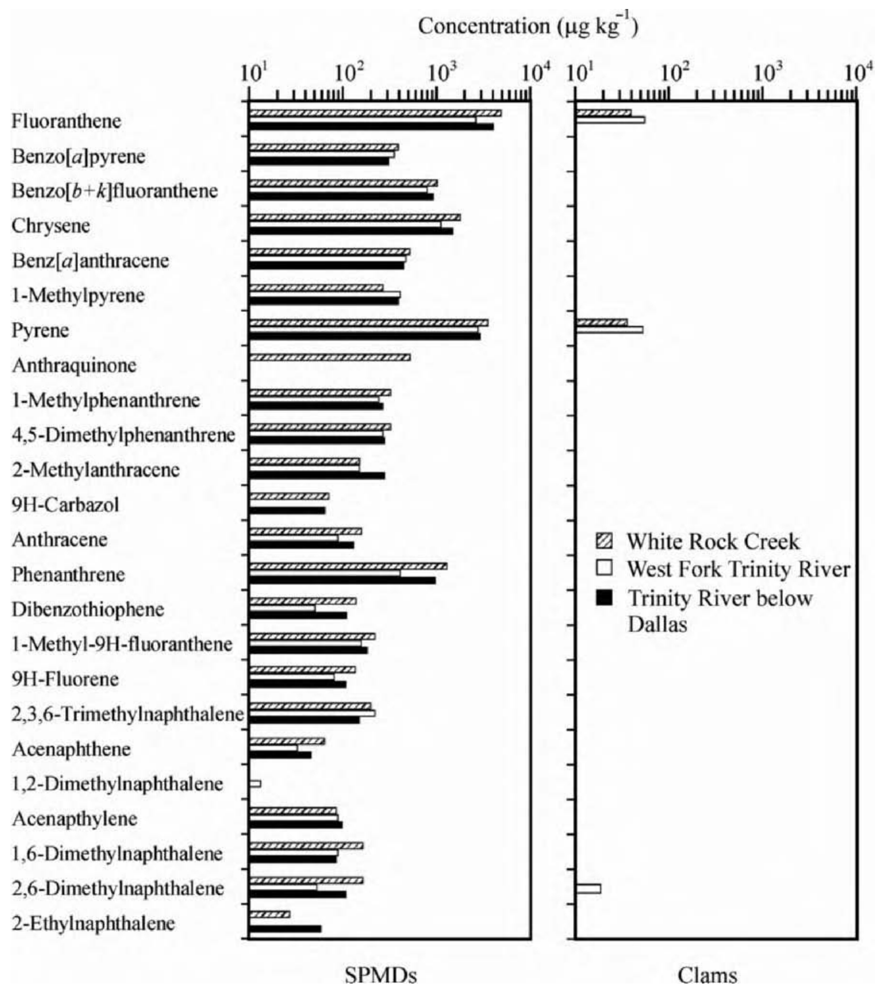

FIGURE 8.4 Comparison of PAHs detected by GC-PID in SPMDs and clams (*Corbicula fuminea*) deployed in the Trinity River, Dallas,Texas, USA. Reprinted from Moring and Rose (1997), copyright (1997); reproduced with permission from Elsevier.

(see Chapter 4) but 152 cm in length and the fish were juvenile hatchery-reared channel catfish (*Ictalurus punctatus*; 8–10 cm).

A number of toxicologically active 2,3,7,8-substituted PCDDs and PCDFs, planar PCBs and PCDD, PCDF, and PCDT homologs were measured in fish, SPMDs, and sediments. Only two target compounds exceeded the detection limits of 0.2–1 pg g^{-1} in SPMD field blanks (see definition in Chapter 5). These exceptions were octachlorodibenzo-*p*-dioxin (OCDD) and octachlorodibenzofuran (OCDF) which were present in SPMDs at about 5 pg g^{-1}. However, negative

control fish contained significant amounts of 1,2,3,4,6,7,8-heptachlorodibenzo-*p*-dioxin (≈ 5 pg g^{-1}), OCDD (≈ 50 pg g^{-1}) and just quantifiable amounts of Cl_{4-6} PCDDs (≈ 1 pg g^{-1}).

Analysis of the three test matrices revealed that congener patterns representing each matrix were constant and distinctive, regardless of sampling site. In general, only the analyte concentrations varied among sites (Figure 8.5). Figure 8.5 (site 5, downstream from Bay City) also shows that patterns of congeners in each homolog group were similar for SPMDs and sediments. More specifically, the number of congeners found and their relative ratios in each homolog group (Cl_3–Cl_7) corresponded well between SPMDs and sediments. The patterns of PCDDs and PCDFs in fish were different from those of either SPMDs or sediments but PCDT patterns showed very little difference among the three matrices (Figure 8.5). The apparent metabolism of PCDDs and PCDFs by channel catfish appeared to be the causal factor in the distinct difference between the residue patterns in the fish and SPMDs (Figure 8.5). Although not shown in Figure 8.5, Gale et al. (1997) found that the coplanar PCB congener 77 or 3,3′,4,4′-tetrachlorobiphenyl was about an order of magnitude higher in SPMDs than in channel catfish, whereas, SPMD and channel catfish concentrations of coplanar PCB congener 81 or 3,4,4′,5-tetrachlorobipheny were within two fold of each other. Structure-specific metabolism appears to be the reason for the difference in the concentrations of the two congeners. Because coplanar PCB congeners are present in technical PCB mixtures at low levels and because of the apparent high specificity of the degradation pathway, the Gale et al. (1997) data does not invalidate the good correlation shown between SPMDs and fish in Figure 7.6.

8.6. USING SPMDs IN CONJUNCTION WITH BIOASSAYS AND CHEMICAL ANALYSIS TO CHARACTERIZE TOXIC POLLUTANTS

Lake Shkodra/Skadar is the largest lake in the Balkan region and is located on the border between Albania and Montenegro. Due to the broad array of rare or endangered plant and animal species it supports, the lake and the extensive associated wetlands have been designated a Ramsar site. The lake is also the focus of an international cooperative investigation by a diverse team of researchers from Albania, Serbia and Montenegro, Germany, Austria and the UK, concerned with the possible detrimental effects of increasing anthropogenic contaminants. From the onset of these investigations, several members of the multinational team expressed concern over the long-term risks posed by increased loads of HOCs on the lake's aquatic biota. However, limited access to suitable facilities and equipment in the Balkan region, and logistical problems associated with the transportation of large quantities of water for analysis delayed investigations into the identity and distribution of HOCs in the lake. These problems were overcome by Rastall et al. (2004a) through the application of SPMD sampling technology. SPMDs were transported to the region, deployed by local workers with knowledge of

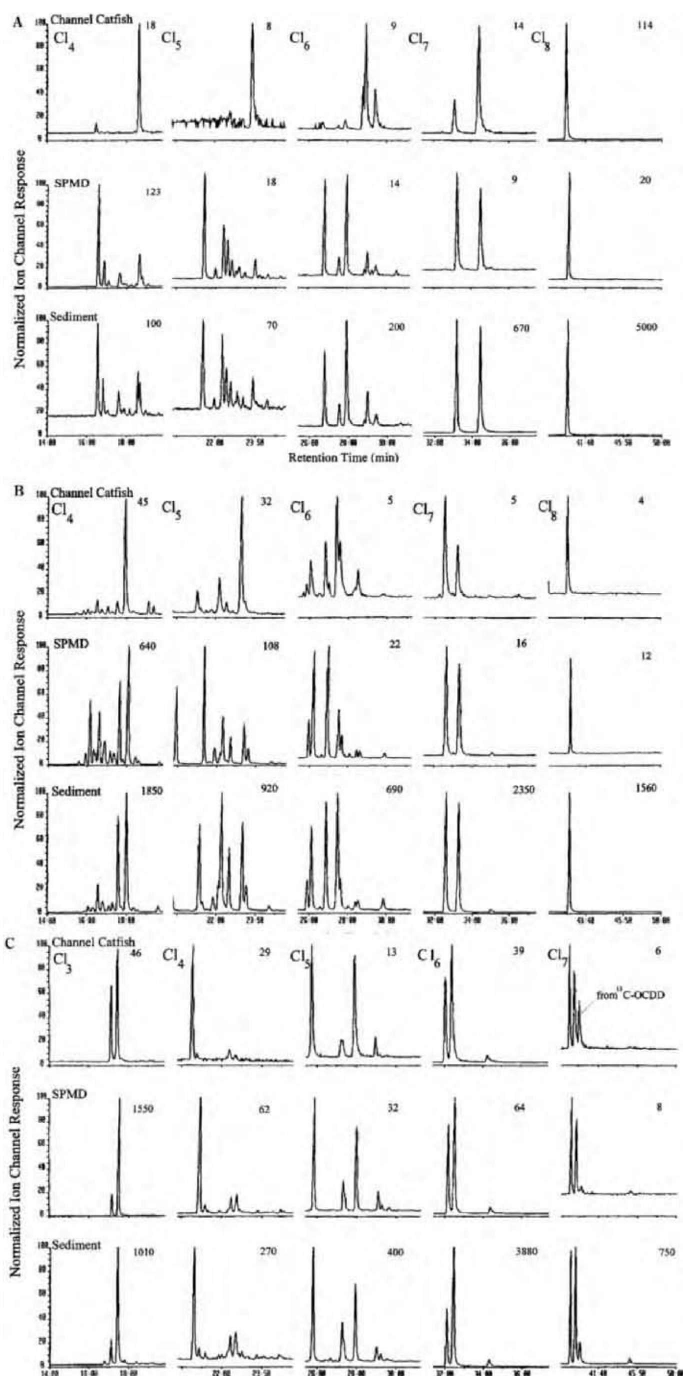

FIGURE 8.5 Ion traces of PCDDs (set A, Cl_4–Cl_8), PCDFs (set B, Cl_4–Cl_8), and PCDTs (set C, Cl_3–Cl_7) in caged channel catfish, SPMDs, and sediment from site 5, downstream from Bay City, MI, USA. The matrix identity is given in the upper left of the first chromatogram of the homolog series and the maximum peak height is given in the upper right of each chromatogram for comparison of peak heights among contaminant homologues and matrices. Reprinted from Gale et al. (1997), copyright (1997); reproduced with permission from American Chemical Society.

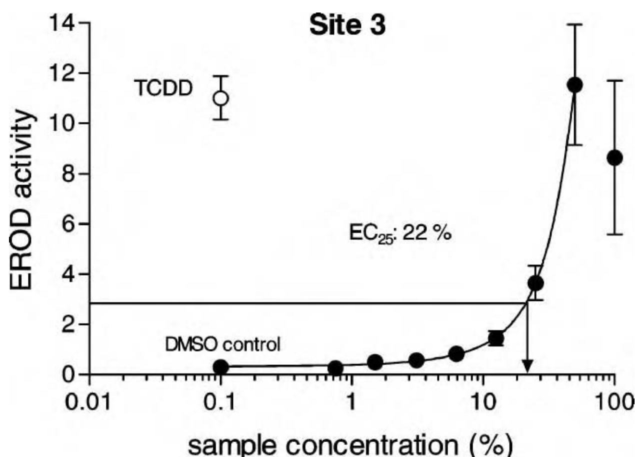

Figure 8.6 Induction of significant activity in the ethoxyresorufin-*O*-deethylase (EROD) screen by an extract of an SPMD sample from Lake Shkodra/Skadar. Reprinted from Rastall et al. (2004a), copyright (2004); reproduced with permission from Environmental Science and Pollution Research.

anthropogenic inputs and influences in the lake, and then returned to the laboratory for analysis. Moreover, SPMDs enabled sequestration of sufficient amounts of chemicals for multiple rounds of bioassay and chemical analysis.

Analysis of the SPMD sample extracts from five of the six sampling sites in this study revealed the presence of a wide variety of waterborne contaminants, including EPA priority pollutants PAHs and their alkylated analogues, atrazine and other agricultural chemicals, and a variety of sterols and sterol derivatives. A total of 39 HOCs were tentatively identified in SPMD extracts but numerous compounds remain unidentified. Extracts from all but one sampling site were found to induce significant concentration dependent ethoxyresorufin-*O*-deethylase (EROD) activity, which is a biomarker of exposure to dioxin-like compounds (Figure 8.6; also see Section 6.3.). Although PAHs were present at relatively high levels in these samples, it appears that EPA priority pollutants represented only 0.06% of the total EROD-inducing potential. Similarly, five of the six sample sites induced significant concentration-dependent activity in the yeast estrogen screen (YES) assay (Figure 8.7; see Section 6.5.). Also, the results of the YES assay from two sites were indicative of an inhibitory or toxic response, i.e., the yeast cells either did not grow or growth was delayed over that observed with controls. No significant activity was observed in any of the blanks or control sample extracts.

These data indicate that hydrophobic chemicals with estrogenic and EROD-inducing potential are widespread in this ecosystem and are readily bioavailable to aquatic organisms living in the system. By incorporating the YES, the recently developed yeast androgen screen, and the EROD assays (Rastall, 2004b) into exposure assessment approaches, a more complete picture of the potential toxicity

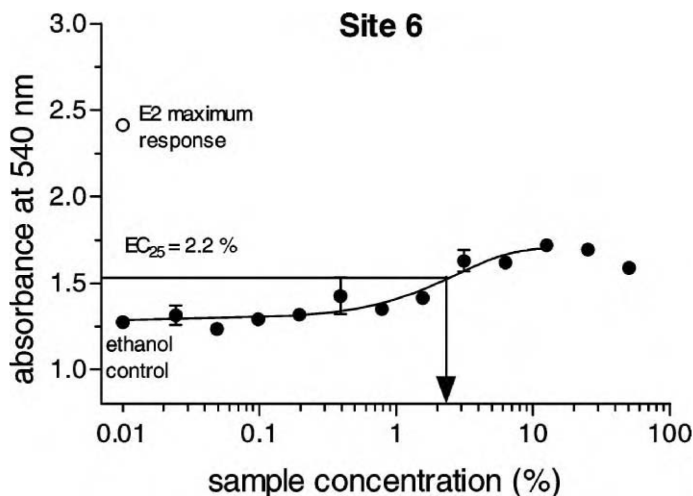

Figure 8.7 Induction of significant activity in yeast estrogen screen (YES) assay by an extract of an SPMD sample from Lake Shkodra/Skadar. Reprinted from Rastall et al. (2004a), copyright (2004); reproduced with permission from Environmental Science and Pollution Research.

of readily bioavailable HOCs is available. Furthermore, as anthropogenic impacts on Lake Shkodra-Skadar increase in the future, SPMD-based sampling is expected to play a central role in surveillance and investigative monitoring, as well as to facilitate research into the effects of HOCs on Lake Shkodra-Skadar's aquatic biota.

8.7. REFERENCES

Booij, K. and van Drooge, B.L. 2001, Polychlorinated biphenyls and hexachlorobenzene in atmosphere, sea-surface microlayer, and water measured with semi-permeable membrane devices (SPMDs). *Chemosphere* **44**: 91–98.

Gale, R.W.; Huckins, J.N.; Petty, J.D.; Peterman, P.H.; Williams, L.L.; Morse, D.; Schwartz, T.R.; Tillitt, D.E. 1997, Comparison of the uptake of dioxin-like compounds by caged channel catfish and semipermeable membrane devices in the Saginaw River, Michigan. *Environ. Sci. Technol.* **32**: 178–187.

Garabetian, F.; Romano, J.-C.; Paul, R.; Sigoillot, J.-C. 1993, Organic matter composition and pollutant enrichment of sea surface microlayer inside and outside slicks. *Mar. Environ. Res.* **35**: 323–339.

Goudreau, S.E.; Neves, R.J.; Sheehan, R. 1993, Effects of wastewater treatment plant effluents of freshwater mollusks in the upper Clinch River, Virginia, USA. *Hydrobiologia* **252**: 211–230.

Hardy, J.T.; Coley, J.A.; Antrim, L.D.; Kiesser, S.L. 1988, A hydrophobic large-volume sampler for collecting aquatic surface microlayers: Characterization and comparison with the glass plate method. *Can. J. Fish. Aquat. Sci.* **45**: 822–826.

Hardy, J.T. and Cleary, J. 1992, Surface microlayer contamination and toxicity in the German Bight. *Mar. Ecol. Prog. Ser.* **91**: 203–210.

Hellou, J.; Steller, S.; Langille, M.A.; Leonard, J.; Tremblay, D. 2004, Partitioning of polycyclic aromatic hydrocarbons between water and particles and bioaccumulation in mussels: A harbour case. *Mar. Environ. Res.* **59**: 101–117.

Huckins, J.N.; Petty, J.D.; Prest, H.F.; Clark, R.C.; Alvarez, D.A.; Orazio, C.E.; Lebo, J.A.; Cranor, W.L.; Johnson, B.T. 2002, *A Guide for the Use of Semipermeable Membrane Devices (SPMDs) as Samplers of Waterborne Hydrophobic Organic Contaminants*; Publication No. 4690; American Petroleum Institute (API): Washington, DC.

Huckins, J.N.; Prest, H.F.; Petty, J.D.; Lebo, J.A.; Hodgins, M.M.; Clark, R.C.; Alvarez, D.A.; Gala, W.R.; Steen, A.; Gale, R.W.; Ingersoll, C.G. 2004, Overview and comparison of lipid-containing semipermeable membrane devices (SPMDs) and oysters (Crassostrea gigas) for assessing chemical exposure. *Environ. Toxicol. Chem.* **23**: 1617–1628.

Moring, J.B. and Rose, D.R. 1997, Occurrence and concentration of polycyclic aromatic hydrocarbons in semipermeable membrane devices and clams in three urban streams of the Dallas-Fort Worth Metropolitan Area, Texas. *Chemosphere* **34**: 551–566.

Petty, J.D.; Huckins, J.N.; Robertson, G.L.; Cranor, W.L.; Gale, R.W.; Alvarez, D.A.; Clark, R.C. 2002, The application of semipermeable membrane devices (SPMDs) as samplers of airborne contaminants in indoor air. Presented at the 53rd Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March 16–22, 2002; New Orleans, LA.

Prest, H.F.; Richardson, B.J.; Jacobson, L.A.; Vedder, J.; Martin, M. 1995, Monitoring organochlorines with semipermeable membrane devices (SPMDs) and mussels (Mytilus edulis) in Corio Bay, Victoria, Australia. *Mar. Pollut. Bull.* **30**: 543–554.

Rastall, A.C.; Neziri, A.; Vukovic, Z.; Jung, C.; Mijovic, S.; Hollert, H.; Nikcevic, S.; Erdinger, L. 2004a, The identification of readily bioavailable pollutants in Lake Shkodra/Skadar using semipermeable membrane devices (SPMDs), bioassays and chemical analysis. *Environ. Sci. Pollut. R.* **11**: 240–253.

Rastall, A.C. 2004b, University of Heidelberg, Germany; Personal communication.

Appendix A

SPMD Calibration Data

A.1. SPMD-WATER PARTITION COEFFICIENTS

Literature values of SPMD-water partition coefficients (K_{sw}s) should be used with caution. Different units of K_{sw} are generated when the concentrations in SPMD and water are expressed on a mass basis (e.g., ng g^{-1}) or a volume basis (e.g., ng mL^{-1}). Depending on the choice of concentration units, K_{sw} values will have units of g g^{-1}, mL mL^{-1}, or mL g^{-1}, or K_{sw} values are given as dimensionless numbers in the former two cases. Care should be taken to distinguish between the different versions of K_{sw}. Preferably, mL mL^{-1} units should be used, because most of the equations for SPMD uptake kinetics use the volume of an SPMD rather than its mass. The two most frequently used versions of K_{sw} are interrelated by

$$K_{sw}(\text{mL mL}^{-1}\text{ units}) = K_{sw}(\text{mLg}^{-1}\text{ units}) \cdot \rho_s \quad (A.1)$$

where ρ_s is the SPMD density (0.91 g mL^{-1}). Hence the difference in the numerical values of the two K_{sw} definitions amounts to a factor of $1/0.91 = 1.10$, which corresponds to 0.04 log units. This value is low, when compared to the magnitude of errors associated with environmental-analytical chemistry, but any data scatter originating from incompatible units should be avoided.

In Tables A.1 through A.3, all K_{sw} values were converted to mL mL^{-1} units where applicable. In the literature sources where the units were not explicitly mentioned, these were inferred from the model equations used. To avoid possible ambiguity in the future, authors are urged to specify the units of their reported K_{sw} values.

TABLE A.1 SPMD-Water Partition Coefficients (K_{sw}s, mL mL^{-1}) of Mono-Aromatic and Polycyclic Aromatic Hydrocarbons

Compound	M	log K_{ow}[a]	log K_{sw}	°C	ref.[b]
benzene	78.1	2.13	1.78	25	1
toluene	92.1	2.69	2.34	25	1
ethylbenzene	106.2	3.13	2.80	25	1
naphthalene	128.2	3.37	3.20	17	5
naphthalene	128.2	3.37	3.36	24	2
1-methylnaphthalene	142.2	3.87	4.20	17	5
acenaphthylene	152.2	4.00	4.20	17	5
acenaphthylene	152.2	4.00	3.63	24	2
acenaphthene	154.2	3.92	4.00	2	4
acenaphthene	154.2	3.92	4.13	13	4
acenaphthene	154.2	3.92	4.50	17	5
acenaphthene	154.2	3.92	4.05	24	2
acenaphthene	154.2	3.92	3.96	30	4
biphenyl	154.2	3.90	4.30	17	5
1,3-dimethylnaphthalene	156.2	4.42	5.10	17	5
fluorene	166.2	4.18	4.80	17	5
fluorene	166.2	4.18	4.21	24	2
anthracene	178.2	4.54	4.67	24	2
phenanthrene	178.2	4.57	4.49	2	4
phenanthrene	178.2	4.57	4.70	8	3
phenanthrene	178.2	4.57	4.66	13	4
phenanthrene	178.2	4.57	4.53	18	3
phenanthrene	178.2	4.57	4.47	24	2
phenanthrene	178.2	4.57	4.29	30	3
phenanthrene	178.2	4.57	4.59	30	4
fluoranthene	202.3	5.22	5.22	2	4
fluoranthene	202.3	5.22	5.22	13	4
fluoranthene	202.3	5.22	4.68	24	2
fluoranthene	202.3	5.22	5.00	30	4
pyrene	202.3	5.18	5.28	2	4
pyrene	202.3	5.18	5.24	13	4
pyrene	202.3	5.18	4.79	24	2
pyrene	202.3	5.18	5.09	30	4
benzo[*a*]anthracene	228.3	5.91	5.45	2	4
benzo[*a*]anthracene	228.3	5.91	5.46	30	4
chrysene	228.3	5.86	5.52	2	4
chrysene	228.3	5.86	5.51	30	4

[a] Adopted from the original reference, from Mackay et al. (1992a), or from US EPA (2003), in order of availability.
[b] 1. Calculated from LDPE-water partition coefficients (Reynolds et al., 1990) and triolein-water partition coefficients (Chiou, 1985); 2. Huckins et al. (1999); 3. Huckins et al. (2002a); 4. Booij et al. (2003); 5. Huckins et al. (2004).

Table A.2 SPMD-Water Partition Coefficients (K_{sw}s, mL mL^{-1}) of Chlorobenzenes and PCBs

Compound	M	log K_{ow}[a]	log K_{sw}	°C	ref.[b]
1,2,3,4-tetrachlorobenzene	215.9	4.50	4.36	2	3
1,2,3,4-tetrachlorobenzene	215.9	4.50	4.58	13	3
1,2,3,4-tetrachlorobenzene	215.9	4.50	4.53	30	3
pentachlorobenzene	250.3	5.00	5.00	30	3
PCB 1	188.7	4.30	4.18	25	1
PCB 4/5/8	223.1	5.13	4.65	25	1
PCB 28	257.5	5.80	5.41	2	3
PCB 28/29	257.5	5.70	5.14	25	1
PCB 28	257.5	5.80	5.50	30	3
PCB 52	292.0	6.10	5.35	2	3
PCB 52	292.0	6.10	5.55	8	2
PCB 52	292.0	6.10	5.66	18	2
PCB 52/47	292.0	6.00	5.35	25	1
PCB 52	292.0	6.10	5.53	30	2
PCB 52	292.0	6.10	5.47	30	3
PCB 98/101	326.4	6.36	5.44	25	1
PCB 153/154	360.9	6.97	5.86	25	1

[a] Adopted from the original reference or from Mackay et al. (1992b), in order of availability.
[b] 1. Calculated from LDPE-water partition coefficients (Lefkovitz et al., 1996) and triolein-water partition coefficients (Chiou, 1985); 2. Huckins et al. (2002a); 3. Booij et al. (2003).

A.2. WATER SAMPLING RATES

SPMD uptake kinetics are commonly reported in terms of sampling rates (R_ss) or uptake rate constants (k_us). Care should be taken to identify the SPMD design and exposure condition for which these parameters are given. The surface area of the SPMD is one of the most important parameters, because R_s values are linearly proportional to the surface area. For this reason, we urge authors to specify the surface area of SPMDs along with R_s values. Sometimes, R_s values have been normalized to the 460 cm^2 surface area of the original (standard) SPMD design (2.54 cm wide, 91.4 cm long LDPE layflat tubing with a wall thickness of 85 μm, containing 1-mL triolein).

The accumulation of chemicals can also be expressed in terms of k_us. Unfortunately, k_us are expressed in several different ways, contributing to uncertainty in data comparability. The symbol "k_u" was initially used in the SPMD related literature as a parameter that describes the equilibration rate constant (Huckins et al., 1993), whereas in later work, the symbol "k_e" was adopted for this parameter (Booij et al., 1998; Huckins et al., 1999). Depending on whether contaminant concentrations in SPMDs are expressed on a mass or a volume basis, k_us may have units of or mL mL^{-1} d^{-1} (i.e., d^{-1}) or mL g^{-1} d^{-1}. These different unit-forms of k_u are interrelated by

$$k_u(d^{-1}\text{units}) = k_u(\text{mLg}^{-1}\,\text{d}^{-1}\text{units}) \cdot \rho_s \tag{A.2}$$

Table A.3 SPMD-Water Partition Coefficients (K_{sw}s, mL mL^{-1}) of Organochlorine Pesticides

Compound	M	log K_{ow}[a]	log K_{sw}	°C	ref.[b]
α-HCH	290.8	3.80	3.29	19	2
α-HCH	290.8	3.80	3.37	19	2
α-HCH	290.8	3.80	3.32	19	2
α-HCH	290.8	3.80	3.31	19	2
β-HCH	290.8	3.80	2.91	19	2
β-HCH	290.8	3.80	2.87	19	2
β-HCH	290.8	3.80	3.17	19	2
β-HCH	290.8	3.80	3.26	19	2
γ-HCH	290.8	3.70	3.01	19	2
γ-HCH	290.8	3.70	3.22	19	2
γ-HCH	290.8	3.70	3.33	19	2
γ-HCH	290.8	3.70	3.22	19	2
δ-HCH	290.8	4.10	3.09	19	2
δ-HCH	290.8	4.10	3.34	19	2
δ-HCH	290.8	4.10	3.56	19	2
p,p′-DDE	318.0	6.14	5.92	8	3
p,p′-DDE	318.0	6.14	6.04	18	3
p,p′-DDE	318.0	6.14	5.93	30	3
trifluralin	335.3	5.10	4.50	[c]	1
chlorpyrifos	350.6	5.00	4.64	[c]	1
heptachlor	373.3	6.10	4.82	[c]	1
dieldrin	380.9	5.40	4.81	[c]	1

[a] Adopted from the original reference or from US EPA (2003), in order of availability.
[b] 1. Sabaliūnas and Södergren (1997); 2. Vrana and Schüürmann (2002); 3. Huckins et al. (2002a).
[c] Not specified.

It may be tempting to use SPMD mass or volume to correct k_u values for differences in SPMD design. However, this approach is only partly valid. For example, by adding more triolein to a standard sized SPMD, the mass of the SPMD is increased while the surface area remains constant. This change results in a decrease of the mass or volume based k_u, but does not change the water sampling rate (L d^{-1}). Therefore, k_u values can only be directly compared among studies when SPMD surface-area-to-volume ratios (AV^{-1}) are similar. Acknowledging that the LDPE thickness for standard-design SPMDs may range between 70 and 95 μm and that the triolein mass fraction should be kept at exactly 20%, standard-design SPMDs may vary in AV^{-1} ratios between 84 and 114 cm^2 cm^{-3} (cm^{-1}), corresponding to a difference of 1.4 fold. It is therefore important that authors clearly specify the SPMD design for which k_u values are reported, i.e., either specify the surface area and the volume or mass, or the ratio between the two (e.g., cm^{-1}).

In the Tables A.4 through A.12, R_s and k_u values are listed for a large number of compounds (one table per study). When necessary, values for 460 cm^2 SPMDs with a mass of 4.5 g ($V = 4.9$ cm^3) were calculated from the reported literature values. The R_s values that were derived from calculated aqueous concentrations were excluded.

TABLE A.4 Water Sampling Rates (R_ss) and Uptake Rate Constants (K_us) of 4.5 g, 460 cm^2 SPMDs at a Temperature of 10, 18, and 26 °C, and a Flow Rate of 0.004 cm s^{-1}(Huckins et al., 1999)

Compounds	M (g mol^{-1})	log K_{ow}[a]	V_{Lebas}(cm^3 mol^{-1})	R_s(L d^{-1})	k_u(L g^{-1} d^{-1})
0.004 cm s^{-1}, 10 °C					
naphthalene	128.2	3.45	147.6	1.9	0.42
acenaphthylene	152.2	4.08	165.7	2.3	0.51
acenaphthene	154.2	4.22	173.0	2.7	0.60
fluorene	166.2	4.38	188.0	3.0	0.67
anthracene	178.2	4.54	197.0	2.9	0.64
phenanthrene	178.2	4.46	199.0	3.8	0.84
fluoranthene	202.3	5.20	217.0	3.6	0.80
pyrene	202.3	5.30	214.0	4.5	1.00
benzo[*a*]anthracene	228.3	5.91	248.0	3.2	0.71
chrysene	228.3	5.61	251.0	3.7	0.82
benzo[*a*]pyrene	252.3	6.35	263.0	3.2	0.71
benzo[*b*]fluoranthene	252.3	5.78	268.9	2.8	0.62
benzo[*k*]fluoranthene	252.3	6.20	268.9	2.9	0.64
benzo[*g,h,i*]perylene	276.3	6.90	277.5	1.8	0.40
indeno[1,2,3-*c,d*]pyrene	276.3	6.51	283.5	2.0	0.44
dibenz[*a,h*]anthracene	278.4	6.75	300.0	3.0	0.67
0.004 cm s^{-1}, 18 °C					
acenaphthylene	152.2	4.08	165.7	1.4	0.31
acenaphthene	154.2	4.22	173.0	2.3	0.51
fluorene	166.2	4.38	188.0	1.7	0.38
anthracene	178.2	4.54	197.0	3.6	0.80
phenanthrene	178.2	4.46	199.0	3.6	0.80
fluoranthene	202.3	5.20	217.0	4.5	1.00
pyrene	202.3	5.30	214.0	5.2	1.16
benzo[*a*]anthracene	228.3	5.91	248.0	3.2	0.71
chrysene	228.3	5.61	251.0	4.8	1.07
benzo[*a*]pyrene	252.3	6.35	263.0	3.7	0.82
benzo[*b*]fluoranthene	252.3	5.78	268.9	3.0	0.67
benzo[*k*]fluoranthene	252.3	6.20	268.9	3.9	0.87
benzo[*g,h,i*]perylene	276.3	6.90	277.5	1.9	0.42
indeno[1,2,3-*c,d*]pyrene	276.3	6.51	283.5	3.0	0.67
dibenz[*a,h*]anthracene	278.4	6.75	300.0	3.8	0.84
0.004 cm s^{-1}, 26 °C					
acenaphthylene	152.2	4.08	165.7	1.7	0.38
acenaphthene	154.2	4.22	173.0	2.4	0.53
fluorene	166.2	4.38	188.0	2.8	0.62
anthracene	178.2	4.54	197.0	4.6	1.02
phenanthrene	178.2	4.46	199.0	5.0	1.11
fluoranthene	202.3	5.20	217.0	6.8	1.51
pyrene	202.3	5.30	214.0	7.6	1.69
benzo[*a*]anthracene	228.3	5.91	248.0	4.7	1.04
chrysene	228.3	5.61	251.0	7.6	1.69
benzo[*a*]pyrene	252.3	6.35	263.0	5.4	1.20

(*Continued*)

TABLE A.4 (*Continued*)

Compounds	M (g mol^{-1})	log K_{ow}[a]	V_{Lebas}(cm^3 mol^{-1})	R_s(L d^{-1})	k_u(L g^{-1} d^{-1})
benzo[*b*]fluoranthene	252.3	5.78	268.9	3.3	0.73
benzo[*k*]fluoranthene	252.3	6.20	268.9	5.5	1.22
benzo[*g,h,i*]perylene	276.3	6.90	277.5	2.4	0.53
indeno[1,2,3-*c,d*]pyrene	276.3	6.51	283.5	3.4	0.76
dibenz[*a,h*]anthracene	278.4	6.75	300.0	4.7	1.04

[a] Adopted from Huckins et al. (1999).

TABLE A.5 Water Sampling Rates (R_ss) and Uptake Rate Constants (k_us) of 4.5 g, 460 cm^2 SPMDs at a Temperature of 25 °C, and Flow Rates of 0.01 and 50 cm s^{-1} (Luellen and Shea, 2002)

Compound	M(g mol^{-1})	log K_{ow}[a]	V_{Lebas}(cm^3 mol^{-1})	R_s(L d^{-1})	k_u(L g^{-1} d^{-1})
0.01 cm s^{-1}, 25 °C					
naphthalene	128.2	3.37	147.6	3.0	0.68
C1-naphthalenes	142.2	3.86	169.8	5.4	1.20
biphenyl	154.2	3.90	184.6	4.4	0.97
C2-naphthalenes	156.2	4.37	192.0	7.3	1.62
fluorene	166.2	4.18	188.0	5.1	1.14
dibenzofuran	168.2	4.12	184.6	5.2	1.16
C3-naphthalenes	170.3	4.90	214.2	6.3	1.39
phenanthrene	178.2	4.46	199.0	4.5	0.99
C1-fluorenes	180.3	4.97	210.0	5.4	1.20
dibenzothiophene	184.3	4.38	191.3	3.0	0.66
C4-naphthalenes	184.3	5.30	236.4	4.3	0.96
C1-phenanthrenes/anthracenes	192.3	5.14	220.0	5.6	1.23
C2-fluorenes	194.3	5.20	232.0	5.5	1.22
C1-dibenzothiophene	198.3	4.80	213.5	3.4	0.74
fluoranthene	202.3	5.22	217.0	4.0	0.89
pyrene	202.3	5.18	214.0	5.8	1.28
C2-phenanthrenes/anthracenes	206.3	5.60	242.0	4.2	0.94
C3-fluorenes	208.3	5.50	254.0	4.5	0.99
C2-dibenzothiophene	212.3	5.50	235.7	2.4	0.54
C1-fluoranthenes-pyrenes	216.3	5.70	237.5	3.9	0.87
C3-phenanthrenes/anthracenes	220.3	5.85	264.0	2.9	0.64
C3-dibenzothiophene	226.3	5.70	257.9	1.3	0.30
benzo[*a*]anthracene	228.3	5.91	248.0	3.5	0.78
chrysene	228.3	5.61	251.0	3.5	0.77
C4-phenanthrenes/anthracenes	234.3	6.50	286.0	2.1	0.46
C1-chrysenes	242.3	6.20	273.2	1.7	0.38
benzo[*b*]fluoranthene	252.3	5.80	268.9	1.7	0.39
benzo[*e*]pyrene	252.3	6.40	263.0	1.5	0.33
C2-chrysenes	256.4	6.50	295.4	1.0	0.22
C3-chrysenes	270.4	6.80	317.6	0.8	0.17

(*Continued*)

TABLE A.5 (*Continued*)

Compound	M(g mol^{-1})	log K_{ow}[a]	V_{Lebas}(cm^3 mol^{-1})	R_s(L d^{-1})	k_u(L g^{-1} d^{-1})
benzo[*g,h,i*]perylene	276.3	7.23	277.0	0.9	0.20
C4-chrysenes	284.4	7.10[b]	339.8	0.4	0.08
50 cm s^{-1}, 25 °C					
naphthalene	128.2	3.37	147.6	3.5	0.77
1-methyl naphthalene	142.2	3.86	169.8	5.0	1.12
2-methyl naphthalene	142.2	3.86	169.8	4.9	1.09
C1-naphthalenes	142.2	3.86	169.8	5.1	1.14
acenaphthylene	152.2	4.07	173.0	3.7	0.81
acenaphthene	154.2	3.92	165.7	3.9	0.87
biphenyl	154.2	3.90	184.6	4.5	1.00
2,6-dimethyl naphthalene	156.2	4.37	192.0	5.7	1.26
C2-naphthalenes	156.2	4.37	192.0	4.8	1.06
50 cm s^{-1}, 25 °C					
fluorene	166.2	4.18	188.0	4.6	1.02
dibenzofuran	168.2	4.12	184.6	4.8	1.06
2,3,5-trimethyl naphthalene	170.3	4.90	214.2	5.9	1.32
C3-naphthalenes	170.3	4.90	214.2	5.7	1.27
anthracene	178.2	4.54	197.0	4.7	1.05
phenanthrene	178.2	4.46	199.0	5.0	1.10
1-methyl fluorene	180.3	4.97	210.0	5.6	1.24
C1-fluorenes	180.3	4.97	210.0	5.8	1.29
dibenzothiophene	184.3	4.38	191.3	3.9	0.86
C4-naphthalenes	184.3	5.30	236.4	4.5	0.99
1-methyl phenanthrene	192.3	5.14	218.7	5.6	1.25
C1-phenanthrenes/anthracenes	192.3	5.14	220.0	5.9	1.30
C2-fluorenes	194.3	5.20	232.0	6.0	1.34
C1-dibenzothiophene	198.3	4.80	213.5	4.1	0.91
fluoranthene	202.3	5.22	217.0	5.5	1.22
pyrene	202.3	5.18	214.0	6.2	1.38
C2-phenanthrenes/anthracenes	206.3	5.60	242.0	4.6	1.02
C3-fluorenes	208.3	5.50	254.0	5.7	1.26
C2-dibenzothiophene	212.3	5.50	235.7	3.8	0.85
C1-fluoranthenes-pyrenes	216.3	5.70	237.5	4.5	0.99
C3-phenanthrenes/anthracenes	220.3	5.85	264.0	3.5	0.77
C3-dibenzothiophene	226.3	5.70	257.9	2.7	0.61
benzo[*a*]anthracene	228.3	5.91	248.0	4.9	1.08
chrysene	228.3	5.61	251.0	4.7	1.04
C4-phenanthrenes/anthracenes	234.3	6.50	286.0	3.1	0.68
C1-chrysenes	242.3	6.20	273.2	4.3	0.95
benzo[*a*]pyrene	252.3	6.04	263.0	3.1	0.69
benzo[*b*]fluoranthene	252.3	5.80	268.9	2.9	0.64
benzo[*e*]pyrene	252.3	6.40	263.0	2.4	0.53
benzo[*k*]fluoranthene	252.3	6.00	268.9	3.1	0.68
perylene	252.3	6.50	263.0	2.5	0.55
C2-chrysenes	256.4	6.50	295.4	3.2	0.70
C3-chrysenes	270.4	6.80	317.6	2.4	0.52

(*Continued*)

TABLE A.5 (*Continued*)

Compound	M(g mol^{-1})	log K_{ow}[a]	V_{Lebas}(cm^3 mol^{-1})	R_s(L d^{-1})	k_u(L g^{-1} d^{-1})
benzo[*g*, *h*, *i*]perylene	276.3	7.23	277.0	1.3	0.29
indeno[1,2,3-*c*, *d*]pyrene	276.3	7.00	283.5	2.2	0.49
dibenz[*a*, *h*]anthracene	278.4	6.75	300.0	1.9	0.41
C4-chrysenes	284.4	7.10[b]	339.8	0.8	0.17
coronene	300.4	7.64	292.0	1.0	0.23

[a] Adopted from Luellen and Shea (2002).
[b] The value listed by the authors (log $K_{ow} = 8$) seems to be unrealistic compared to the values for C1-, C2-, and C3-chrysenes.

TABLE A.6 Water Sampling Rates (R_ss) and Uptake Rate Constants (k_us) of 4.5 g, 460 cm^2 SPMDs at a Temperature of 16.5 °C and a Flow Rate of 0.1 cm s^{-1} (Huckins et al., 2004)

Compound	M(g mol^{-1})	log K_{ow}^a	V_{Lebas}(cm^3 mol^{-1})	R_s(L d^{-1})	k_u(L g^{-1} d^{-1})
0.1 cm s^{-1}, 16.5 °C					
naphthalene	128.2	3.40	147.6	0.5	0.11
benzo[*b*]thiophene	134.2	3.10	139.7	1.0	0.22
1-methyl naphthalene	142.2	3.90	169.8	1.9	0.42
2-methyl naphthalene	142.2	3.86	169.8	2.0	0.44
acenaphthylene	152.2	4.10	165.7	1.8	0.40
acenaphthene	154.2	4.20	173.0	2.0	0.45
biphenyl	154.2	3.90	184.6	1.9	0.43
1,3-dimethylnaphthalene	156.2	4.30	192.0	2.3	0.50
1-ethyl naphthalene	156.2	4.40	192.0	2.2	0.48
fluorene	166.2	4.40	188.0	2.1	0.46
4-methyl biphenyl	168.2	4.63	206.8	2.2	0.48
2,3,5-trimethyl naphthalene	170.3	4.80	214.2	2.3	0.51
anthracene	178.2	4.50	197.0	2.3	0.52
phenanthrene	178.2	4.50	199.0	2.3	0.51
1-methyl fluorene	180.3	4.97	210.0	2.2	0.49
dibenzothiophene	184.3	4.20	191.3	2.2	0.49
2-methyl phenanthrene	192.3	5.15	218.7	2.5	0.56
fluoranthene	202.3	5.20	217.0	2.4	0.54
pyrene	202.3	5.30	214.0	2.5	0.55
3,6-dimethyl phenanthrene	206.3	5.25	240.9	2.7	0.60
2-methyl fluoranthene	216.3	5.30	236.0	2.7	0.59
benzo[*a*]anthracene	228.3	5.76	248.0	2.3	0.52
chrysene	228.3	5.60	251.0	1.5	0.34
benzo[*b*]naphtho[2,1-*d*]thiophene	234.3	5.19	242.9	2.4	0.53
benzo[*a*]pyrene	252.3	6.40	263.0	1.6	0.36
benzo[*b*]fluoranthene	252.3	5.80	268.9	1.8	0.40
benzo[*e*]pyrene	252.3	6.04	263.0	1.6	0.36
benzo[*k*]fluoranthene	252.3	6.20	268.9	1.4	0.30
perylene	252.3	6.25	263.0	1.7	0.38
benzo[*g,h,i*]perylene	276.3	6.90	277.0	1.6	0.36
indeno[1,2,3-*c,d*]pyrene	276.3	6.50	283.5	1.8	0.41
dibenz[*a,h*]anthracene	278.4	6.80	300.0	1.6	0.36

[a] Adopted from Huckins et al. (2004).

TABLE A.7 Water Sampling Rates (R_ss) and Uptake Rate Constants (k_us) of 4.5 g, 460 cm^2 SPMDs at Temperatures of 2, 13, and 30 °C, and a Flow Rate of 90 cm s^{-1} (Booij et al., 2003)

Compound	M(g mol^{-1})	log $K_{ow}{}^a$	V_{Lebas}(cm^3 mol^{-1})	R_s(L d^{-1})	k_u(L g^{-1} d^{-1})
90 cm s^{-1}, 2 °C					
acenaphthene	154.2	3.92	173.0	21.2	4.72
phenanthrene	178.2	4.57	199.0	40.2	8.93
fluoranthene	202.3	5.22	217.0	44.3	9.85
pyrene	202.3	5.18	214.0	53.1	11.81
benzo[*a*]anthracene	228.3	5.91	248.0	58.3	12.95
chrysene	228.3	5.86	251.0	51.5	11.44
benzo[*a*]pyrene	252.3	6.04	263.0	47.4	10.54
1,2,3,4-tetrachlorobenzene	215.9	4.64	180.0	25.8	5.74
pentachlorobenzene	250.3	5.18	200.0	54.8	12.18
hexachlorobenzene	284.8	5.73	221.4	73.6	16.36
PCB 28	257.5	5.80	247.3	84.4	18.75
PCB 52	292.0	6.10	268.2	72.9	16.20
PCB 118	326.4	6.40	289.1	44.1	9.80
PCB 153	360.9	6.90	310.0	42.9	9.54
PCB 170	395.3	6.90	330.9	46.2	10.27
PCB 194	429.8	7.40	351.8	67.3	14.96
90 cm s^{-1}, 13 °C					
acenaphthene	154.2	3.92	173.0	52.1	11.58
phenanthrene	178.2	4.57	199.0	71.5	15.88
fluoranthene	202.3	5.22	217.0	101.7	22.59
pyrene	202.3	5.18	214.0	108.7	24.17
benzo[*a*]anthracene	228.3	5.91	248.0	98.9	21.98
chrysene	228.3	5.86	251.0	99.8	22.17
benzo[*a*]pyrene	252.3	6.04	263.0	100.4	22.30
benzo[*e*]pyrene	252.3	6.04	263.0	100.0	22.22
pentachlorobenzene	250.3	5.18	200.0	96.1	21.35
PCB 52	292.0	6.10	268.2	116.8	25.95
PCB 118	326.4	6.40	289.1	97.4	21.65
PCB 153	360.9	6.90	310.0	97.6	21.69
PCB 170	395.3	6.90	330.9	83.7	18.59
PCB 194	429.8	7.40	351.8	78.4	17.42
90 cm s^{-1}, 30 °C					
acenaphthene	154.2	3.92	173.0	68.0	15.12
phenanthrene	178.2	4.57	199.0	104.9	23.30
fluoranthene	202.3	5.22	217.0	125.2	27.83
pyrene	202.3	5.18	214.0	130.1	28.92
benzo[*a*]anthracene	228.3	5.91	248.0	169.3	37.63
chrysene	228.3	5.86	251.0	181.2	40.26
benzo[*a*]pyrene	252.3	6.04	263.0	197.4	43.86
benzo[*e*]pyrene	252.3	6.04	263.0	182.0	40.44
90 cm s^{-1}, 30 °C					
1,2,3,4-tetrachlorobenzene	215.9	4.64	180.0	145.3	32.29

(*Continued*)

TABLE A.7 (*Continued*)

Compound	M(g mol^{-1})	log K_{ow}[a]	V_{Lebas}(cm^3 mol^{-1})	R_s(L d^{-1})	k_u(L g^{-1} d^{-1})
pentachlorobenzene	250.3	5.18	200.0	87.0	19.34
hexachlorobenzene	284.8	5.73	221.4	120.4	26.75
PCB 28	257.5	5.80	247.3	210.4	46.75
PCB 52	292.0	6.10	268.2	187.5	41.66
PCB 118	326.4	6.40	289.1	165.5	36.79
PCB 153	360.9	6.90	310.0	142.5	31.67
PCB 170	395.3	6.90	330.9	131.0	29.11
PCB 194	429.8	7.40	351.8	121.5	27.01

[a] Adopted from Booij et al. (2003).

TABLE A.8 Water Sampling Rates (R_ss) and Uptake Rate Constants (k_us) of 4.5 g, 460 cm^2 SPMDs at a Temperature of 12 °C and a Flow Rate of 0.004 cm s^{-1} (Meadows et al., 1998)

Compound	M(g mol^{-1})	log K_{ow}[a]	V_{Lebas}(cm^3 mol^{-1})	R_s(L d^{-1})	k_u(L g^{-1} d^{-1})
0.004 cm s^{-1}, 12 °C					
PCB 6	223.1	5.10	226.4	13.2	2.93
PCB 18	257.5	5.20	247.3	9.6	2.12
PCB 19	257.5	5.00	247.3	5.5	1.21
PCB 22	257.5	5.60	247.3	5.9	1.31
PCB 25	257.5	5.70	247.3	5.9	1.31
PCB 26	257.5	5.70	247.3	5.9	1.31
PCB 28	257.5	5.70	247.3	8.6	1.92
PCB 31	257.5	5.70	247.3	7.3	1.62
PCB 40	292.0	5.70	268.2	6.8	1.52
PCB 41	292.0	5.70	268.2	6.4	1.42
PCB 42	292.0	5.80	268.2	6.4	1.42
PCB 43	292.0	5.80	268.2	6.4	1.42
PCB 44	292.0	5.80	268.2	7.7	1.72
PCB 45	292.0	5.50	268.2	8.2	1.82
PCB 46	292.0	5.50	268.2	4.6	1.01
PCB 47	292.0	5.80	268.2	7.7	1.72
PCB 48	292.0	5.80	268.2	3.6	0.81
PCB 49	292.0	5.80	268.2	5.5	1.21
PCB 51	292.0	5.60	268.2	5.0	1.11
PCB 52	292.0	5.80	268.2	6.4	1.42
PCB 53	292.0	5.60	268.2	5.0	1.11
PCB 63	292.0	6.20	268.2	5.5	1.21
PCB 64	292.0	6.00	268.2	7.7	1.72
PCB 66	292.0	6.20	268.2	5.5	1.21
PCB 67	292.0	6.20	268.2	5.5	1.21
PCB 70	292.0	6.20	268.2	7.3	1.62
PCB 74	292.0	6.20	268.2	6.4	1.42
PCB 81	292.0	6.40	268.2	5.0	1.11
PCB 82	326.4	6.20	289.1	4.6	1.01

(*Continued*)

TABLE A.8 (*Continued*)

Compound	M(g mol^{-1})	log K_{ow}[a]	V_{Lebas}(cm^3 mol^{-1})	R_s(L d^{-1})	k_u(L g^{-1} d^{-1})
PCB 83	326.4	6.30	289.1	5.0	1.11
PCB 84	326.4	6.00	289.1	4.6	1.01
PCB 85	326.4	6.30	289.1	5.0	1.11
PCB 87	326.4	6.30	289.1	5.5	1.21
PCB 90	326.4	6.40	289.1	6.4	1.42
PCB 91	326.4	6.10	289.1	4.6	1.01
PCB 92	326.4	6.40	289.1	5.5	1.21
PCB 95	326.4	6.10	289.1	6.4	1.42
PCB 97	326.4	6.30	289.1	4.6	1.01
PCB 99	326.4	6.40	289.1	4.6	1.01
0.004 cm s^{-1}, 12 °C					
PCB 101	326.4	6.40	289.1	6.4	1.42
PCB 105	326.4	6.60	289.1	4.1	0.91
PCB 107	326.4	6.70	289.1	5.5	1.21
PCB 110	326.4	6.50	289.1	5.9	1.31
PCB 114	326.4	6.60	289.1	4.6	1.01
PCB 118	326.4	6.70	289.1	5.0	1.11
PCB 119	326.4	6.60	289.1	4.6	1.01
PCB 128	360.9	6.70	310.0	4.6	1.01
PCB 129	360.9	6.70	310.0	3.6	0.81
PCB 130	360.9	6.80	310.0	4.1	0.91
PCB 134	360.9	6.60	310.0	5.0	1.11
PCB 136	360.9	6.20	310.0	5.5	1.21
PCB 137	360.9	6.80	310.0	3.6	0.81
PCB 138	360.9	6.80	310.0	5.0	1.11
PCB 141	360.9	6.80	310.0	5.0	1.11
PCB 146	360.9	6.90	310.0	5.0	1.11
PCB 149	360.9	6.70	310.0	5.9	1.31
PCB 151	360.9	6.60	310.0	5.5	1.21
PCB 153	360.9	6.90	310.0	3.6	0.81
PCB 156	360.9	7.20	310.0	2.7	0.61
PCB 157	360.9	7.20	310.0	2.7	0.61
PCB 158	360.9	7.00	310.0	3.6	0.81
PCB 172	395.3	7.30	330.9	1.4	0.30
PCB 174	395.3	7.10	330.9	3.2	0.71
PCB 176	395.3	6.80	330.9	2.3	0.51
PCB 178	395.3	7.10	330.9	3.2	0.71
PCB 179	395.3	6.70	330.9	2.3	0.51
PCB 180	395.3	7.40	330.9	2.7	0.61
PCB 183	395.3	7.20	330.9	3.2	0.71
PCB 187	395.3	7.20	330.9	3.6	0.81
PCB 194	429.8	7.80	351.8	1.4	0.30
PCB 199	429.8	7.60	351.8	1.8	0.40
PCB 201	429.8	7.30	351.8	1.8	0.40
PCB 207	464.2	7.70	372.7	0.3	0.06

[a] Adopted from Meadows et al. (1998).

Table A.9 Water Sampling Rates (R_ss) and Uptake Rate Constants (k_us) of 4.5 g, 460 cm^2 SPMDs at a Temperature of 11 and 19 °C and a Flow Rate of 8 cm s^{-1} (Rantalainen et al., 2000)

Compound	M(g mol^{-1})	log K_{ow}[a]	V_{Lebas}(cm^3 mol^{-1})	R_s(L d^{-1})	k_u(L g^{-1} d^{-1})
8 cm s^{-1}, 11 °C					
PCB 77	292.0	6.36	268.2	2.5	0.56
PCB 78	292.0	6.35	268.2	3.8	0.85
PCB 79	292.0	6.42	268.2	4.4	0.98
PCB 81	292.0	6.36	268.2	3.2	0.71
PCB 126	326.4	6.89	289.1	1.9	0.43
PCB 127	326.4	6.95	289.1	1.4	0.31
PCB 169	360.9	7.42	310.0	1.8	0.40
2,3,7,8-TCDF	306.0	6.53	268.2	2.2	0.48
1,2,3,7,8-PeCDF	340.4	6.79	289.1	1.7	0.39
2,3,4,7,8-PeCDF	340.4	6.92	289.1	1.6	0.36
1,2,3,4,7,8-HxCDF	374.9	7.00	310.0	1.1	0.24
1,2,3,6,7,8-HxCDF	374.9	7.00	310.0	1.1	0.24
1,2,3,7,8,9-HxCDF	374.9	7.00	310.0	0.8	0.19
2,3,4,6,7,8-HxCDF	374.9	7.00	310.0	1.1	0.24
1,2,3,4,6,7,8-HpCDF	409.3	7.92	330.9	0.6	0.14
OCDF	443.8	7.97	351.8	0.4	0.09
2,3,7,8-TCDD	322.0	6.42	275.6	2.2	0.48
1,2,3,7,8-PeCDD	356.4	6.64	296.5	1.6	0.35
1,2,3,4,7,8-HxCDD	390.9	7.80	317.4	1.2	0.28
1,2,3,6,7,8-HxCDD	390.9	7.80	317.4	1.2	0.26
1,2,3,7,8,9-HxCDD	390.9	7.80	317.4	1.1	0.24
1,2,3,4,6,7,8-HpCDD	425.2	8.00	338.3	0.6	0.14
OCDD	459.8	8.20	359.2	1.1	0.25
8 cm s^{-1}, 19 °C					
PCB 77	292.0	6.36	268.2	3.8	0.85
PCB 78	292.0	6.35	268.2	4.5	0.99
PCB 79	292.0	6.42	268.2	4.5	1.01
PCB 81	292.0	6.36	268.2	4.3	0.95
PCB 126	326.4	6.89	289.1	3.7	0.81
PCB 127	326.4	6.95	289.1	3.6	0.79
PCB 169	360.9	7.42	310.0	5.1	1.13
OCDF	443.8	7.97	351.8	1.6	0.35
8 cm s^{-1}, 19 °C					
2,3,7,8-TCDF	306.0	6.53	268.2	3.2	0.71
1,2,3,7,8-PeCDF	340.4	6.79	289.1	3.3	0.74
2,3,4,7,8-PeCDF	340.4	6.92	289.1	3.7	0.81
1,2,3,4,7,8-HxCDF	374.9	7.00	310.0	2.3	0.51
1,2,3,6,7,8-HxCDF	374.9	7.00	310.0	2.5	0.56
1,2,3,7,8,9-HxCDF	374.9	7.00	310.0	2.0	0.44
2,3,4,6,7,8-HxCDF	374.9	7.00	310.0	2.6	0.57
1,2,3,4,6,7,8-HpCDF	409.3	7.92	330.9	2.3	0.51

(*Continued*)

Table A.9 (*Continued*)

Compound	M(g mol^{-1})	log K_{ow}[a]	V_{Lebas}(cm^3 mol^{-1})	R_s(L d^{-1})	k_u(L g^{-1} d^{-1})
2,3,7,8-TCDD	322.0	6.42	275.6	3.3	0.74
1,2,3,7,8-PeCDD	356.4	6.64	296.5	2.9	0.65
1,2,3,4,7,8-HxCDD	390.9	7.80	317.4	3.5	0.78
1,2,3,6,7,8-HxCDD	390.9	7.80	317.4	2.7	0.61
1,2,3,7,8,9-HxCDD	390.9	7.80	317.4	2.5	0.56
1,2,3,4,6,7,8-HpCDD	425.2	8.00	338.3	1.9	0.43
OCDD	459.8	8.20	359.2	2.6	0.58

[a] Adopted from Rantalainen et al. (2000).

Table A.10 Water Sampling Rates (R_ss) and Uptake Rate Constants (k_us) of 4.5 g, 460 cm^2SPMDs at a Temperature of 19 °C and Flow Rates of 0.06, 0.28, and 1.14 cm s^{-1} (Vrana and Schüürmann, 2002)

Compound	M(g mol^{-1})	log K_{ow}[a]	V_{Lebas}(cm^3 mol^{-1})	R_s(L d^{-1})	k_u(L g^{-1} d^{-1})
0.06 cm s^{-1}, 19 °C					
pentachlorobenzene	250.3	5.20	200.0	3.3	0.74
hexachlorobenzene	284.8	5.50	221.4	1.4	0.30
α-HCH	290.8	3.80	243.6	2.3	0.52
β-HCH	290.8	3.80	243.6	3.6	0.79
γ-HCH	290.8	3.70	243.6	2.5	0.56
δ-HCH	290.8	4.10	243.6	3.1	0.69
0.28 cm s^{-1}, 19 °C					
pentachlorobenzene	250.3	5.20	200.0	10.3	2.29
hexachlorobenzene	284.8	5.50	221.4	13.2	2.93
α-HCH	290.8	3.80	243.6	2.4	0.54
β-HCH	290.8	3.80	243.6	2.0	0.44
γ-HCH	290.8	3.70	243.6	2.3	0.52
δ-HCH	290.8	4.10	243.6	3.8	0.84
1.14 cm s^{-1}, 19 °C					
pentachlorobenzene	250.3	5.20	200.0	8.2	1.81
hexachlorobenzene	284.8	5.50	221.4	14.8	3.28
α-HCH	290.8	3.80	243.6	1.9	0.42
β-HCH	290.8	3.80	243.6	0.9	0.20
γ-HCH	290.8	3.70	243.6	1.3	0.28
δ-HCH	290.8	4.10	243.6	1.8	0.41

[a] Adopted from Vrana and Schüürmann (2002).

TABLE A.11 Water Sampling Rates (R_ss) and Uptake Rate Constants (k_us) of 4.5 g, 460 cm^2SPMDs at a Temperature of 10, 18, and 26 °C and a Flow Rate of 0.004 cm s^{-1} (Huckins et al., 2002b)

Compound	M(g mol^{-1})	log $K_{ow}{}^{a}$	V_{Lebas}(cm^3 mol^{-1})	R_s(L d^{-1})	k_u(L g^{-1} d^{-1})
0.004 cm s^{-1}, 10 °C					
pentachloroanisole	280.4	5.48	231.8	2.9	0.64
hexachlorobenzene	284.8	5.71	221.4	2.0	0.44
α-HCH	290.8	3.86	243.6	0.9	0.20
γ-HCH	290.8	3.71	243.6	0.7	0.16
o,p′-DDE	318.0	5.56	305.2	2.3	0.51
p,p′-DDE	318.0	6.14	305.2	2.8	0.62
o,p′-DDD	320.1	6.08	312.6	2.5	0.56
p,p′-DDD	320.1	5.75	312.6	2.3	0.51
dacthal	332.0	4.26	301.6	0.6	0.13
p,p′-methoxychlor	345.7	4.61	354.3	1.2	0.27
o,p′-DDT	354.5	5.59	333.5	2.0	0.44
p,p′-DDT	354.5	5.47	333.5	2.0	0.44
heptachlor	373.3	5.19	308.2	2.6	0.58
endrin	380.9	4.63	318.2	2.3	0.51
dieldrin	380.9	4.60	318.2	1.3	0.29
heptachlor epoxide	389.3	4.51	309.6	1.3	0.29
cis-chlordane	409.8	5.38	336.5	2.6	0.58
trans-chlordane	409.8	5.38	336.5	2.4	0.53
oxychlordane	423.8	5.48	334.1	2.3	0.51
cis-nonachlor	444.2	6.20	357.4	2.2	0.49
trans-nonachlor	444.2	6.35	357.4	2.7	0.60
mirex	545.6	6.89	403.2	3.0	0.67
0.004 cm s^{-1}, 18 °C					
pentachloroanisole	280.4	5.48	231.8	2.5	0.56
hexachlorobenzene	284.8	5.71	221.4	2.6	0.58
α-HCH	290.8	3.86	243.6	1.4	0.31
γ-HCH	290.8	3.71	243.6	1.1	0.24
o,p′-DDE	318.0	5.56	305.2	2.4	0.53
p,p′-DDE	318.0	6.14	305.2	2.7	0.60
o,p′-DDD	320.1	6.08	312.6	2.3	0.51
p,p′-DDD	320.1	5.75	312.6	2.5	0.56
dacthal	332.0	4.26	301.6	1.8	0.40
o,p′-DDT	354.5	5.59	333.5	3.3	0.73
p,p′-DDT	354.5	5.47	333.5	3.7	0.82
endrin	380.9	4.63	318.2	3.2	0.71
dieldrin	380.9	4.60	318.2	2.6	0.58
heptachlor epoxide	389.3	4.51	309.6	1.4	0.31
cis-chlordane	409.8	5.38	336.5	1.7	0.38
trans-chlordane	409.8	5.38	336.5	2.0	0.44
oxychlordane	423.8	5.48	334.1	1.9	0.42
cis-nonachlor	444.2	6.20	357.4	2.0	0.44
trans-nonachlor	444.2	6.35	357.4	1.9	0.42
mirex	545.6	6.89	403.2	2.4	0.53

(*Continued*)

Table A.11 (*Continued*)

Compound	M(g mol^{-1})	log K_{ow}[a]	V_{Lebas}(cm^3 mol^{-1})	R_s(L d^{-1})	k_u(L g^{-1} d^{-1})
0.004 cm s^{-1}, 26 °C					
pentachloroanisole	280.4	5.48	231.8	7.2	1.60
hexachlorobenzene	284.8	5.71	221.4	5.6	1.24
α-HCH	290.8	3.86	243.6	1.8	0.40
β-HCH	290.8	3.86	243.6	1.6	0.36
γ-HCH	290.8	3.71	243.6	2.3	0.51
o,p′-DDE	318.0	5.56	305.2	6.0	1.33
p,p′-DDE	318.0	6.14	305.2	6.8	1.51
o,p′-DDD	320.1	6.08	312.6	5.5	1.22
p,p′-DDD	320.1	5.75	312.6	6.1	1.36
dacthal	332.0	4.26	301.6	2.0	0.44
p,p′-methoxychlor	345.7	4.61	354.3	2.5	0.56
o,p′-DDT	354.5	5.59	333.5	4.0	0.89
p,p′-DDT	354.5	5.47	333.5	4.1	0.91
heptachlor	373.3	5.19	308.2	6.8	1.51
endrin	380.9	4.63	318.2	7.6	1.69
dieldrin	380.9	4.60	318.2	4.6	1.02
heptachlor epoxide	389.3	4.51	309.6	5.3	1.18
cis-chlordane	409.8	5.38	336.5	6.0	1.33
trans-chlordane	409.8	5.38	336.5	6.0	1.33
oxychlordane	423.8	5.48	334.1	5.6	1.24
cis-nonachlor	444.2	6.20	357.4	4.9	1.09
trans-nonachlor	444.2	6.35	357.4	6.0	1.33
mirex	545.6	6.89	403.2	5.8	1.29

[a] Adopted from Huckins et al. (2002b) or from US EPA (2003).

Table A.12 Water Sampling Rates (R_ss) and Uptake Rate Constants (k_us) of 4.5 g, 460 cm^2 SPMDs at an Unknown Temperature and a Flow Rate of 0.006 cm s^{-1} (Sabaliūnas and Södergren, 1997)

Compound	M(g mol^{-1})	log K_{ow}[a]	V_{Lebas}(cm^3 mol^{-1})	R_s(L d^{-1})	k_u(L g^{-1} d^{-1})
0.006 cm s^{-1}, °C unknown					
trifluralin	335.3	5.34	295.9	3.6	0.80
chlorpyrifos	350.6	4.96	298.8	5.2	1.16
heptachlor	373.4	6.10	308.2	5.0	1.11
dieldrin	380.9	5.40	318.2	6.8	1.51
fenvalerate	419.9	6.20	479.6	2.6	0.58
deltamethrin	505.2	6.20	462.5	2.5	0.56

[a] Adopted from Sabaliūnas and Södergren (1997) or from US EPA (2003).

A.3. AIR SAMPLING RATES

Air sampling rates are available from laboratory exposures and field deployments. In the latter case, vapor phase concentrations (C_a) were determined by traditional high-volume sampling (HiVol), using a glass fiber filter in combination with a solid-phase adsorbent. Vapor-phase concentrations in the field may be highly variable, and some uncertainty exists to what extent the intermittently determined C_a values reflect the average concentration during the SPMD exposure. The R_ss from studies that fail to simultaneously determine vapor phase concentrations are excluded from this appendix. As discussed in Chapter 3, it should be noted that air-exposed SPMDs may sample particle-bound contaminants such as PAHs $\geq$ 5-rings. In Tables A.13 through A.16, R_s values are listed for those studies in which vapor phase concentrations were determined and particulate contributions could be neglected.

TABLE A.13 Air Sampling Rates (R_ss) and Uptake Rate Constants (k_us) of 4.5 g, 460 cm^2 SPMDs at Various Flow Rates and Temperatures (Ockenden et al., 1998)

Compound	M(g mol^{-1})	log K_{oa}[a]	V_{Lebas}(cm^3 mol^{-1})	R_s(m^3 d^{-1})	k_u(m^3 g^{-1} d^{-1})
460 cm s^{-1}, 4 °C					
PCB 28	257.5	9.0	247.3	4.5	1.00
PCB 52	292.0	9.3	268.2	6.2	1.38
PCB 101	326.4	10.1	289.1	11.0	2.44
PCB 118	326.4	11.3	289.1	14.0	3.11
PCB 138	360.9	10.9	310.0	18.0	4.00
PCB 153	360.9	10.9	310.0	15.0	3.33
PCB 180	395.3	11.4	330.9	13.0	2.89
unknown flow rate, 14 °C					
PCB 28	257.5	8.5	247.3	2.8	0.63
PCB 52	292.0	8.8	268.2	4.5	1.01
PCB 101	326.4	9.5	289.1	7.2	1.61
PCB 118	326.4	10.7	289.1	8.5	1.89
PCB 138	360.9	10.4	310.0	7.2	1.60
PCB 153	360.9	10.3	310.0	6.3	1.41
PCB 180	395.3	10.9	330.9	7.0	1.56
270 cm s^{-1}, 18 °C					
PCB 52	292.0	8.6	268.2	1.3	0.29
PCB 101	326.4	9.3	289.1	3.3	0.73
PCB 118	326.4	10.5	289.1	6.9	1.53
PCB 138	360.9	10.2	310.0	4.3	0.96
PCB 153	360.9	10.1	310.0	4.5	1.00
PCB 180	395.3	10.7	330.9	4.9	1.09

[a] Adopted from Kömp and MacLachlan (1997), evaluated at the exposure temperature.

Table A.14 Air Sampling Rates (R_ss) and Uptake Rate Constants (k_us) of 4.5 g, 460 cm^2 SPMDs at Unknown Flow Rates and Temperatures of 25 and 26 °C (Huckins et al., 1994; Petty et al., 1993)

Compound	M(g mol^{-1})	log K_{oa}[a]	V_{Lebas}(cm^3 mol^{-1})	R_s(m^3 d^{-1})	k_u(m^3 g^{-1} d^{-1})
unknown flow rate, 25 °C					
PCB 7	223.1	7.4	226.4	0.9	0.20
PCB 17	223.1	7.6	226.4	0.9	0.19
PCB 18	257.5	7.6	247.3	0.9	0.21
PCB 22	257.5	8.0	247.3	2.6	0.58
PCB 52	292.0	8.4	268.2	3.0	0.66
PCB 74	292.0	9.1	268.2	5.7	1.28
PCB 95	326.4	9.1	289.1	3.6	0.80
PCB 101	326.4	9.3	289.1	5.3	1.19
PCB 110	326.4	9.0	289.1	5.7	1.27
PCB 138	360.9	10.1	310.0	7.1	1.59
PCB 153	360.9	10.0	310.0	7.0	1.56
PCB 174	395.3	10.3	330.9	7.7	1.71
PCB 183	395.3	10.3	330.9	5.6	1.25
PCB 201	429.8	10.9	351.8	9.6	2.14
unknown flow rate, 26 °C					
PCB 52		8.2		3.0	0.67

[a] Adopted from Kömp and MacLachlan (1997) or from Harner and Bidleman (1996).

Table A.15 Air Sampling Rates (R_ss) and Uptake Rate Constants (k_us) of 4.5 g, 460 cm^2 SPMDs at a Flow Rate of 0.001 cm s^{-1} and a Temperature of 23 °C (Shoeib and Harner, 2002)

Compound	M(g mol^{-1})	log K_{oa}[a]	V_{Lebas}(cm^3 mol^{-1})	R_s(m^3 d^{-1})	k_u(m^3 g^{-1} d^{-1})
0.001 cm s^{-1}, 23 °C					
PCB 28	257.5	8.12	247.3	3.5	0.78
PCB 44	292.0	8.61	268.2	3.3	0.72
PCB 52	292.0	8.43	268.2	3.6	0.81
PCB 77	292.0	9.75	268.2	3.3	0.72
PCB 81	292.0	9.67	268.2	3.4	0.76
PCB 99	326.4	9.24	289.1	3.1	0.68
PCB 101	326.4	9.19	289.1	3.2	0.70
PCB 105	326.4	10.2	289.1	3.7	0.83
PCB 114	326.4	10.0	289.1	3.9	0.87
PCB 118	326.4	9.96	289.1	4.0	0.89
PCB 126	326.4	10.4	289.1	9.2	2.04
PCB 128	360.9	10.4	310.0	4.8	1.07
PCB 137/138	360.9	10.1	310.0	5.0	1.12
PCB 153	360.9	9.91	310.0	3.8	0.85
PCB 156	360.9	10.8	310.0	4.6	1.01
PCB 180	395.3	10.7	330.9	7.3	1.63
tetrachloronaphthalenes	266.0	8.4	231.2	2.8	0.62
pentachloronaphthalenes	300.4	9.1	252.1	3.0	0.66
hexachloronaphthalenes	334.8	10.1	273.0	4.7	1.05

[a] PCBs: Shoeib and Harner (2002); PCNs: Harner and Bidleman (1998).

Table A.16 Air Sampling Rates (R_ss) and Uptake Rate Constants (k_us) of 4.5 g, 460 cm^2 SPMDs at a Flow Rate of 3.4 cm s^{-1} and a Temperature of 25 °C (Robertson, 2004)

Compound	M(g mol^{-1})	log K_{oa}[a]	V_{Lebas}(cm^3 mol^{-1})	R_s(m^3 d^{-1})	k_u(m^3 g^{-1} d^{-1})
3.4 cm s^{-1}, 25 °C					
diazinon	304.4	9.1	349.0	2.6	0.58
p, p′-DDE	318.0	9.3	305.2	6.9	1.53
p, p′-DDD	320.1	9.6	312.6	6.9	1.53
chlorpyrifos	350.6	8.9	325.8	5.1	1.13
p, p′-DDT	354.5	10.4	333.5	5.5	1.22
cis-permethrin	391.3	10.6	427.4	3.4	0.76
trans-permethrin	391.3	10.6	427.4	5.5	1.22
trans-chlordane	409.8	8.9	336.5	5.1	1.13
cis-chlordane	409.8	8.9	336.5	5.5	1.22
cyfluthrin	434.3	10.4	459.1	4.1	0.91
cypermethrin	434.3	10.8	454.1	0.7	0.16
fipronil	437.2	11.5	358.5	2.3	0.51
fluorene	166.2	6.8	188.0	2.4	0.53
phenanthrene	178.2	7.6	199.0	4.3	0.96
anthracene	178.2	7.3	197.0	3.7	0.82
fluoranthene	202.3	8.9	217.0	6.4	1.42
pyrene	202.3	8.8	214.0	6.9	1.53
benz[*a*]anthracene	228.3	9.5	248.0	15.0	3.33
chrysene	228.3	10.4	251.0	13.0	2.89
benzo[*b*]fluoranthene	252.3	10.4	268.9	8.7	1.93
benzo[*k*]fluoranthene	252.3	11.2	268.9	6.0	1.33
benzo[*a*]pyrene	252.3	10.8	263.0	6.0	1.33

[a] fluorene, phenanthrene, fluoranthene, pyrene: Harner and Bidleman (1998); other PAHs: calculated from log K_{ow}s and Henry's law constants (Mackay et al. 1992b); pesticides: calculated from log K_{ow}s and Henry's law constants (US EPA, 2003).

A.4. REFERENCES

Booij, K.; Sleiderink, H.M.; Smedes, F. 1998, Calibrating the uptake kinetics of semipermeable membrane devices using exposure standards. *Environ. Toxicol. Chem.* **17**: 1236–1245.

Booij, K.; Hofmans, H.E.; Fischer, C.V.; van Weerlee, E.M. 2003, Temperature-dependent uptake rates of non-polar organic compounds by semipermeable membrane devices and low-density polyethylene membranes. *Environ. Sci. Technol.* **37**: 361–366.

Chiou, C.T. 1985, Partition coefficients of organic compounds in lipid-water systems and correlations with fish bioconcentration factors. *Environ. Sci. Technol.* **19**: 57–62.

Harner, T. and Bidleman, T.F. 1996, Measurements of octanol-air partition coefficients for polychlorinated biphenyls. *J. Chem. Eng. Data* **41**: 895–899.

Harner, T. and Bidleman, T.F. 1998, Measurement of octanol-air partition coefficients for polycyclic aromatic hydrocarbons and polychlorinated naphthalenes. *J. Chem. Eng. Data* **43**: 40–46.

Huckins, J.N.; Manuweera, G.K.; Petty, J.D.; Mackay, D.; Lebo, J.A. 1993, Lipid-containing semipermeable membrane devices for monitoring organic contaminants in water. *Environ. Sci. Technol.* **27**: 2489–2496.

Huckins, J.N.; Petty, J.D.; Orazio, C.E.; Zajicek, J.L.; Gibson, V.L.; Clark, R.C.; Echols, K.R. 1994, Semipermeable Membrane Device (SPMD) Sampling Rates for Trace Organic Contaminants in Air and Water. *15th Annual meeting of Society of Environmental Toxicology and Chemistry;* Denver, CO.; Abstract MB01.

Huckins, J.N.; Petty, J.D.; Orazio, C.E.; Lebo, J.A.; Clark, R.C.; Gibson, V.L.; Gala, W.R.; Echols, K.R. 1999, Determination of uptake kinetics (sampling rates) by lipid-containing semipermeable membrane devices (SPMDs) for polycyclic aromatic hydrocarbons (PAHs) in water. *Environ. Sci. Technol.* **33**: 3918–3923.

Huckins, J.N.; Petty, J.D.; Lebo, J.A.; Almeida, F.V.; Booij, K.; Alvarez, D.A.; Cranor, W.L.; Clark, R.C.; Mogensen, B.B. 2002a, Development of the permeability/performance reference compound approach for in situ calibration of semipermeable membrane devices. *Environ. Sci. Technol.* **36**: 85–91.

Huckins, J.N.; Petty, J.D.; Prest, H.F.; Clark, R.C.; Alvarez, D.A.; Orazio, C.E.; Lebo, J.A.; Cranor, W.L.; Johnson, B.T. 2002b, *A Guide for the Use of Semipermeable Membrane Devices (SPMDs) as Samplers of Waterborne Hydrophobic Organic Contaminants;* Publication No. 4690; American Petroleum Institute (API): Washington, DC.

Huckins, J.N.; Prest, H.F.; Petty, J.D.; Lebo, J.A.; Hodgins, M.M.; Clark, R.C.; Alvarez, D.A.; Gala, W.R.; Steen, A.; Gale, R.W.; and Ingersoll, C.G. 2004, Overview and comparison of lipid-containing semipermeable membrane devices (SPMDs) and oysters (Crassostrea gigas) for assessing organic chemical exposure. *Environ. Toxicol. Chem.* **23**: 1617–1628.

Kömp, P. and McLachlan, M.S. 1997, Octanol/air partitioning of polychlorinated biphenyls. *Environ. Toxicol. Chem.* **16**: 2433–2437.

Lefkovitz, L.; Crecelius, E.; McElroy, N. 1996, The use of Polyethylene Alone to Predict Dissolved-phase Organics in the Columbia River. *17th Annual Meeting of Society of Environmental Toxicology Chemistry*; November 17–21, 1996; Washington, D.C.; Abstract PO523.

Luellen, D.R. and Shea, D. 2002, Calibration and field verification of semipermeable membrane devices for measuring polycyclic aromatic hydrocarbons in water. *Environ. Sci. Technol.* **36**: 1791–1797.

Mackay, D.; Shiu, W.Y.; Ma, K.C. 1992a, *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals: Polynuclear Aromatic Hydrocarbons, Polychlorinated Dioxins, and Dibenzofurans*; Lewis Publishers: Chelsea, MI.; Vol. II.

Mackay, D.; Shiu, W.Y.; Ma, K.C. 1992b,*Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals: Monoaromatic Hydrocarbons, Chlorobenzenes, and PCBs*; Lewis Publishers: Chelsea, MI.; Vol. I.

Meadows, J.C.; Echols, K.R.; Huckins, J.N.; Borsuk, F.A.; Carline, R.F.; Tillitt, D.E. 1998, Estimation of uptake rate constants for PCB congeners accumulated by semipermeable membrane devices and brown trout (Salmo trutta). *Environ. Sci. Technol.* **32**: 1847–1852.

Ockenden, W.A.; Prest, H.F.; Thomas, G.O.; Sweetman, A.; Jones, K.C. 1998, Passive air sampling of PCBs: Field calculation of atmospheric sampling rates by triolein-containing semipermeable membrane devices. *Environ. Sci. Technol.* **32**: 1538–1543.

Petty, J.D.; Huckins, J.N.; Zajicek, J.L. 1993, Application of semipermeable membrane devices (SPMDs) as passive air samplers. *Chemosphere* **27**: 1609–1624.

Rantalainen, A.-L.; Cretney, W.; Ikonomou, M.G. 2000, Uptake rates of semipermeable membrane devices (SPMDs) for PCDDs, PCDFs and PCBs in water and sediment. *Chemosphere* **40**: 147–158.

Reynolds, G.W.; Hoff, J.T.; Gillham, G.W. 1990, Sampling bias caused by materials used to monitor halocarbons in groundwater. *Environ. Sci. Technol.* **24**: 135–140.

Robertson, G, 2004, U.S. EPA, National Exposure Research Laboratory: Las Vegas, NV;. Personal communication.

Sabalinas, D. and Södergren, A. 1997, Use of semi-permeable membrane devices to monitor pollutants in water and assess their effects: A laboratory test and field verification. *Environ. Pollut.* **96**: 195–206.

Shoeib, M. and Harner, T. 2002, Characterization and comparison of three passive air samplers for persistent organic pollutants. *Environ. Sci. Technol.* **36**: 4142–4151.

US EPA 2003, Estimation Program Interface (EPI) Suite. Version 3.11; U.S. Environmental Protection Agency; http://www.epa.gov/opptintr/exposure/docs/episuite.htm (accessed on November, 2004).

Vrana, B. and Schüürmann, G. 2002, Calibrating the uptake kinetics of semipermeable membrane devices in water: Impact of hydrodynamics. *Environ. Sci. Technol.* **36**: 290–296.

Appendix B

SPMD Bibliography

Over the last decade, the growth in SPMD research and applications has been remarkable. Reports on this work have been in the form of graduate degree (masters and Ph.D.) theses, abstracts from presentations, laboratory reports, journal articles and book chapters. Herein, we provide the reader with a list of SPMD related peer-reviewed journal articles and book chapters. However, we do not claim that this list is complete and apologize in advance to authors of articles not included. In light of the current rate of the publication of SPMD related articles, additional papers will undoubtedly be available by the time this book is published.

Anderson, K.A. and Johnson, E. 2001, Bioavailable organochlorine pesticides in a semi-arid region of Eastern Oregon, USA, as determined by gas chromatography with electron capture detection. *J. AOAC* **84**: 1371–1382.

Axelman, J.; Næs, K.; Näf, C.; Broman, D. 1999, Accumulation of polycyclic aromatic hydrocarbons in semipermeable membrane devices and caged mussels (Mytilus edulis) in relation to water column phase distribution. *Environ. Toxicol. Chem.* **18**: 2454–2461.

Balmer, M.E.; Poiger, T.; Droz, C.; Romanin, K.; Bergqvist, P.-A.; Müller, M.D.; Buser, H.-R. 2004, Occurrence of methyl triclosan, a transformation product of the bactericide triclosan in fish from various lakes in Switzerland. *Environ. Sci. Technol.* **38**: 390–395.

Bartkow, M.E.; Huckins, J.N.; Müller, J.F. 2004, Field-based evaluation of semipermeable membrane devices (SPMDs) as passive air samplers of polyaromatic hydrocarbons (PAHs). *Atmos. Environ.* **38**: 5983–5900.

Baussant, T.; Sanni, S.; Jonsson, G.; Skadsheim, A.; Børseth, J.F. 2001, Bioaccumulation of polycyclic aromatic compounds: 1. Bioconcentration in two marine species and in semipermeable membrane devices during chronic exposure to dispersed crude oil.*Environ. Toxicol. Chem.* **20**: 1175–1184.

Bennett, E.R.; Metcalfe, T.L.; Metcalfe, C.D. 1996, Semipermeable membrane devices (SPMDs) for monitoring organic contaminants in the Otanabee River, Ontario. *Chemosphere* **33**: 363–375.

Bennett, E.R. and Metcalfe, C.D. 2000, Distribution of degradation products of alkylphenol ethoxylates near sewage treatment plants in the lower Great Lakes, North America. *Environ. Toxicol. Chem.* **19**: 784–792.

Bergqvist, P.-A.; Strandberg, B.; Hjelt, M.; Rappe, C. 1990, Nondestructive steps for the lipid reduction in PCDD and PCDF analyses. *Organohal. Comp.* **2**: 103–106.

Bergqvist, P.-A.; Strandberg, B.; Ekelund, R.; Rappe, C.; Granmo, Å. 1998a, Temporal monitoring of organochlorine compounds in seawater by semipermeable membranes following a flooding episode in Western Europe. *Environ. Sci. Technol.* **32**: 3887–3892.

Bergqvist, P.-A.; Strandberg, B.; Rappe, C. 1998b, Lipid removal using semipermeable membranes in PCDD and PCDF analysis of fat-rich environmental samples. *Chemosphere* **38**: 933–943.

Booij, K.; Sleiderink, H.M.; Smedes, F. 1998, Calibrating the uptake kinetics of semipermeable membrane devices using exposure standards. *Environ. Toxicol. Chem.* **17**: 1236–1245.

Booij, K. and van Drooge, B.L. 2001, Polychlorinated biphenyls and hexachlorobenzene in atmosphere, sea-surface microlayer, and water measured with semi-permeable membrane devices (SPMDs). *Chemosphere* **44**: 91–98.

Booij, K.; Zegers, B.N.; Boon, J.P. 2000, Levels of some polybrominated diphenyl ether (PBDE) flame retardants along the Dutch coast as derived from their accumulation in SPMDs and blue mussels (Mytilus edulis). *Organohal. Comp.* **47**: 89–92.

Booij, K.; Smedes, F.; van Weerlee, E.M. 2002a, Spiking of performance reference compounds in low density polyethylene and silicone passive water samplers. *Chemosphere* **46**: 1157–1161.

Booij, K.; Zegers, B.N.; Boon, J.P. 2002b, Levels of some polybrominated diphenyl ether (PBDE) flame retardants along the Dutch coast as derived from their accumulation in SPMDs and blue mussels (Mytilus edulis).*Chemosphere* **46**: 683–688.

Booij, K.; Hofmans, H.E.; Fischer, C.V.; van Weerlee, E.M. 2003, Temperature-dependent uptake rates of nonpolar organic compounds by semipermeable membrane devices and low-density polyethylene membranes.*Environ. Sci. Technol.* **37**: 361–366.

Bridges, C.M. and Little, E.E. 2003, *Using Semipermeable Membrane Devices (SPMDs) to Assess the Toxicity and Teratogenicity of Aquatic Amphibian Habitats*. ASTM Special Technical Publication No. 1443; pp. 159–168.

Bridges, C.M.; Little, E.E.; Gardiner, D.M.; Petty, J.D.; Huckins, J.D. 2004, Assessing the toxicity of teratogenicity of pond water in North-Central Minnesota to amphibians. *Environ. Sci. Pollut. R.* **11**: 233–239.

Čáslavskŷ, J.; Zdrahal, Z.; Vytopilova, M. 2000, Application of SPMDs for PAH sampling in the DEZA chemical factory. *Polycyclic Aromat. Compd.***20**: 123–141.

Čáslavskŷ, J. and Kotlaříková, P. 2003, High-molecular-weight polycyclic aromatic hydrocarbons in the area and vicinity of the DEZA chemical plant, Czech Republic. *Polycyclic Aromat. Compd.* **23**: 327–352.

Čáslavskŷ, J.; Kotlaříková, P.; Benešová, K. 2004, Sampling of airborne polycyclic aromatic hydrocarbons with semipermeable membrane devices. *Environ. Chem. Letters* **2**: 89–92.

Chambers, D.B. 1999, Semipermeable membrane devices used to estimate bioconcentration of polychlorinated biphenyls. *J. Am. Water Res. Assoc.* **33**: 143–154.

Cleveland, L.; Little, E.E.; Petty, J.D.; Johnson, B.T.; Lebo, J.A.; Orazio, C.E.; Dionne. J.; Crockett, A. 1997, Toxicological and chemical screening of Antarctica sediments: Use of whole sediment toxicity tests, Microtox, Mutatox, and semipermeable membrane devices (SPMDs). *Mar. Pollut. Bull.* **34**: 194–202.

Corrigan, B.P. and Jones, K.C. 2002, Passive sampling survey of PBDEs and PCBs in UK air. *Organohal. Comp.* **56**: 449–452.

Crunkilton, R.L. and DeVita, W.M. 1997, Determination of aqueous concentrations of polycyclic aromatic hydrocarbons (PAHs) in an urban stream. *Chemosphere* **35**: 1447–1463.

De la Torre, A.I.; Fernandez, C.; Tarazona, J.V.; Muñoz, M.J. 1995, Detection of aroclor, DDT, malathion, and HCB using semipermeable membranes as concentration method. *Chemosphere* **31**: 2727–2737.

De la Torre, A.I.; Fernandez, C.; Tarazona, J.V.; Muñoz, M.J. 1998, Combination of semipermeable membranes and toxicity bioassays for the detection of lipophylic toxic chemicals in environmental samples. *Ecotoxicol. Environ. Restoration* **1**: 78–84.

De la Torre, A.I.; Jimenez, J.A.; Carballo, M.; Fernandez, C.; Roset, J.; Muñoz, M.J. 2000, Ecotoxicological evaluation of a pig slurry. *Chemosphere* **41**: 1629–1635.

DeVita, W.M. and Crunkilton, R.L. 1998, Quality Control Associated with Use of Semipermeable Membrane Devices. In *Environmental Toxicology & Risk Assessment*, *Seventh Volume;* Little, E.E., Delonay, A.J., Greenberg, B.M., Eds.; ASTM STP 1333; American Society for Testing and Materials: West Conshocken, PA; pp 237–245.

Echols, K.R.; Gale, R.W.; Schwartz, T.R.; Huckins, J.N.; Williams, L.L.; Meadows, J.C.; Morse, D.; Petty, J.D.; Orazio, C.E.; Tillitt, D.E. 2000, Comparing polychlorinated biphenyl concentrations and patterns in the Saginaw River using sediment, caged fish, and semipermeable membrane devices. *Environ. Sci. Technol.* **34**: 4095–4102.

Ellis, G.S.; Huckins, J.N.; Rostad, C.E.; Schmitt, C.J.; Petty J.D.; MacCarthy, P. 1995, Evaluation of lipid-containing semipermeable membrane devices (SPMDs) for monitoring organochlorine contaminants in the Upper Mississippi River. *Environ. Toxicol. Chem.* **14**: 1875–1884.

Følsvik, N.; Brevik, E.M.; Berge, J.A. 2000, Monitoring of organotin compounds in seawater using semipermeable membrane devices (SPMDs)—tentative results. *J. Environ. Monitor.* **2**: 281–284.

Følsvik, N.; Brevik, E.M.; Berge, J.A. 2002, Organotin compounds in a Norwegian fjord. A comparison of concentration levels in semipermeable membrane devices (SPMDs), blue mussels (Mytilus edulis) and water samples. *J. Environ. Monitor.* **4**: 280–283.

Franke, S.; Meyer, C.; Heinzel, N.; Gaterman, R.; Huehnerfuss, H.; Rimkus, G.; Koenig, W.A.; Francke, W. 1999, Enantiomeric composition of the polycyclic musks HHCB and AHTN in different aquatic species. *Chirality* **11**: 795–801.

Gale, R.W.; Huckins, J.N.; Petty, J.D.; Peterman, P.H.; Williams, L.L.; Morse, D.; Schwartz, T.R.; Tillitt, D.E. 1997, Comparison of the uptake of dioxin-like compounds by caged channel catfish and semipermeable membrane devices in the Saginaw River, Michigan. *Environ. Sci. Technol.* **32**: 178–187.

Gale, R.W. 1998, Three-compartment model for contaminant accumulation by semipermeable membrane devices. *Environ. Sci. Technol.* **32**: 2292–2300.

Gatermann, R.; Siselli, S.; Hühnerfuss, H.; Rimkus, G.G.; Franke, S.; Hecker, M.; Kallenborn, R.; Karbe, L.; König, W.A. 2002a, Synthetic musks in the environment. Part 2: Enantioselective transformation of the polycyclic musk fragrances HHCB, AHTN, AHDI, and ATII in freshwater fish. *Arch. Environ. Con. Tox.* **42**: 447–453.

Gatermann, R.; Siselli, S.; Hühnerfuss, H.; Rimkus, G. G.; Hecker, M.; Karbe, L. 2002b, Synthetic musks in the environment. Part 1: Species-dependent bioaccumulation of polycyclic and nitro musk fragrances in freshwater fish and mussels. *Arch. Environ. Con. Tox.* **42**: 437–446.

Granmo, Å.; Ekelund, R.; Berggren, M.; Brorström-Lunden, E.; Bergqvist, P.-A. 2000, Temporal trend of organochlorine marine pollution indicated by concentrations in mussels, semipermeable membrane devices, and sediment. *Environ. Sci. Technol.* **34**: 3323–3329.

Gustavson, K.E.; DeVita, W.; Revis, A.; Harkin, J.M. 2000a, A novel use of a dual-zone restricted access sorbent: Normal phase separations of methyl oleate and polynuclear aromatic hydrocarbons stemming from semipermeable membrane devices. *J. Chromatogr. A* **883**: 143–149.

Gustavson, K.E. and Harkin, J.M. 2000b; Comparison of sampling techniques and evaluation of semipermeable membrane devices (SPMDs) for monitoring polynuclear aromatic hydrocarbons (PAHs) in groundwater. *Environ. Sci. Technol.* **34**: 4445–4451.

Hajšlova, J. and Šetkova, L. 2004, Synthetic Musks in Bioindicators: Monitoring Data of Fish and Human Milk Samples from the Czech Republic. *The Handbook of Environmental Chemistry*, Springer-Verlag: Heidelberg, Germany; Vol. 3X; pp. 151–188.

Harner, T.; Ikonomou, M.; Shoeib, M.; Stern, G.; Diamond, M. 2002, Passive air sampling results for polybrominated diphenyl ethers along an urban-rural transect. *Organohal. Comp.* **57**: 33–36.

Harner, T.; Shoeib, M.; Diamond, M.; Stern, G.; Rosenberg, B. 2004, Using passive air samplers to assess urban-rural trends for persistent organic pollutants. 1. Organochlorine pesticides. *Environ. Sci. Technol.* **38**: 4474–4483.

Herve, S.; Paukku, R.; Paasivirta, J.; Heinonen, P.; Sodergren, A. 1991, Uptake of organochlorines from lake water by hexane-filled dialysis membranes and by mussels. *Chemosphere* **22**: 997–1001.

Herve, S.; Prest, H.F.; Heinonen, P.; Hyötyläinen, T.; Koistinen, J.; Paasivirta, J. 1995, Lipid-filled semipermeable membrane devices and mussels as samplers of organochlorine compounds in lake water. *Environ. Sci. Pollut. R.* **2**: 24–30.

Hewitt, L.M.; Pryce, A.C.; Parrott, J.L.; Marlatt, V.; Wood, C.; Oakes, K.; Van der Kraak, G.J. 2003, Accumulation of ligands for aryl hydrocarbon and sex steroid receptors in fish exposed to treated effluent from a bleached sulfite/groundwood pulp and paper mill. *Environ. Toxicol. Chem.* **22**: 2890–2897.

Hofelt, C.S. and Shea, D. 1997, Accumulation of organochlorine pesticides and PCBs by semipermeable membrane devices and Mytilus edulis in New Bedford Harbor. *Environ. Sci. Technol.* **31**: 154–159.

Huckins, J.N.; Tubergen, M.W.; Lebo, J.A.; Gale, R.W.; Schwartz, T.R. 1990a, Polymeric film dialysis in organic solvent media for cleanup of organic contaminants. *J. AOAC* **73**: 290–293.

Huckins, J.N.; Tubergen, M.W.; Manuweera, G.K. 1990b, Semipermeable membrane devices containing model lipid: A new approach to monitoring the availability of lipophilic contaminants and estimating their bioconcentration potential. *Chemosphere* **20**: 533–552.

Huckins, J.N.; Manuweera, G.K.; Petty, J.D.; Mackay, D.; Lebo, J.A. 1993, Lipid-containing semipermeable membrane devices for monitoring organic contaminants in water. *Environ. Sci. Technol.* **27**: 2489–2496.

Huckins, J.N.; Petty, J.D.; Lebo, J.A.; Orazio, C.E.; Prest, H.F.; Tillitt, D.E.; Ellis, G.S.; Johnson, B.T.; Manuweera, G.K. 1996, Semipermeable Membrane Devices (SPMDs) for the Concentration and Assessment of Bioavailable Organic Contaminants in Aquatic Environments. In *Techniques in Aquatic Toxicology*; Ostrander, G.K., Ed.; CRC Press: Boca Raton, FL; pp. 625–655.

Huckins, J.N.; Petty, J.D.; Orazio, C.E.; Lebo, J.A.; Clark, R.C.; Gibson, V.L.; Gala, W.R.; Echols, K.R. 1999, Determination of uptake kinetics (sampling rates) by lipid-containing semipermeable membrane devices (SPMDs) for polycyclic aromatic hydrocarbons (PAHs) in water. *Environ. Sci. Technol.* **33**: 3918–3923.

Huckins, J.N.; Petty, J.D.; Lebo, J.A.; Almeida, F.V.; Booij, K.; Alvarez, D.A.; Cranor, W.L.; Clark, R.C.; Mogensen, B.B. 2002, Development of the permeability/performance reference compound (PRC) approach for in situ calibration of semipermeable membrane devices (SPMDs). *Environ. Sci. Technol.* **36**: 85–91.

Huckins, J.N.; Prest, H.F.; Petty, J.D.; Lebo, J.A.; Hodgins, M.M.; Clark, R.C.; Alvarez, D.A.; Gala, W.R.; Steen, A.; Gale, R.W.; Ingersoll, C.G. 2004, Overview and comparison of lipid-containing semipermeable membrane devices (SPMDs) and oysters (Crassostrea gigas) for assessing chemical exposure. *Environ. Toxicol. Chem.* **23**: 1617–1628.

Hühnerfuss, H.; Biselli, S.; Gaterman, R. 2004, Enantioselective Analysis of Polycyclic Musks as a Versatile Tool for the Understanding of Environmental Processes. *The Handbook of Environmental Chemistry*, Springer-Verlag: Heidelberg, Germany; Vol. 3X, pp. 213–231.

Ikonomou, M.G.; Rayne, S.; Addison, R.F. 2002a, Exponential increases of the brominated flame retardants, polybrominated diphenyl ethers, in the Canadian Arctic from 1981 to 2000. *Environ. Sci. Technol.* **36**: 1886–1892.

Ikonomou, M.G.; Rayne, S.; Fischer, M.; Fernandez, M.P.; Cretney, W. 2002b, Occurrence and congener profiles of polybrominated diphenyl ethers in environmental samples from Coastal British Columbia, Canada. *Chemosphere* **46**: 649–663.

Isidora, M.; Ferrara, M.; Lavorgna, M.; Nardelli, A.; Parrella, A. 2003, In situ monitoring of urban air in Southern Italy with the Tradescantia micronucleus bioassay and semipermeable membrane devices (SPMDs). *Chemosphere* **52**: 121–126.

Jaward, F.M.; Meijer, S.N.; Steinnes, E.; Thomas, G.O.; Jones, K.C. 2004, Further studies on the latitudinal and temporal trends of persistent organic pollutants in Norwegian and U.K. background air. *Environ. Sci. Technol.* **38**: 2523–2530.

Jegorova, I. 2002, Monitoring with Semipermeable Membrane Device (SPMD) Technology for Persistent Organic Pollutants (POPs) Analysis. In *Principles of Instrumental Analysis;* Leary, J, Skoog, D, Eds.; 4th Ed.; Harcourt Brace Jovanovich: Orlando, FL.

Johnson, B.T.; Petty, J.D.; Huckins, J.N. 2000, Collection and detection of lipophilic chemical contaminants in water, sediment, soil, and air. *Environ. Toxicol.* **15**: 248–252.

Johnson, B.T.; Petty, J.D.; Huckins, J.N.; Lee, K. 2004, Hazard assessment of simulated oil spill on intertidal areas of the St. Lawrence River with SPMD-TOX. *Environ. Toxicol.* **19**: 329–335.

Kŏcí, V.; Ocelka, T.; Kochánková, L. 2001a, SPMD–a modern approach to passive sampling. *Vodni Hospodarstvi* **51**: 331–332.

Kŏcí, V.; Ocelka, T.; Kochánková, L. 2001b, SPMD–description of perspective method of POP monitoring in water bodies. *Vodni Hospodarstvi* **51**: 345–348.

Kŏcí, V.;Mlejnek, M.; Kochánková, L. 2003, Toxicological evaluations of exposed SPMD membranes. *Cen. Eur. J. Chem.* **1**: 28–34.

Kŏci, V.; Lukavsky, J.; Mlejnek, M.; Kochánková, L.; Grabic, R.; Ocelka, T. 2004a, Application of a semipermeable membrane device (SPMD) for assessment of organic toxicants dangerous to the green microalga Scenedesmus subspicatus. *Arch. Hydrobiol.* **150**: 173–186.

Kŏcí, V.; Ocelka, T.; Mlejnek, M.; Grabic, R. 2004b, Efficiency assessment of wastewater treatment plant based on SPMD sampling. *Cen. Eur. J. Chem.* **2**: 91–112.

Koistinen, J.; Lehtonen, M.; Tukia, K.; Soimasuo, M.; Lahtipera, M.; Oikari, A. 1998a, Identification of lipophilic pollutants discharged from a Finnish pulp and paper mill. *Chemosphere* **37**: 219–235.

Koistinen, J.; Soimasuo, M.; Tukia, K.; Oikari, A.; Blankenship, A.; Giesy, J.P. 1998b, Induction of EROD activity in HEPA-1 mouse hepatoma cells and estrogenicity in MC-7 human breast cancer cells by extracts of pulp mill effluents, sludge, and sediment exposed to effluents. *Environ. Toxicol. Chem.* **17**: 1499–1507.

Kolok, A.S.; Huckins, J.N.; Petty, J.D.; Oris, J.T. 1996, The role of water ventilation and sediment ingestion in the uptake of benzo[*a*]pyrene in gizzard shad (Dorosoma cepedianum). *Environ. Toxicol. Chem.* **10**: 1752–1759.

Kot, A.; Zabiegata, B.; Namieśnik, J. 2000, Passive sampling for long-term monitoring of organic pollutants in water. *Trends Anal. Chem.* **9**: 446–459.

Kukkonen, J.V.K.; Rantalainen, A.-L.; Mikkelson, P.; Lyytikäinen, M.; Hamäläinen, H.; Passivirta, J. 1998, Bioavailability of polychlorinated diphenylethers (PDPEs) in contaminated sediments: Comparison of benthic organisms and semipermeable membrane devices (SPMDs). *Organohal. Comp.* **39**: 5–8.

Lebo, J.A.; Zajicek, J.L.; Huckins, J.N.; Petty, J.D.; Peterman, P.H. 1992, Use of semipermeable membrane devices for in situ monitoring of polycyclic aromatic hydrocarbons in aquatic environments. *Chemosphere* **25**: 697–718.

Lebo, J.A.; Gale, R.W.; Petty, J.D.; Tillitt, D.E.; Huckins, J.N.; Meadows, J.C.; Orazio, C.E.; Echols, K.R.; Schroeder, D.J.; Inmon, L.E. 1995, Use of the semipermeable membrane device (SPMD) as an in situ sampler of waterborne bioavailable PCDD and PCDF residues at sub-part-per-quadrillion concentrations. *Environ. Sci. Technol.* **29**: 2886–2892.

Lebo, J.A.; Zajicek, J.L.; Orazio, C.E.; Petty, J.D.; Huckins, J.N.; Douglas, E.H. 1996, Use of the semipermeable membrane device (SPMD) to sample polycyclic aromatic hydrocarbon pollution in a lotic system. *Polycyclic Aromat. Compd.***8**: 53–65.

Lebo, J.A.; Huckins, J.N.; Petty, J.D.; Ho, K.T.; Stern, E.A. 2000, Selective removal of organic contaminants from sediments: A methodology for toxicity identification evaluations (TIEs). *Chemosphere* **40**: 811–819.

Lebo, J.A.; Almeida, F.V.; Cranor, W.L.; Petty, J.D.; Huckins, J.N.; Rastall, A.; Alvarez, D.A.; Mogensen, B.B.; Johnson, B.T. 2004, Purification of triolein for use in semipermeable membrane devices (SPMDs). *Chemosphere* **54**: 1217–1224.

Leppanen, H. and Kukkonen, V.K. 2000, Effect of sediment-chemical contact time on availability of sediment-associated pyrene and benzo[*a*]pyrene to oligochaete worms and semipermeable membrane devices. *Aquat. Toxicol.* **49**: 227–241.

Lindström, A.; Buerge, I.J.; Poiger, T.; Bergqvist, P.A.; Müller, M.D.; Buser, H.R. 2002, Occurrence and environmental behavior of the bactericide triclosan and its methyl derivative in surface waters and in wastewater. *Environ. Sci. Technol.* **36**: 2322–2329.

Lohmann, R.; Corrigan, B.P.; Howsak, M.; Jones, K.; Ockenden, W.A. 2001, Further developments in the use of semipermeable membrane devices (SPMDs) as passive air samplers for persistent organic pollutants: Field application in a spatial survey of PCDD/Fs and PAHs. *Environ. Sci. Technol.* **35**: 2576–2582.

Louch, J.; Allen, G.; Erickson, C.; Wilson, G.; Schmedding, D. 2003, Interpreting results from field deployments of semipermeable membrane devices. *Environ. Sci. Technol.* **37**: 1202–1207.

Lu, Y.; Wang, Z.; Huckins, J.N. 2002, Review of the background of triolein-containing semipermeable membrane devices in aquatic environmental study. *Aquat. Toxicol.* **60**: 139–153.

Lu, Y. and Wang, Z. 2003, Accumulation of organochlorinated pesticides by triolein-containing semipermeable membrane device (triolein-SPMD) and rainbow trout. *Water Res.* **37**: 2419–2425.

Luellen, D.A. and Shea, D. 2002, Calibration and field verification of semipermeable membrane devices for measuring polycyclic aromatic hydrocarbons in water. *Environ. Sci. Technol.* **36**: 1791–1797.

Luellen, D.A. and Shea, D. 2003, Semipermeable membrane devices accumulate conserved ratios of sterane and hopane petroleum biomarkers. *Chemosphere* **53**: 705–713.

Lyytikäinen, M.; Hirva, P.; Minkkinen, P.; Hämäläinen, H.; Rantalainen, A.-L.; Mikkelson, P.; Paasivirta, J.; Kukkonen, J.V.K. 2003a, Bioavailability of sediment-associated PCDD/Fs and PCDEs: Relative importance of contaminant and sediment characteristics and biological factors. *Environ. Sci. Technol.* **37**: 3926–3934.

Lyytikäinen, M.; Rantalainen, A.-L.; Mikkelson, P.; Hämäläinen, H.; Paasivirta, J.; Kukkonen, J.V.K. 2003b, Similarities in bioaccumulation patterns of polychlorinated dibenzo-p-dioxins and furans and polychlorinated diphenyl ethers in laboratory-exposed oligochaetes and semipermeable membrane devices and in field-collected chironomids. *Environ. Toxicol. Chem.* **22**: 2405–2415.

Ma, M.; Wang, Y.; Wang; Z. 1999, Sample pretreatment for toxic assessment of organic pollutants in river water. *Huanjing Kexue/Environ. Sci.* **20**: 80–83.

MacRae, J.D. and Hall, K.J. 1998, Comparison of methods used to determine the availability of polycyclic aromatic hydrocarbons in marine sediment. *Environ. Sci. Technol.* **32**: 3809–3815.

McCarthy, J.F.; Southworth, G.R.; Palmer, J.A.; Ham, K.D. 2000, Time-integrated, flux-based monitoring using semipermeable membrane devices to estimate the contribution of industrial facilities to regional polychlorinated biphenyl budgets. *Environ. Toxicol. Chem.* **19**: 352–359.

McCarthy, K.A. and Gale, R.W. 2001, Evaluation of persistent hydrophobic organic compounds in the Columbia River Basin using semipermeable membrane devices. *Hydrological Processes* **15**: 1271–1283.

Meadows, J.C.; Tillitt, D.E.; Huckins, J.N.; Schroeder, D. 1993, Large-scale dialysis of sample lipids using a semipermeable membrane device. *Chemosphere* **26**: 1993–2006.

Meadows, J.C.; Tillitt, D.E.; Schwartz, T.R.; Schroeder, D.J.; Echols, K.R.; Gale, R.W.; Powell, D.C.; Bursian, S.J. 1996, Organochlorine contaminants in double-crested cormorants from Green Bay, Wisconsin: 1. Large-scale extraction and isolation from eggs using semi-permeable membrane dialysis. *Arch. Environ. Con. Tox.* **31**: 218–224.

Meadows, J.C.; Echols, K.R.; Huckins, J.N.; Borsuk, F.A.; Carline, R.F.; Tillitt, D.E. 1998, Estimation of uptake rate constants for PCB congeners accumulated by semipermeable membrane devices and brown trout (Salmo trutta). *Environ. Sci. Technol.* **32**: 1847–1852.

Meijer, S.N.; Ockenden, W.A.; Steinnes, E.; Corrigan, B.P.; Jones, K.C. 2003, Spatial and temporal trends of POPs in Norwegian and UK background air: Implications for global cycling. *Environ. Sci. Technol.* **37**: 454–461.

Metcalfe, T.L.; Metcalfe, C.D.; Bennett, E.R.; Haffner, G.D. 2000, Distribution of toxic organic contaminants in water and sediments in the Detroit River. *J. Great Lakes Res.* **26**: 55–64.

Miege, C.; Durand, S.; Garric, J.; Gourlay, C.; Wang, D.; Mouchel, J.M.; Tusseau-Vuillemin, M.H. 2004, Semipermeable membrane device-availability of polycyclic aromatic hydrocarbons in river waters and wastewater treatment plant effluents. *Polycyclic Aromat. Compd.***24**: 805–825.

Moring, J.B. and Rose, D.R. 1997, Occurrence and concentration of polycyclic aromatic hydrocarbons in semipermeable membrane devices and clams in three urban streams of the Dallas-Fort Worth Metropolitan Area, Texas. *Chemosphere* **34**: 551–566.

Norrgren, L.; Pettersson, U.; Örn, S.; Bergqvist, P.A. 2000, Environmental monitoring of the Kafue River, located in the Copperbelt, Zambia. *Arch. Environ. Con. Tox.* **38**: 334–341.

Ocelka, T.; Prazak, J.; Kǒcí, J.; Raclavska, H.; Grabic, R. 2003, Application of the SPMD method for POPs monitoring and toxicity assessment in waste waters. *Vodni Hospodarstvi*. **53**: 211–214.

Ockenden, W.A.; Prest, H.F.; Thomas, G.O.; Sweetman, A.; Jones, K.C. 1998a, Passive air sampling of PCBs: Field calculation of atmospheric sampling rates by triolein-containing semipermeable membrane devices. *Environ. Sci. Technol.* **32**: 1538–1543.

Ockenden, W.A.; Sweetman, A.J.; Prest, H.F.; Steinnes, E.; Jones, K.C. 1998b, Toward an understanding of the global atmospheric distribution of persistent organic pollutants: The use of semipermeable membrane devices as time-integrated passive samplers. *Environ. Sci. Technol.* **32**: 2795–2803.

Ockenden, W.A.; Corrigan, B.P.; Howsam, M.; Jones, K.C. 2001, Further developments in the use of semipermeable membrane devices as passive air samplers: Application to PCBs. *Environ. Sci. Technol.* **35**: 4536–4543.

Pablos, M.V.; Fernandez, C.; Garcia-Hortiguela, P.; Valdovinos, C.; Tarazona, J.V. 1999, Comparison of different extraction procedures for organic-fraction toxicity testing of urban sewages. *Toxicol. Environ. Chem.* **70**: 115–127.

Palowitch, A.W. 1996, Semipermeable membrane devices. *Sea Technology* **37**: 73–79.

Parrott, J.L. and Tillitt, D.E. 1997, The use of Semipermeable Membrane Devices (SPMDs) to Concentrate Inducers of Fish Hepatic Mixed Function Oxygenase (MFO). In *Ecotoxicology: Responses, Biomarkers, and Risk Assessment. An OECD Workshop;* Zelikoff, J.T., Ed.; SOS Publications: Fair Haven, NJ.; pp. 185–196.

Parrott, J.L.; Backus, S.M.; Borgmann, A.I.; Swyripa, M. 1999, The use of semipermeable membrane devices to concentrate chemicals in oil refinery effluent on the Mackenzie River. *Arctic* **52**: 125–138.

Petty, J.D.; Huckins, J.N.; Zajicek, J.L. 1993, Application of semipermeable membrane devices (SPMDs) as passive air samplers. *Chemosphere* **27**: 1609–1624.

Petty, J.D.; Huckins, J.N.; Martin, D.B.; Adornato, T.G. 1995a, Use of semipermeable membrane devices (SPMDs) to determine bioavailable organochlorine pesticide residues in streams receiving irrigation drainwater. *Chemosphere* **30**: 1891–1903.

Petty, J.D.; Huckins, J.N.; Orazio, C.E, Lebo, J.A.; Poulton, B.C.; Gale, R.W.; Charbonneau, C.S.; Kaiser, E.M. 1995b, Determination of bioavailable organochlorine pesticide residues in the Lower Missouri River. *Environ. Sci. Technol.* **29**: 2561–2566.

Petty, J.D.; Poulton, B.C.; Charbonneau, C.S.; Huckins, J.N.; Jones, S.B.; Cameron, J.T.; Prest, H.F. 1998, Determination of bioavailable contaminants in the Lower Missouri River following the flood of 1993. *Environ. Sci. Technol.* **32**: 837–842.

Petty, J.D.; Jones, S.B.; Huckins, J.N.; Cranor, W.L.; Parris , J.T.; McTague, T.B.; Boyle, T.P. 2000a, An approach for assessment of water quality using semipermeable membrane devices (SPMDs) and bioindicator tests. *Chemosphere* **41**: 311–321.

Petty, J.D.; Orazio, C.E.; Huckins, J.N.; Gale, R.W.; Lebo, J.A.; Meadows, J.C.; Echols, K.R.; Cranor, W.I. 2000b, Considerations involved with the use of semipermeable membrane devices for monitoring environmental contaminants. *J. Chromatogr. A* **879**: 83–95.

Petty, J.D.; Huckins, J.N.; Alvarez, D.A.; Brumbaugh, W.G.; Cranor, W.L.; Gale, R.W.; Rastall, A.C.; Jones-Lepp, T.L.; Leiker, T.J.; Rostad C.E.; Furlong, E.T. 2004, A holistic passive integrative sampling approach for assessing the presence and potential impacts of waterborne environmental contaminants.*Chemosphere* **54**: 695–705.

Peven, C.S.; Uhler, A.D.; Querzoli, F.J. 1996, Caged mussels and semipermeable membrane devices as indicators of organic contaminant uptake in Dorchester and Duxbury Bays, Massachusetts. *Environ. Toxicol. Chem.* **15**: 144–149.

Poiger, T.; Buser, H.-R.; Balmer, M.E.; Bergqvist, P.-A.; Müller, M.D. 2004, Occurrence of UV filter compounds from sunscreens in surface waters: Regional mass balance in two Swiss lakes. *Chemosphere* **55**: 951–963.

Prest, H.F.; Jarman, W.M.; Burns, S.A.; Weismuller, T.; Martin, M.; Huckins, J.N. 1992, Passive water sampling via semipermeable membrane devices (SPMDs) in concert with bivalves in the Sacramento/San Joachin river delta. *Chemosphere* **25**: 1811–1824.

Prest, H.F.; Huckins, J.N.; Petty, J.D.; Herve, S.; Paasivirta, J.; Heinonen, P. 1995a, A survey of recent results in passive sampling of water and air by semipermeable membrane devices. *Mar. Pollut. Bull.* **31**: 306–312.

Prest, H.F.; Jacobson, L.A.; Huckins, J.N. 1995b, Passive sampling of water and coastal air via semipermeable membrane devices. *Chemosphere* **30**: 1351–1361.

Prest, H.F, Richardson, B.J.; Jacobson, L.A.; Vedder, J.; Martin, M. 1995c, Monitoring organochlorines with semipermeable membrane devices (SPMDs) and mussels (Mytilus edulis) in Corio Bay, Victoria, Australia. *Mar. Pollut. Bull.* **30**: 543–554.

Prest, H.F.; Jacobson, L.A.; Wilson, M. 1997, Passive water sampling for polynuclear aromatic hydrocarbons using lipid-containing semipermeable membrane devices (SPMDs): Application to contaminant residence times. *Chemosphere* **35**: 3047–3063.

Rantalainen, A.-L.; Ikonomou, M.G.; Rogers, I.H. 1998a, Lipid-containing semipermeable-membrane devices (SPMDs) as concentrators of toxic chemicals in the Lower Fraser River, British Columbia.*Chemosphere* **37**: 1119–1138.

Rantalainen, A-.L.; Paasivirta, J.; Herve, S. 1998b, Uptake of chlorohydrocarbons from soil by lipid-containing semipermeable membrane devices (SPMDs).*Chemosphere* **36**: 1415–1437.

Rantalainen, A.-L.; Hyötyläinen, T.; Saramo, M.; Niskanen, I. 1999, Passive sampling of PAHs in indoor air in Nepal. *Toxicol. Environ. Chem.* **68**: 335–348.

Rantalainen, A.-L.; Cretney, W.; Ikonomou, M.G. 2000a, Uptake rates of semipermeable membrane devices (SPMDs) for PCDDs, PCDFs, and PCBs in water and sediment. *Chemosphere* **40**: 147–158.

Rantalainen, A.-L.; Crewe, N.F.; Ikonomou, M.G. 2000b, Comparison of three techniques for lipid removal from seal blubber: Gel permeation, acid treatment, and dialysis with semipermeable membrane. *Int. J. Environ. An. Ch.* **76:** 31–47.

Rastall, A.C.; Neziri, A.; Vukovic, Z.; Jung, C.; Mijovic, S.; Hollert, H.; Nikcevic, S.; Erdinger, L. 2004, The identification of readily bioavailable pollutants in Lake Shkodra/Skadar using semipermeable membrane devices (SPMDs), bioassays and chemical analysis. *Environ. Sci. Pollut. R.* **11**: 240–253.

Rayne, S. and Ikonomou, M.G. 2002, Reconstructing source polybrominated diphenyl ether congener patterns from semipermeable membrane devices in the Fraser River, British Columbia, Canada: Comparison to commercial mixtures. *Environ. Toxicol. Chem.* **21**: 2292–2300.

Richardson, B.J.; Zheng, G.J.; Tse, E.S.C.; Lam, P.K.S. 2001, A comparison of mussels (Perna viridis) and semi-permeable membrane devices (SPMDs) for monitoring chlorinated trace organic contaminants in Hong Kong coastal waters. *Chemosphere* **45**: 1201–1208.

Richardson, B.J.; Lam, P.K.S.; Zheng, G.J.; McClellan, K.E.; De Luca-Abbott, S.B. 2002, Biofouling confounds the uptake of trace organic contaminants by semi-permeable membrane devices. *Mar. Pollut. Bull.* **44**: 1372–1379.

Richardson, B.J.; Zheng, G.J.; Tse, E.S.C.; De Luca-Abbott, S.B.; Siu, S.Y.M, Lam, P.K.S. 2003, A comparison of polycyclic aromatic hydrocarbon and petroleum hydrocarbon uptake by mussels

(Perna viridis) and semi-permeable membrane devices (SPMDs) in Hong Kong Coastal Waters. *Environ. Pollut.* **122**: 223–227.

Robertson, G.; Lebowitz, M.; Needham, L.; O'Rourke, M.K.; Rogan, S.; Petty, J.D.; Huckins, J.N. 2002, Distribution of Residential Organochlorine Pesticide Residuals along the Arizona/Mexico Border. *Proceedings: 9th International Conference on Indoor Air Quality and Climate*; Monterey, CA, June 2002; pp. 63–68.

Rogers, H.R. 1997, Influence of suspended solids and back diffusion on organic contaminant uptake by semi-permeable membranes (SPMDs). *Chemosphere* **35**: 1651–1658.

Rohr, A.C.; Hall, E.R.; Hall, K.J. 1996, Use of semipermeable membrane devices for monitoring pulp mill effluents: A preliminary assessment. *Water Qual. Res. J. Can.* **31**: 85–100.

Sabaliūnas, D. and Sodergren, A. 1996, Uptake of organochlorine pesticides by solvent-filled cellulose and polyethylene membranes. *Ecotox. Environ. Safe.* **35**: 150–155.

Sabaliūnas, D. and Sodergren, A. 1997, Use of semipermeable membrane devices to monitor pollutants in water and assess their effects: A laboratory test and field verification.*Environ. Pollut.* **96**: 195–205.

Sabaliūnas, D.; Ellington, J.; Neuman, J. 1998a, Semipermeable Membrane Devices for Monitoring Pollutants in Aquatic Ecosystems of Lithuania. *CRC Critical Reviews in Analytical Chemistry*, Vol. 2812; CRC Press: Boca Raton, FL.; p. 50.

Sabaliūnas, D.; Lazutka, J.; Sabaliūniene, I.; Sodergren, A. 1998b, Use of semipermeable membrane devices for studying effects of organic pollutants: Comparison of pesticide uptake by semipermeable membrane devices and mussels. *Environ. Toxicol. Chem.* **17**: 1815–1824.

Sabaliūnas, D.; Ellington, J.; Sabaliūniene, I. 1999, Screening bioavailable hydrophobic toxicants in surface waters with semipermeable membrane devices: Role of inherent oleic acid in toxicity evaluations. *Ecotox. Environ. Safe.* **44**: 160–167.

Sabaliūnas, D.; Lazutka, J.R.; Sabaliūniene, I. 2000, Acute toxicity and genotoxicity of aquatic hydrophobic pollutants sampled with semipermeable membrane devices. *Environ. Pollut.* **109**: 251–265.

Sabaliūnas, D.; Webb, S.F.; Hauk, A.; Jacob, M.; Eickhoff, W.S. 2003, Environmental fate of triclosan in the River Aire Basin, UK.*Water Res.* **37**: 3145–3154.

Scott, G.I.; Fulton, M.H.; Wirth, E.F.; Chandler, G.T.; Key, P.B.; Daugomah, J.W.; Bearden, D.; Chung, K.W.; Strozier, E.D.; DeLorenzo, M.; Sivertsen, S.; Dias, A.; Sanders, M.; Macauley, J.M.; Goodman, L.R.; LaCroix, M.W.; Thayer, G.W.; Kuclick, J. 2002, Toxicological studies in tropical ecosystems: An ecotoxicological risk assessment of pesticide runoff in South Florida estuarine ecosystems. *J. Agr. Food Chem.* **50**: 4400–4408.

Shaw, M.; Tibbetts, I.R.; Müller, J.F. 2004, Monitoring PAHs in the Brisbane River and Moreton Bay, Australia, using semipermeable membrane devices and EROD activity in yellowfin bream, Acanthopagrus australis. *Chemosphere* **3**: 237–246.

Shigenaka, G. and Henry, C.B. Jr. 1995, Use of Mussels and Semipermeable Membrane Devices To Assess Bioavailability of Residual Polynuclear Aromatic Hydrocarbons Three Years After the Exxon Valdez Oil Spill. In *Exxon Valdez Oil Spill: Fate and Effects in Alaskan Waters;* Wells, P.G., Butler, J.N., Hughes, J.S, Eds.; American Society for Testing and Materials: Philadelphia, PA.; pp. 239–260.

Shim, S.M.; Santerre, C.R.; Dorworth, L.E.; Miller, B.K.; Stahl, J.R.; Deardorff, D.C. 2004, Prediction of PCB content in sportfish using semipermeable membrane devices (SPMDs). *J. Environ. Sci. Health, Part B* **39**: 263–271.

Shoeib, M. and Harner, T. 2002, Characterization and comparison of three passive air samplers for persistent organic pollutants. *Environ. Sci. Technol.* **36**: 4142–4151.

Söderström, H.S. and Bergqvist, P.-A. 2003, Polycyclic aromatic hydrocarbons in a semiaquatic plant and semipermeable membrane devices exposed to air in Thailand. *Environ. Sci. Technol.* **37**: 47–52.

Söderström, H.S. and Bergqvist, P.-A. 2004, Passive air sampling using semipermeable membrane devices at different wind-speeds in situ calibrated by performance reference compounds. *Environ. Sci. Technol.* **38**: 4828–4834.

Strandberg, B.; Wagman, N.; Bergqvist, P.-A.; Haglund, P.; Rappe, C. 1997, Semipermeable membrane devices as passive samplers to determine organochlorine pollutants in compost. *Environ. Sci. Technol.* **31**: 2960–2965.

Strandberg, B.; Bergqvist, P.-A.; Rappe, C. 1998, Dialysis with semipermeable membranes as an efficient lipid removal method in the analysis of bioaccumulative chemicals. *Anal. Chem.* **70**: 526–533.

Stuer-Lauridsen, F. and Dahl, B. 1995, Tributyltin transport at a marine water/sediment interface-A field study. *Chemosphere* **30**: 831–845.

Stuer-Lauridsen, F. and Kjlholt, J. 2000, Identification of selected hydrophobic organic contaminants in wastewater with semipermeable membrane devices (SPMDs). *Water Res.* **34**: 3478–3482.

Sztamberek-Gola, I.; Grochowalski, A.; Chrzaszcz, R. 2003, Monitoring of PCDDs, PCDFs, and PAHs in wastewater with use of semipermeable membrane devices (SPMD). *Organohal. Comp.* **60**: 45–48.

Tandlich, R.; Vrana, B.; Balaz, S. 2003, Monitoring of Polychlorinated Biphenyls in Slovakian Freshwater Sediments: Use of Semipermeable Membrane Devices. In *The Utilization of Bioremediation to Reduce Soil Contamination: Problems and Solutions*; Sasek, V., Glaser, J., Baveye, P. Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands; 221–226.

Utvik, T.I.R.; Durell, G.S.; Johnsen, S. 1999a, Determining produced water originating polycyclic aromatic hydrocarbons in North Sea waters: Comparison of sampling techniques. *Mar. Pollut. Bull.* **38**: 977–989.

Utvik, T.I.R. and Johnsen, S. 1999b, Bioavailability of polycyclic aromatic hydrocarbons in the North Sea. *Environ. Sci. Technol.* **33**: 1963–1969.

Van der Oost, R.; Beyer, J.; Vermeulen, N.P.E. 2003, Fish bioaccumulation and biomarkers in environmental risk assessment: A review. *Environ. Toxicol. Phar.* **13**: 57–149.

Van Stee, L.L.P.; Leonards, P.E.G.; van Loon, W.M.G.M.; Hendriks, A.J.; Maas, J.L.; Struijs, J.; Brinkman, U.A.Th. 2002, Use of semi-permeable membrane devices and solid-phase extraction for the wide-range screening of microcontaminants in surface waters by GC-AED/MS. *Water Res.* **36**: 4455–4470.

Verweij, F.; Booij, K.; Satumalay, K.; van der Molen, N.; van der Oost, R. 2004, Assessment of bioavailable PAH, PCB, and OCP concentrations in water using semipermeable membrane devices (SPMDs), sediments and caged carp. *Chemosphere* **11**: 1675–1689.

Villeneuve, D.L.; Crunkilton, R.L.; DeVita, W.M. 1997, Aryl hydrocarbon receptor-mediated toxic potency of dissolved lipophilic organic contaminants collected from Lincoln Creek, Milwaukee, Wisconsin, USA, to PLHC-1 (Poeciliopsis lucida) fish hepatoma cells. *Environ. Toxicol. Chem.* **16**: 977–984.

Villeneuve, J.Y.; Niimi, A.J.; Metcalfe, C.D. 2000, Distribution and bioaccumulation of chlorinated diphenyl ethers in a contaminated embayment of Lake Ontario. *J. Great Lakes Res.* **25**: 760–771.

Voie, Ø.A.; Johnsen, A.; Rossland, H.K. 2002, Why biota still accumulate high levels of PCB after removal of PCB contaminated sediments in a Norwegian Fjord *Chemosphere* **46**: 1367–1372.

Vrana, B.; Paschke, A.; Popp, P. 2001a, Polyaromatic hydrocarbon concentrations and patterns in sediments and surface water of the Mansfield Region, Saxony-Anhalt, Germany. *J. Environ. Monitor.* **3**: 602–609.

Vrana, B.; Paschke, A.; Popp, P.; Schüürmann, G. 2001b, Use of semipermeable membrane devices (SPMDs): Determination of bioavailable organic contaminants in the industrial region of Bitterfeld, Saxony-Anhalt, Germany. *Environ. Sci. Pollut. R.* **8**: 27–34.

Vrana, B. and Schüürmann, G. 2002, Calibrating the uptake kinetics of semipermeable membrane devices in water: Impact of hydrodynamics. *Environ. Sci. Technol.* **36**: 290–296.

Wågman N, Strandberg B, Tysklind M. 1998, Passive sampling of PCBs from in—and outdoor air with semipermeable membrane devices (SPMDs). *Organohal. Comp.* 35: 209–212.

Wang, C.; Wang, Y.; Kiefer, F.; Yediler, A.; Wang, Z.; Kettrup, A. 2003, Ecotoxicological and chemical characterization of selected treatment process effluents of municipal sewage treatment plant. *Ecotox. Environ. Safe.* **56**: 211–217.

Wang, Y.; Wang, C.; Wang, Z. 1998, Uptake of moderately hydrophobic chlorophenols from water by semipermeable membrane devices (SPMDs) and by goldfish (Crassius auratus). *Chemosphere* **37**: 327–339.

Wang, Y.; Wang, Z.; Liu, J.; Ma, M.; Belzile, N. 1999a, Monitoring priority pollutants in the Yangtze River by dichloromethane extraction and semipermeable membrane device (SPMD). *Chemosphere* **39**: 113–131.

Wang, Y.; Wang, Z.; Wang, C.; Wang, W. 1999b, Uptake of moderately hydrophobic nitroaromatics from water by semipermeable membrane devices (SPMDs) and by goldfish (Crassius auratus). *Chemosphere* **38**: 51–66.

Wang, Y.; Wang, Z.; Liu, J.; Ma, M.; Wang, C; Mo, Z. 2001, Monitoring priority pollutants in a sewage treatment process by dichloromethane extraction and triolein-semipermeable membrane devices (SPMDs). *Chemosphere* **43**: 339–346.

Wang, Y.; Huang, Y.; Huckins, J.N.; Petty, J.D. 2004, Compound-specific carbon and hydrogen isotope analysis of sub-parts per billion level waterborne petroleum hydrocarbons. *Environ. Sci. Technol.* **38**: 3689–3697.

Wang, Z.; Lu, Y. Wang, Y.; Ma, M. 2002a, Assessing the ecological risk of substituted benzenes in Huaihe River, China. *Acta Sci. Circumstantiae* **22**: 300–304.

Wang, Z.; Wang, Y.; Ma, M.; Lu, Y.; Huckins, J.N. 2002b, Use of triolein-SPMD to assess the bioconcentration processes of hydrophobic organic contaminants in the Huaihe River, China. *Environ. Toxicol. Chem.* **21**: 2378–2384.

Whyte, J.J.; Karrow, N.A.; Boermans, H.J.; Dixon, D.G.; Bols, N.C. 2000, Combined methodologies for measuring exposure of rainbow trout (Oncorhynchus mykiss) to polycyclic aromatic hydrocarbons (PAHs) in creosote contaminated microcosms. *Polycyclic Aromat. Compd.* **18**: 71–98.

Williamson, K.S.; Petty, J.D.; Huckins, J.N.; Lebo, J.A.; Kaiser, E.M. 2002a, HPLC-PFD determination of priority pollutant PAHs in water, sediment, and semipermeable membrane devices. *Chemosphere* **49**: 703–715.

Williamson, K.S.; Petty, J.D.; Huckins, J.N.; Lebo, J.A.; Kaiser, E.M. 2002b, Sequestration of priority pollutant PAHs from sediment pore water employing semipermeable membrane devices. *Chemosphere* **49**: 717–729.

Zabiegala, B.; Kot, A.; Namieśnik, J. 2000, Long-term monitoring of organic pollutants in water–Application of passive dosimetry. *Chem. Anal-Warsaw* **45**: 645–657.

Zajicek, J.L.; Tillitt, D.E.; Huckins, J.N.; Petty, J.D.; Potts, M.E.; Nardone, D.A. 1996, Application of Enzyme-Linked Immunosorbent Assay (ELISA) for Measurement of Polychlorinated Biphenyls (PCBs) from Hydrophobic Solutions: Extracts of Fish and Dialysates of Semipermeable Membrane Devices (SPMDs). In *Environmental Immunochemical Methods*; ACS Symposium Series 646; American Chemical Society: Washington, D.C.; Chapter 26, pp. 307–325.

Zhang, J. and Zhang, Y. 2001, Development and application of SPMD technology to environmental research. *Mar. Environ. Sci.* **20**: 67–74.

Zhu, Y.-X.; Zhang, Y.; Zhang, J.; Zhuang, Y.-T.; Poon, K.-F.; Lam, M.H.W.; Hong, H.-S.; Wu, R.S.S. 2001, Monitoring polynuclear aromatic hydrocarbons in sediment porewater by SPMD. *Chin. J. Oceanol. Limnol.* **19**: 382–388.

Zimmerman, L.R.; Thurman, E.M.; Bastian, K.C. 2000, Detection of persistent organic pollutants in the Mississippi Delta using semipermeable membrane devices. *Sci.Total Environ.* **248**: 169–179.

Glossary

The units specified for symbols in the table below are only recommendations. Other units may (and sometimes should) be used, as long as the units on the right-hand sides of the relevant equation matches the units on the left-hand sides. For example, if time is measured in days in Eq. 3.22, and R_s is given in L d^{-1}, then the SPMD volume should be given in L, rather than in cm^3, because of the argument that the exponent ($R_s\, t/V_s K_{sw}$) should be dimensionless. Similarly, when the absorbed amount is given in ng, and the SPMD volume is given in L, then the aqueous concentration calculated from Eq. 3.22 has units of ng L^{-1}.

Symbol	Quantity	Recommended units[a]
A	Surface area	cm^2
B_m	Antilog of the log k_m − log K_{ow} intercept	cm d^{-1}
B_w	Antilog of the log k_w − logK_{ow} intercept	cm d^{-1}
C_B	Concentration in a biomonitoring organism	g g^{-1}
C_c	Concentration of concern	ng cm^{-3}
C_f	Concentration in food	g g^{-1}
C_L	Concentration in the triolein	ng cm^{-3}
C_s	Concentration in SPMD	ng cm^{-3}
C_t	Total (dissolved + *DOC*-bound) concentration in the water	ng cm^{-3}
C_w	Aqueous concentration	ng cm^{-3}
CF	Concentration factor	cm^3 cm^{-3}
$C.V.$	Coefficient of variation	%
d	Characteristic length scale	cm

(*Continued*)

Glossary (*Continued*)

Symbol	Quantity	Recommended units[a]
D_a	Diffusion coefficient in air	$cm^2\ d^{-1}$
D_b	Diffusion coefficient in the biofilm	$cm^2\ d^{-1}$
D_i	Diffusion coefficient in the rate-limiting barrier	$cm^2\ d^{-1}$
D_m	Diffusion coefficient in the membrane	$cm^2\ d^{-1}$
D_w	Diffusion coefficient in water	$cm^2\ d^{-1}$
$[DOC]$	Concentration of dissolved organic carbon	$g\ cm^{-3}$
ΔE_a	Activation energy	$J\ mol^{-1}$
E_v	Volume of sample medium cleared of chemical	mL
E_t	Fraction of total sample injected	—
F	Feeding rate	$g\ g^{-1}\ d^{-1}$
f_r	Faction of quickly equilibrating particle-bound contaminants	—
F_w	Groundwater flow rate	$m^3\ d^{-1}$
H	Henry's law constant	$Pa\ m^3\ mol^{-1}$
Δh	Hydraulic head	m
I	Transport resistance ($1/k$)	$d\ cm^{-1}$
j_b	Flux through the biofilm	$ng\ cm^{-2}\ d^{-1}$
j_m	Flux through the membrane	$ng\ cm^{-2}\ d^{-1}$
j_w	Flux through the water boundary layer	$ng\ cm^{-2}\ d^{-1}$
j_x	Flux in the x direction	$ng\ cm^{-2}\ d^{-1}$
K	Bulk sediment-water partition coefficient	$cm^3\ cm^{-3}$
k_2	Sediment desorption rate constant	d^{-1}
k_a	Mass transfer coefficient for the air boundary layer	$cm\ d^{-1}$
k_b	Mass transfer coefficient for the biofilm	$cm\ d^{-1}$
K_{bw}	Biofilm-water partition coefficient	$cm^3\ cm^{-3}$
K_{DOC}	*DOC*-water partition coefficient	$cm^3\ g^{-1}$
k_e	Equilibration rate constant or release rate constant	d^{-1}
k_{ea}	Equilibration rate constant for air	d^{-1}
k_{em}	Rate constant for HOC metabolism	d^{-1}
k_{ew}	Equilibration rate constant for water	d^{-1}
k_{Ld}	Mass transfer coefficient for the lipid-derived film	$cm\ d^{-1}$
K_{Lda}	"Lipid derived film" to air partition coefficient	$cm^3\ cm^{-3}$
K_{Lm}	Lipid-membrane partition coefficient	$cm^3\ cm^{-3}$
k_m	Mass transfer coefficient for the membrane	$cm\ d^{-1}$
K_{ma}	Membrane-air partition coefficient	$cm^3\ cm^{-3}$
K_{mL}	Membrane-lipid partition coefficient	$cm^3\ cm^{-3}$
K_{mw}	Membrane-water partition coefficient	$cm^3\ cm^{-3}$
k_o	Overall mass transfer coefficient	$cm\ d^{-1}$
K_{oa}	Octanol-air partition coefficient	$cm^3\ cm^{-3}$
K_{ow}	Octanol-water partition coefficient	$cm^3\ cm^{-3}$
k_p	Mass transfer coefficient for a polymer film	$cm\ d^{-1}$
K_{pa}	Polymer-air partition coefficient	$cm^3\ cm^{-3}$
K_{pw}	Polymer-water partition coefficient	$cm^3\ cm^{-3}$
K_{sa}	SPMD-air partition coefficient	$cm^3\ cm^{-3}$
K_{sw}	SPMD-water partition coefficient	$cm^3\ cm^{-3}$
k_u	Uptake rate constant (CRK model)	$cm^3\ cm^{-3}d^{-1}$
k_w	Mass transfer coefficient for the water boundary layer	$cm\ d^{-1}$

(*Continued*)

(*Continued*)

Symbol	Quantity	Recommended units[a]
L_f	Length of water-bearing strata	m
M	Molar mass	g mol^{-1}
m_L	Mass of lipid	g
m_{Leq}	Lipid-equivalent mass	g
m_m	Mass of membrane	g
m_{oc}	Mass of sedimentary organic carbon	g
M_{wb}	Whole body tissue mass	g
N	Absorbed amount	ng
n	Number of observations	—
N_0	Amount prior to exposure	ng
P_{hc}	Hydraulic permeability	m d^{-1}
P_r	Procedural recovery of analyte	%
Q	*DOC* quality (K_{DOC}/K_{ow} ratio)	cm^3 g^{-1}
R	Gas constant	J mol^{-1} K^{-1}
r	Correlation coefficient (regression models)	—
Re	Reynolds number	—
R_s	Sampling rate	cm^3 d^{-1}
R_v	Ventilation rate across gills	cm^3 d^{-1}
S	Fractional assimilation efficiency across gut	g g^{-1}
s	Standard deviation	same as the dependent variable
S_a	Solubility coefficient for an amorphous polymer	cm^3 cm^{-3}
Sc	Schmidt number	—
Sh	Sherwood number	—
s_n	Number of standard SPMDs per mL carrier solvent	SPMD mL^{-1}
S_p	Solubility coefficient	cm^3 cm^{-3}
T	Absolute temperature	K
t	Time	d or s
$t_{1/2}$	First order half-life	d
t_{95}	Time to 95% of equilibrium	d
t_L	Lag time	d or s
t_m	Residence time	d or s
t_r	Response time	d or s
V	LeBas molar volume or unit volume	cm^3 mol^{-1}
ν	Kinematic viscosity	cm^2 s^{-1}
V_c	Volume of carrier solvent used in a bioassay	mL
V_{gw}	Well water volume	cm^3
V_i	Volume of standard injected	μL
V_L	Lipid or triolein volume	cm^3
V_m	LeBas molar volume	cm^3 mol^{-1}
V_p	Polymer volume	cm^3
V_s	SPMD volume	cm^3
V_T	Tissue volume	cm^3
V_{tox}	Volume of SPMD per day eliciting a toxicological response	mL d^{-1}
V_w	Water volume	cm^3
V_{w-tox}	Volume of water extracted eliciting a toxicological response	cm^3
α	Compound-specific effect on the sampling rate	—

(*Continued*)

Glossary (*Continued*)

Symbol	Quantity	Recommended units[a]
β	Exposure-specific effect on the sampling rate	—
δ_i	Thickness of rate-limiting barrier	cm
δ_b	Biofilm thickness	cm
δ_m	Membrane thickness	cm
δ_p	Polymer film thickness	cm
δ_w	Effective water boundary layer thickness	cm
ϕ	Porosity	—
ϕ_a	Amorphous volume fraction of polymer	$cm^3\ cm^{-3}$
θ	Tortuosity	—
π	3.14159 . . .	—

[a] As discussed above other units may be used.

Index

Activation energies, mass transfer, 55, 56
Active Sampling, definition of and methods, 3–6
Air boundary layer (ABL): *see* Boundary layer
Air diffusion coefficient: *see* Diffusion coefficients
Air flow, effects on sampling: *see* Exposure conditions
Air sampling rates: *see* Sampling rates (R_s), SPMD
Air-water partition coefficient: *see* Partition coefficients
Ames mutagenicity test: *see* Bioassay of SPMD extracts
Amorphous region: *see* Rubbery region, polymer
Arrhenius equation, 55
Aqueous boundary layer: *see* Boundary layer
Artifacts, procedural, 81, 117

Bioaccumulation, defination of and parameters, 2, 122, 143, 158
Bioaccumulation factor (*BAF*), 6, 140–144, 153, 158, 160, 161
Bioassays of SPMD extracts (also *see* Toxicity endpoints):
  Ames mutagenicity assay, 121
  Daphtoxkit F, 121
  enzyme-linked immunosorbent assay (ELISA), 121, 134
Bioassays of SPMD (*Cont.*)
  ethoxyresorufin-*O*-deethylase (EROD) activity, 121, 127, 128, 151, 179
  Microtox, 121, 124, 125, 126
  Mutatox, 91, 121, 124, 125, 127
  sister chromatid exchange, 121
  vitellogenin production (VGT), 121, 131
  yeast androgen screen, 179
  yeast estrogen screen (YES), 113, 121, 135, 179, 180
Bioavailability, definition of, 3
Bioconcentration, definition of, 2
Bioconcentration factor (*BCF*), 2, 34, 35, 55, 122, 141–143, 158, 159, 161
Biofilm or periphyton, 21, 22, 45, 47, 69, 71, 72, 108
Biofouling, effects on sampler performance and control of, 14, 21, 22, 72, 75
Biomagnification, 116, 153, 160
Biomagnification factor (BMF), 160
Biomarkers or bioindicators: *see* Bioassay of SPMD extracts
Biomimetic, 32, 35, 160, 161
Biomonitoring organisms (BMOs), 6, 139–162
Blanks, QC samples for SPMD analysis:
  fabrication, 104, 106, 111
  field, 97, 105, 111, 114, 135
  process, 104, 106, 111, 135
  reagent, 105

Blanks, QC samples for SPMD analysis: (*Cont.*)
trip, 105
Boundary layer, passive sampler:
air (ABL), 9, 23, 77–79, 148
water (WBL), 15, 16, 19, 21, 39, 45–48, 60, 63–65, 69, 72, 73, 141, 146, 148, 149

Calibration data: *see* SPMD
Chemical reaction kinetic (CRK) models: *see* Mathematical models
Clearance capacity, 8, 13
Concentration factor (*CF*), 18, 153, 154
Conductivity, definition of and models, 48, 69, 72
Crystallinity, polymer, 14
Curvilinear uptake phase: *see* Uptake phases

Daphtoxkit F: *see* Bioassays of SPMD extracts
Darcy's Law, 74
Deployment devices or canisters: *see* SPMD
Deployment precautions: *see* SPMD
Depuration rate constant: *see* Rate constants
Dialysis, organic solvent (OSD): *see* SPMD
Dietary uptake, 143, 154, 160, 162
Diffusion coefficients:
air, 72, 75–77, 79
biofilm, 72
membrane or LDPE or polymer, 41, 63, 68
water, 71
Dissipation rate constant: *see* Rate constants
Dissolved organic carbon (*DOC*), 4, 51–53, 66, 68, 69
DOC-water partition coefficient: *see* Partition coefficients

Elimination rate constant: *see* Rate constants
Empore extraction disk, 4, 12
Encounter-volume, 3, 32, 33, 39
Endocrine disruption: *see* Toxicity endpoints
Enzyme-linked immunosorbent assay (ELISA): *see* Bioassay of SPMDs
Episodic exposure events, 122, 157
Equilibrium partition (EP) theory, 116, 140–142, 153, 161
Equilibrium samplers, 4, 8, 15, 49, 50
Estimation of ambient concentration, 7, 14, 21, 29, 34, 35, 51, 62, 69, 70, 73, 76, 78
Exposure adjustment factor (*EAF*), 59
Exposure conditions, effects on sampling rates:
biofouling, 12, 14, 19, 21, 22, 69, 72, 75, 96
flow-turbulence, 10, 14, 19, 21, 58, 60, 63–65, 76, 78, 96, 98, 147, 148
temperature, 14, 21, 55, 57, 79, 114, 140

Fabrication Blank: *see* Blanks
Fick's law, 38, 40, 49
Field blank: *see* Blanks
First-order kinetics: *see* Kinetics
Fish lipid: *see* SPMD liquid phases
Flow-turbulence: *see* Exposure conditions; effects on sampling
Flux, equations for, 47, 71, 72
Food chain, 116, 154, 160
Free volume of polymer, 11, 15, 21, 30, 63
Fugacity, 2, 7, 8

Gas constant, 56
Genotoxicity: *see* Toxicity endpoints
Gill extraction efficiencies, 143, 148
Gills or respiratory lamellae, fish, 3, 143, 145, 147, 148, 161
Goulden large sample extractor, 5
Grab sampling, 3–5
Groundwater sampling, 34, 35, 74, 75
Gut assimilation (also *see* dietary uptake), 143, 148

Half-life ($t_{1/2}$), 36, 91, 155, 159
Hayduk-Laudie equation, 65
Henry's law constants (H), 75–79
High-volume air sampler (HiVol), 6, 10, 76, 81, 198
Hildebrand and Hansen solubility parameters, 11, 20

Immunoassays, 121, 134
Impedance (I_o), 48
Impurities (SPMD): *see* Triolein impurities and Polyethylene waxes
Infiltrix sampler, 5, 6
Integrative sampling, definition of, 6, 8, 37, 122
Interferences, bioassays, 134, 135
Isotropic exchange, 21

Kinematic viscosity, 65
Kinetics:
first-order, 14, 19, 36, 40, 143, 153
Michaelis-Menten, 143

Lag time, membrane diffusion, 41
LDPE strips: *see* Passive samplers
LDPE-water partition coefficient: *see* Partition coefficients
LeBas molar volume, 56, 65
Lipid-derived or surficial film, SPMD, 75, 80
LDPE-water partition coefficient: *see* Partition coefficients

Low-density polyethylene (LDPE) membrane, 9, 11, 12, 18–20, 30, 63, 88, 89, 91

Mass transfer coefficient (MTC) models: *see* Mathematical models
Mathematical models:
  chemical Reaction Kinetics (CRK), 46, 49
  mass Transfer Coefficient (MTC), 47, 49
Membrane-air partition coefficient: *see* Partition coefficients
Membrane-lipid partition coefficient: *see* Partition coefficients
Membrane rate control: *see* Rate control
Membrane-water partition coefficient: *see* Partition coefficients
Method detection limits (MDL), 114
Method quantitation limit (MQL), 5, 90, 114
Methyl oleate: *see* Triolein impurities
Michaelis-Menten kinetics: *see* Kinetics
Microtox: *see* Bioassay of SPMDs
Mixed function oxygenase (MFO), 121, 127
Molecular diffusion coefficient: *see* Diffusion coefficients
Mussel-SPMD comparisons, 148, 150–153, 174
Mutatox: *see* Bioassay of SPMDs

Narcosis: *see* Toxicity endpoints
Neurotoxicity: *see* Toxicity endpoints
Nonporous polymers, definition of, 10

Octanol-air partition coefficient: *see* Partition coefficients
Octanol-water partition coefficient: *see* Partition coefficients
Oleic acid: *see* Triolein impurities
Organic solvent dialysis (OSD), *see* SPMD dialysis
Oyster-SPMD comparisons, 149, 153–155, 157

Particulate organic carbon (*POC*), 4, 16, 51
Partition coefficients:
  air-water *(H/RT)*, 76, 170
  biofilm-water, 47, 72
  DOC-water, 52
  lipid- or triolein-water (K_{Lw}), 19, 29, 48, 142
  membrane-air (K_{ma}), 14, 23, 79
  membrane (LDPE)-water (K_{mw}), 14, 39, 60, 61, 68, 79, 146
  membrane-lipid (K_{mL}), 115, 116
  octanol-air (K_{oa}), 2, 33, 76, 115
  octanol-water (K_{ow}), 2, 29, 51, 52, 122
  particle-water, 51

Partition coefficients (*Cont.*)
  polymer-air (also *see* Partition coefficients, membrane-air), 8
  polymer-water (also *see* Partition coefficients, membrane-water), 16
  sediment organic carbon-water (K_{oc}), 15, 16, 74
  sediment-water (K), 71, 73
  SPMD-air (K_{sa}), 40, 75, 93
  SPMD-water (K_{sw}), 35, 37, 39, 47, 48, 50, 53–55, 74, 76, 93, 142, 153, 158, 159, 161, 183, 184–186
  triolein-membrane (also *see* Partition coefficients, membrane-lipid), 19, 49
Passive samplers:
  PES (LDPE or LDPE strips), 12–14, 16–20, 35
  PDM (personal diffusional monitors), 8, 9, 15
  PISCES (passive *in situ* concentration and extraction sampler), 12, 13, 19
  POCIS (polar organic chemical integrative sampler), 12, 13, 33
  POG (polymer coated glass), 8, 9, 13, 15, 16
  PSS (passive sampling system), 12, 13
  PUF (polyurethane foam) disk, 10
  Silastic SPMD, 14, 18–20
  SPME (solid-phase micro extraction), 4, 13, 15–17
  ST (silastic or silicone tubing/sheets of PDMS), 11, 14, 15
Passive sampling, definition of, 7
PDMs: *see* Passive samplers
Performance reference compounds (PRCs) for passive sampling, 14, 15, 21, 22, 35, 39, 50, 51, 59, 60, 68, 69, 72, 81, 92, 93, 98, 105, 114
Periphyton: *see* Biofilm
Permeability, polymer and groundwater, 10, 35, 39, 74, 80
Pervaporation, 9, 87
Photolysis, effects of sunlight or solar radiation on chemicals, 90, 91, 97
PISCES: *see* Passive samplers
POCIS: *see* Passive samplers
POG: *see* Passive samplers
Polar organic chemical integrative sampler (POCIS): *see* Passive samplers
Polydimethyl siloxane (PDMS) samplers: *see* Passive samplers
Polymer-air partition coefficient: *see* Partition coefficients
Polymer coated glass (POG): *see* Passive samplers

Polymer diffusion coefficient: *see* Diffusion coefficients
Polymer-water partition coefficient: *see* Partition coefficients
Pore water sampling, 16, 34, 35, 72–74
Principle components analysis (PCA), SPMD samples, 151, 152
Process Blank: *see* Blanks
PSS: *see* Passive samplers
PUF disk: *see* Passive samplers

Quality control (QC), SPMDs, 87, 93, 98, 103–107
Quantitation limit: *see* Method quantitation limit
Quantitative-structure-activity relationships (QSARs), 1, 2
Quantitative-structure-property relationships (QSPRs), 2, 3

Rate constants:
- depuration or elimination (k_e; organisms), 141–144, 156
- desorption (sediment), 74
- release or elimination (k_e; passive samplers), 9, 37, 39, 46, 51, 114, 155, 156
- uptake (k_u; passive samplers and organisms), 22, 46, 49, 117, 141, 142, 144, 146, 148, 151, 161, 185–200

Rate control or limiting (a step in or barrier to chemical exchange):
- air boundary layer (ABL), 9, 77–79
- membrane, 8, 12, 15, 39, 41, 60–63, 77–79, 146, 148
- sediment desorption, 73
- water boundary layer (WBL), 39, 40, 63, 69, 146, 148

Reagent blank: *see* Blanks
Release rate constant: *see* Rate constants
Residence time (t_m), 40, 157
Resistance to mass transfer, equations of, 48
Response time (t_r), 40
Reynolds number (Re), 14, 64
Rubbery regions, polymer, 10

Sample preservation, 88, 93
Sample set, 104
Sampling rates (R_s), SPMD:
- air, 23, 75, 81, 198–200
- water, 39, 50, 51, 57, 59–61, 63, 65, 68, 72, 146, 159, 185–197

Schmidt number (Sc), 64
Sea surface microlayer (SSM), sampling, 170
Sediment organic carbon-water partition coefficient: *see* Partition coefficients
Sediment-water partition coefficient: *see* Partition coefficients
Semipermeable membrane device (SPMD): *see* SPMD
Semi-volatile organic compounds (SVOCs), 5, 8, 9, 36
Sherwood number (Sh), 64
Shielding from sunlight or solar radiation, importance of, 91
Silicone fluid as a liquid phase for SPMDs, 20, 29
Size exclusion chromatography (SEC), 88, 101, 109–113, 127, 129
Solid-phase microextraction (SPME): *see* Passive samplers
Solubility coefficient, polymer (S_p), 14
SPMD:
- analysis, 103–113, 171, 174–177
- applications, 33–35, 98, 169
- assembly or preparation, 87–89
- biofouling: *see* Exposure conditions and Biofilm
- blanks: *see* Blanks
- calibration data, 50, 51, 57, 66, 81, 183–200
- cleaning, external membrane surface, 88, 108, 109, 111
- cleanup, extracts or dialysates, 102–104, 109–112, 127, 135
- comparison to BMOs, 139, 141, 144, 147, 150, 153, 154, 158, 161, 173, 175, 177
- comparison to other passive samplers, 13, 14, 17, 19, 20
- contamination, sample (also *see* Quality control), 87, 96–98 104, 105, 114
- data quality and format, 34, 107, 113–117
- density, 49, 183
- deployment devices or canisters, 10, 79, 90–96
- deployment considerations/precautions (also *see* Quality control), 87, 89–97
- dialysis, organic solvent (OSD), 20, 21, 30, 34, 107–109, 123, 127
- handling precautions (also *see* Quality control), 95, 97
- liquid phase, 18, 20, 29
- partition coefficients: *see* Partition coefficients
- processing, sample, 103, 104, 106, 107
- sampling rates: *see* Sampling rates (R_s)

SPMD: (*Cont.*)
standard design specifications, 19, 20, 89
storage (stored, also *see* Sample preservation), 88, 93, 94
tether loops, 89, 96
transport, 93, 94
types of chemicals sampled, 30, 32, 35, 96, 101, 171, 172
SPME: *see* Passive samplers
ST: *see* Passive samplers
Steric impedance or size discrimination, polymer, 30, 32, 147
Surface-area-to-sorbent-volume ratios (AV^1), 9–13, 16, 18, 89

Temperature effects: *see* Exposure conditions
Time-weighted average (TWA) concentration, definition, 6
Toxicity endpoints (also *see* Bioassays of SPMD extracts)
deformities, frogs, 132–134
endocrine disruption, 131, 180
genotoxicity, 125–127
narcosis, 126
neurotoxicity, 130, 131
Toxicity identification evaluation (TIE), 34, 132
Triolein cleanup method, 109, 112
Triolein impurities
oleic acid, 20, 23, 80, 111, 112, 134, 135
methyl oleate, 20, 23, 80, 111, 112, 135
Triolein-membrane partition coefficient: *see* Partition coefficients
Triolein-water partition coefficient: *see* Partition coefficients
Trip blank: *see* Blanks

Uptake rate constant: *see* Rate constants
Uptake kinetics: *see* Kinetics
Uptake phases
curvilinear, 36, 37, 40, 93
equilibrium, 36, 37, 40, 49, 50
linear, 36, 37, 40, 49, 50

Ventilation rate, gills, 143, 147, 148
Vitellogenin (VGT): *see* Bioassay of SPMDs)
Volatile organic compound (VOC), 5, 8, 9, 17

Water or aqueous boundary layer (WBL); *see* Boundary layer
Water quality, effects on sampling, 30

XAD resins, 5, 9, 52

Yeast androgen screen: *see* Bioassay of SPMD extracts
Yeast estrogen screen (YES): *see* Bioassay of SPMD extracts