ELSEVIER

Journal of Chromatography A, 879 (2000) 83–95

JOURNAL OF CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Review

Considerations involved with the use of semipermeable membrane devices for monitoring environmental contaminants

J.D. Petty*, C.E. Orazio, J.N. Huckins, R.W. Gale, J.A. Lebo, J.C. Meadows, K.R. Echols, W.L. Cranor

US Geological Survey, Columbia Environmental Research Center, 4200 New Haven Road, Columbia, MO 65201, USA

Abstract

Semipermeable membrane devices (SPMDs) are used with increasing frequency, and throughout the world as samplers of organic contaminants. The devices can be used to detect a variety of lipophilic chemicals in water, sediment/soil, and air. SPMDs are designed to sample nonpolar, hydrophobic chemicals. The maximum concentration factor achievable for a particular chemical is proportional to its octanol–water partition coefficient. Techniques used for cleanup of SPMD extracts for targeted analytes and for general screening by full-scan mass spectrometry do not differ greatly from techniques used for extracts of other matrices. However, SPMD extracts contain potential interferences that are specific to the membrane–lipid matrix. Procedures have been developed or modified to alleviate these potential interferences. The SPMD approach has been demonstrated to be applicable to sequestering and analyzing a wide array of environmental contaminants including organochlorine pesticides, polychlorinated biphenyls, polycyclic aromatic hydrocarbons, polychlorinated dioxins and dibenzofurans, selected organophosphate pesticides and pyrethroid insecticides, and other nonpolar organic chemicals. We present herein an overview of effective procedural steps for analyzing exposed SPMDs for trace to ultra-trace levels of contaminants sequestered from environmental matrices.

Keywords: Reviews; Environmental analysis; Water analysis; Semipermeable membrane devices; Membranes; Organochlorine compounds; Pesticides; Polynuclear aromatic hydrocarbons; Polychlorinated biphenyls

Contents

*Corresponding author.

0021-9673/00/$ – see front matter
PII: S0021-9673(00)00315-0

1. Introduction

Due to the myriad potential chronic effects (particularly reproductive effects) associated with exposure of organisms to environmental pollutants, environmental scientists are increasingly concerned with determining trace (i.e., <1 part per billion) and ultra-trace (i.e., <1 part per trillion) levels of bioavailable hydrophobic chemicals in water [1]. Because organisms often bioconcentrate these seemingly innocuous levels of contaminants to relatively high levels (parts per million) in their lipids, determination of the bioavailable portion of environmental pollutants is critical to assessing the potential for detrimental biological impacts. Unfortunately, modifications in traditional sampling methods (e.g., liquid–liquid extraction, solid-phase extraction, etc.) for sequestering these pollutants from water have been only partially successful due to problems associated with sampling and processing the large (e.g., >50 l) water volumes required for analysis of ultra-trace concentrations.

These limitations in methods for the direct measurement of contaminant water concentrations have often prompted the use of biomonitoring organisms for assessing the exposure of organisms to trace/ultra-trace levels of hydrophobic chemicals. This organism-based approach also has inherent problems, including biotransformation and depuration of contaminants, and inapplicability in many exposure situations due to the effects of stress on the biomonitoring organisms that often lead to a lack of proportionality between biomonitoring organism tissue concentrations and ambient exposure concentrations. Because accurate exposure estimates are a fundamental element of hazard assessment, innovative approaches for sampling and analyzing trace/ultra-trace levels of waterborne hydrophobic chemicals are needed.

The passive processes of biomembrane diffusion and partitioning between an organism's lipids and its environment (i.e., water, soil/sediment, or air) are widely accepted as the major mechanisms accounting for high but often variable concentrations of a broad spectrum of nonpolar organic chemicals in organisms. Employing a mimetic chemistry approach (i.e., use of processes in simple or uniform media to mimic complex biological systems), scientists at the US Geological Survey's Columbia Environmental Research Center (CERC) have developed a passive, integrative sampler that simulates hydrophobic chemical bioconcentration [2–7]. The uncertainty of estimating exposure concentrations from tissue concentrations in biomonitoring organisms is thereby avoided. This sampler, the semipermeable membrane device (SPMD) operates passively, and integratively samples only the readily bioavailable (dissolved and vapor phase) portion of hydrophobic contaminants [2,5].

The SPMD consists of a thin film of the neutral lipid, triolein, sealed inside a layflat, thin-walled tube of nonporous (i.e., no fixed pores; only transient thermally mediated cavities) low-density polyethylene (LDPE). The diameters of the transient cavities range up to about 10 Å, effectively precluding sampling of any contaminant molecules associated with dissolved organic matter or particulates. This cavity size limitation has an important consequence: in general only dissolved chemicals with molecular masses less than about 600 are sampled by SPMDs [8], and this molecular mass limitation is very similar to that imposed by the pores of biomembranes [9].

At saturation, the capacity of the SPMD for a hydrophobic chemical [2] is generally, related to the compound's octanol–water partition coefficient (K_{OW}) i.e., the higher a compound's K_{OW}, the greater the capacity of the SPMD for that chemical. Due to the very high concentration factors attained, even ultra-trace levels of hydrophobic contaminants are

readily analyzed resulting in improved exposure assessment [4].

In this paper we present a summary of considerations for effectively and efficiently using SPMDs to monitor environmental contaminants.

2. Project considerations

2.1. Applicability of semipermeable membrane devices

The primary question to be addressed before applying the SPMD samplers, relates to the suitability of the sampling technique for the chemicals of interest. Standard SPMDs are designed to sequester and concentrate hydrophobic chemicals such as polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), etc. SPMDs are not designed to concentrate ionic species such as ionic metals, salts of organic acids, or very polar organic chemicals. Neutral organic chemicals that are hydrophobic (i.e., with $\log K_{OW}$ values ≥ 3) will be concentrated significantly above ambient levels. In reality, any compound with a $\log K_{OW} \geq 1$ will be concentrated by the SPMD, but for compounds with $\log K_{OW}$ values less than 3, there is no significant advantage in using SPMDs in preference to other sampling procedures.

SPMDs will, in general, concentrate all neutral hydrophobic chemicals having molecular masses <600 from water. No other sampling approach offers this broad a range of applicability with respect to chemical class or molecular mass. Examples of environmental contaminants that have been effectively sampled by SPMDs include; PAHs, PCBs, OCPs, polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), alkylated phenols (e.g., nonylphenol), moderately polar organophosphate insecticides (e.g., diazinon, chlorpyrifos), pyrethroid insecticides, neutral organometallic compounds, and certain heterocyclic aromatic compounds. Other neutral chemicals that have been found in dialysates from field-deployed SPMDs include polybrominated diphenyl ethers, trifluralin, pendimethalin, etc., [3,10].

In general, SPMDs can be advantageously used in the following broad areas of application: (1) determination of pollution point sources; (2) estimation of time-weighted average dissolved or vapor phase chemical concentrations; (3) in situ mimetic concentration of bioavailable chemicals for bioindicator or immunoassay tests; (4) contaminant sequestration in toxicity identification and evaluation (TIE) procedures; and (5) estimation of organisms' exposure and bioconcentration potential. It is possible to deploy SPMDs in a wide variety of situations including sediments/soils, sediment–water interfaces, flowing and quiescent aquatic systems, and atmospheric systems. To ensure that the SPMDs are employed successfully, a number of SPMD-specific concerns must be addressed, and a general understanding of the principles of operation of SPMDs is necessary. A brief summary of the latter discussion point is presented below.

As a first approximation, from a mechanistic viewpoint, hydrophobic chemicals encounter the LDPE membrane of the SPMD, dissolve into the membrane, diffuse through the membrane to the interior surface of the membrane, and finally dissolve into the sequestration phase, i.e., the triolein. A more detailed description of the basic theory relating to the uptake of chemicals by SPMDs has been published, as have several mathematical models for estimating ambient water concentrations from analyte concentrations in SPMDs [2,11]. Briefly, the SPMD sampling rates have been demonstrated to be independent of water concentrations and salinity. Information about sampling rates for PAHs [12], OCs [13], and PCBs [14] are available. Also, the amounts of accumulated chemicals have been determined to be proportional to ambient concentrations of dissolved chemicals. As would be expected, sampling rates generally increase with temperature and $\log K_{OW}$ (i.e., sampling rates increase with increasing hydrophobicity) up to a $\log K_{OW}$ of about 6. A decrease in sampling rates is observed for compounds with $\log K_{OW}$ values >6; a similar phenomenon is observed in bioconcentration rates in fish [15]. Current velocity–turbulence and biofouling can also affect sampling rates. A more detailed discussion of the factors affecting chemical uptake by SPMDs is beyond the scope of this paper, but is available elsewhere [16].

Potential pitfalls that specifically relate to the

SPMD sampling technique include improper handling, storage, and transportation to and from the field. Also, during SPMD handling and subsequent dialysate fractionation and enrichment procedures, care must be taken to minimize analytical interferences related to the SPMD membrane and lipid. These topics are briefly addressed below.

2.2. Standard semipermeable membrane devices

The standard, commercially available SPMD, usually consists of a piece of 106 cm by 2.5 cm wide layflat LDPE tube having a wall thickness of 75–90 μm, that contains 1 ml of ≥95% pure triolein. The surface area–volume ratio (SA–V) is about 80 cm^2 per ml of SPMD (membrane plus triolein) or about 460 cm^2 per ml of triolein. The device weighs approximately 4.50 g and is about 20% triolein (i.e., 20% lipid). Any length SPMD with a SA–V ratio of about 460 cm^2 per ml of triolein, an approximate 0.2 lipid-to-membrane mass ratio, and a 75–90 μm wall thickness is considered to be (or to be proportional to, e.g., 4-fold) a ''standard'' SPMD. Use of standard SPMDs ensures that existing SPMD sampling rate calibration data are applicable for estimating ambient water concentrations of analytes.

2.3. Handling precautions

Because SPMDs can sequester a wide variety of chemicals, care must be taken to prevent their inadvertent contamination. Proper handling and processing of SPMDs includes logical precautions and adherence to general good laboratory practices. Until deployment, SPMDs must be stored in the vapor-tight cans provided by the supplier, and ideally should be maintained frozen (≤−15°C) until deployed.

The samplers are used in a broad array of situations, but the following general considerations apply to all deployment scenarios. SPMDs exposed to air will concentrate vapor-phase chemicals [5]. For example, based on phenanthrene's aqueous sampling rate of about 3 l per day for a standard SPMD, we estimate a phenanthrene vapor-phase sampling rate of about 2 m^2 per day (i.e., the phenanthrene vapors in 1.4 l of air would be sampled each minute that an SPMD is exposed to the atmosphere). Because there are many sources of vapor phase contaminants including engine exhausts, gasoline, diesel fuel, oils, tars, paints, solvents, cigarette smoke, etc., it is critical (for aquatic deployment and during subsequent processing of the SPMDs) that the samplers be open to the atmosphere for only as long as necessary. Consequently, during deployment in and retrieval from aquatic systems, it is important to open the sealed metal containers only after all preparations for deployment or retrieval of the samplers have been completed. Also, the deployment area should be examined for potential contamination sources and exposure to these sources minimized. If surficial waterborne chemicals such as sheens of oil, gasoline, etc., are present, care must be exercised to prevent coating the samplers during deployment in the water. Hand lotions, cologne, perfume, powered gloves, etc., must not be used because these materials contain chemicals that can be sequestered by the SPMDs. Finally, after retrieval, the samplers must be placed back into the airtight metal containers and frozen (≤−15°C) as soon as possible if storage before shipment to the processing laboratory is required. The SPMD containers should be shipped to the processing laboratory frozen on dry ice or cooled by blue ice or similar coolants.

2.4. Deployment method

SPMDs have been deployed in many types of protective housings [3,4,8]. We have also found the commercially available deployment hardware (i.e., from Environmental Sampling Technologies) convenient and easy to use. Certain guidelines should be used in the construction of any SPMD deployment device. Metal surfaces (stainless steel is preferred) must be free of cutting oils or other potential interferences. Use of plastic components should be minimized due to the possible presence of leachable organic compounds. Hardware must be designed so as to minimize abrasion of the membrane, especially in turbulent environments. Because flow-rates can influence sampling rates, some buffering of external flow is desirable so long as adequate water exchange rates are maintained. SPMDs should be arranged to ensure maximum exposure of membrane surface. Certain contaminants (e.g., PAHs) are vulnerable to photodegradation; therefore deployments in low tur-

bidity waters may require shading the SPMDs. The apparatus must be adequately tethered, and perhaps adequately camouflaged to prevent loss. Also, for deployments at the sediment water interface, care must be exercised to minimize ''silting in''.

2.5. Deployment duration and environmental variables

Due to the integrative nature of the sampling process, SPMDs can be deployed for sampling intervals ranging from days to months depending on the expected levels of contaminants. In general, we have found a deployment of 14 to 30 days sufficient to sequester quantifiable levels of most environmentally relevant hydrophobic contaminants. However, selection of an appropriate interval for integratively sampling via SPMDs should take into account several factors. Among these are the types of analytes and the analytical sensitivity (i.e., method detection limits and method quantitation limits) required, the time resolution needed for defining changes in waterborne chemical concentrations, and environmental variables (e.g., flow-rate, temperature, expected level of biofouling, potential for vandalism or other damage to SPMDs, etc.).

Because environmental variables affect the SPMD uptake of all types of chemicals, it is very important to record as much data as possible regarding each deployment site and the field conditions during deployment and retrieval. For multiple site deployments involving relational comparisons, investigators should select sites with similar flow regimes. Temperatures (at a minimum, at the beginning and end of SPMD exposure), visual assessment of the extent of biofouling (e.g., light, medium, heavy, none), and an estimation of flow-rates should be noted and recorded.

2.6. Permeability reference compounds

Recent research indicates that the uptake rates of many analytes by SPMDs can be influenced somewhat by flow-rates during aquatic exposures [16]. While it is beyond the scope of this presentation, a detailed discussion of this topic and of the use of permeation reference compounds (PRCs) to provide an overall correction factor for variations in SPMD uptake rates for analytes is available [16]. PRCs are analytically non-interfering compounds, such as perdeuterated PAHs, with moderate to fairly high SPMD fugacity, that are added to SPMD lipid prior to deployment. The losses of the PRCs during the field exposure compared to their losses under controlled laboratory conditions are used to correct for the effects of variations of temperature, diffusion layer thickness, and degree of biofouling on SPMD sampling rates. We assume, when perdeuterated PAHs are used as PCRs, that the native and perdeuterated forms of the same compounds have identical uptake and loss rates. Because the direct use of laboratory SPMD calibration data to predict analyte concentrations in diverse field environments may not always provide the most accurate results (e.g., flow-rates are often significantly greater than those used in the sampling rate calibration studies), the use of PRCs is recommended for enhancing the utility of SPMD-derived data for calculating ambient concentrations of contaminants. The PRC concept is the subject of ongoing research at CERC.

3. Analysis of semipermeable membrane devices

3.1. Quality control

Perhaps the single most important design consideration in any SPMD deployment and sample analysis project is the quality control (QC) parameters necessary to ensure data of the highest quality. At a minimum, QC samples must address sampler contamination during deployment and retrieval, and residue recovery during dialytic recovery, and fractionation and enrichment procedures. The exact level of QC effort appropriate for a study should be defined during the development of the experimental design and data quality objective phase of a project. The following are representative of basic QC parameters and should not be viewed as all encompassing.

Field blank SPMDs (a minimum of one for each field deployment site in aquatic systems) must accompany the samplers during transport, deployment, and retrieval. Cans containing these field blanks are opened during deployment of the sampler arrays, are subsequently resealed and stored frozen at $\leq -15^{\circ}C$ until retrieval of the exposed SPMDs when they are

again exposed to the atmosphere during sampler retrieval. Such field blanks account for the contamination of the SPMDs by airborne chemicals. They are processed and analyzed exactly as deployed SPMDs.

For air sampling deployments, trip blanks are used. These trip blanks consist of SPMDs sealed in airtight metal cans that accompany the deployed SPMDs during transport to the deployment sites and upon retrieval of the deployed samplers to the processing laboratory. The cans containing the trip blanks are never opened to the atmosphere. These trip-blank SPMDs account for potential interferences introduced during transport of the samplers.

Similarly, laboratory SPMD controls (at least one per sample set) are included in the QC assessment. These controls consist of freshly prepared SPMDs that are subjected to the analytical scheme to account for contributions of the SPMD membrane and sequestration phase to the totality of residues found in the field-deployed SPMDs. SPMD controls (i.e., day zero SPMDs) can be prepared along with the SPMDs used in the deployment, and stored frozen (≤ -15°C) until the exposed SPMDs are analysed.

Reagent blanks (at least one per sample set) consisting of equivalent portions of all solvents used during the processing, enrichment, and analysis of SPMD samples, are carried through the entire analytical sequence as if they were samples. Such blanks provide information regarding the laboratory background associated with the entire analytical process.

Analytical recoveries for known analytes are determined by fortifying the triolein of non-exposed SPMDs with appropriate levels of the analytes. Generally, such SPMDs are spiked with chemicals at levels equivalent to the midpoint of the appropriate calibration curve. Recoveries through the analytical procedures employed at CERC are generally $>75\%$, with good precision (i.e., $\leq 20\%$ RSD). The RSDs for the analysis of replicate samples (i.e., SPMDs deployed at the same sites and treated identically) are often $<10\%$. In general, QC samples represent 20 to 30% of a sample set. DeVita and Crunkilton [17] have presented an independent assessment of the performance of SPMDs as related to QC parameters and comparison to selected US Environmental Protection Agency (EPA) methods that can be viewed as a supplement to this overview of quality control considerations.

3.2. Sample processing and residue enrichment

Recovery of sequestered chemicals from field-deployed SPMDs (and the subsequent analyte fractionation, enrichment, and analysis) has been described in detail [3–8]. In summary, processing of the SPMDs generally involves the following steps: (1) removal of exterior surficial periphyton and debris; (2) organic solvent dialysis; (3) size-exclusion chromatography (SEC); and (4) chemical class-specific fractionation using Florisil, silica gel and/or alumina sorption chromatography. Reversed-phase chromatography can also be applied for appropriate chemical classes [18]. Detection and quantitation of sequestered contaminants can be accomplished using techniques such as gas chromatography (GC) with a variety of detectors, GC–mass spectrometry, high-performance liquid chromatography (HPLC), etc. Fig. 1 is a generalized representation of the analytical scheme.

Following removal of the surficial biofouling and debris using hexane rinses, gentle brushing, and immersion in dilute acid, the surfaces of the SPMDs are rinsed with water, acetone, then isopropanol. The cleaned SPMDs are subsequently dialyzed in hexane (125 ml of hexane per standard SPMD) for 18 h at 18°C, followed by a second dialytic period (with 125 ml of fresh hexane) of 6 h. The two dialysates are combined, reduced in volume to about 1 ml and subjected to SEC cleanup. The SEC apparatus includes an HPLC solvent delivery system and a Phenogel SEC column [250×22.5 mm I.D., 10-μm particles (10-nm pore size), Phenomonex Torrance, CA, USA] and either 100% dichloromethane or 2% methanol in dichloromethane as the mobile phase. Our standard protocol limits sample loading on the SEC system to a maximum of the (combined) dialysates from one SPMD per 1-ml injection. The SEC system is calibrated on a daily basis using a solution containing diethylhexylphthalate (DEHP), biphenyl, naphthalene, coronene, and elemental sulfur. The five calibration materials elute from the SEC in the above order. The chromatographic run time is set to be sufficiently long to allow sulfur to elute from the column prior to injection of the next sample. The ‘‘collect’’ fraction is initiated at the point 70% of the retention time between the apex of the DEHP peak and the apex of the biphenyl peak and terminated prior to the onset of the sulfur peak.

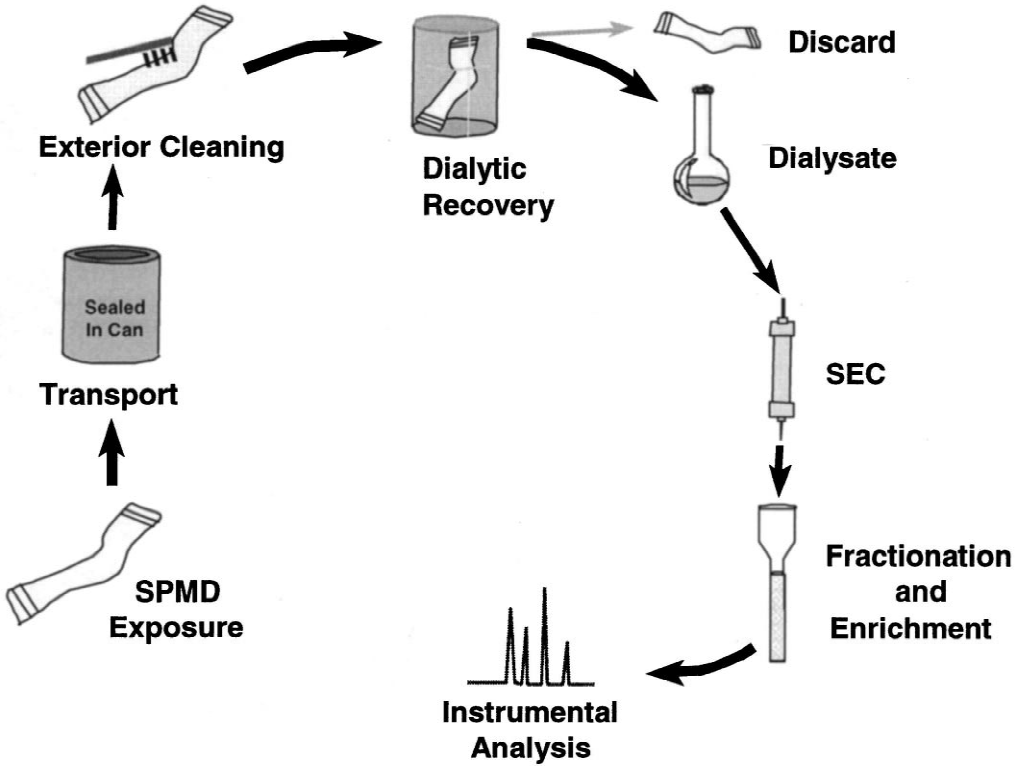

Fig. 1. Key aspects of SPMD sample processing and analysis.

This effectively eliminates SPMD-sequestered elemental sulfur and coextracted materials. Components eluted from the SEC column before the ''collect'' window and prior to the next sample injection are dumped to waste.

Following SEC, sample extracts can be fractionated and enriched using a variety of chromatographic techniques. As an example, sample extracts (i.e., eluates collected from SEC) to be analyzed by GC at CERC are generally divided into two equal portions. One portion, destined for analysis for PAHs, is treated using a tri-adsorbent column consisting of, from top to bottom; 3 g phosphoric acid impregnated silica gel, 3 g potassium silicate (KS), and 3 g silica gel [18] in a 1-cm I.D. glass column. To recover the PAHs, the three tandem sorbents are eluted with 50 ml of 4% methyl *tert*.-butyl ether in hexane. Following solvent exchange into hexane and volume reduction to 1 ml, the eluates from the tri-adsorbent column are analyzed by capillary GC with photoionization detection (PID). The other half of the eluates collected from SEC are applied to 5 g of Florisil contained in a 1-cm I.D. glass column. The analytes (PCBs, OCPs, and various other contaminants of potential analytical interest) are eluted with 60 ml of 25% hexane in methyl *tert*.-butyl ether [3,7,18]. After volume reduction and exchange into hexane, the concentrated eluates from Florisil are applied to 5 g of silica gel contained in a 1-cm I.D. glass column. The first fraction (SG-1), produced with 46 ml of hexane, contains PCBs and a few of the least polar OCPs. The second fraction (SG-2), produced with 55 ml of 40% methyl *tert*.-butyl ether in hexane, contains more polar ones. Both fractions are reduced in volume to 1 ml (or a lesser volume depending on the amounts of contaminant residues present) and are subsequently analyzed by capillary GC with electron-capture detection (ECD).

3.3. Instrumental analysis

The enriched fractions, and in some situations, the SPMD dialysates immediately after SEC cleanup, can be analyzed using a wide variety of instrumental

techniques, including GC, HPLC, and GC–MS. Any analytical technique used to analyze other environmental matrices for organic contaminants can be applied to the analysis of chemicals in SPMDs. The types and levels of chemicals expected to be present in the sample extracts will dictate the analytical instrumentation to be used.

The majority of analyses involving SPMD-derived samples at CERC have used GC (equipped with ECD and PID), and the methods have been reported in detail [2–8]. Typical examples are presented here for illustrative purposes. For nearly all analyses, 1.0 μl of purified sample extract is injected, using the ''cool, on-column'' technique, with hydrogen as the carrier gas. The most current analytical methods follow: analysis of PAHs is performed using a Hewlett–Packard GC System (Hewlett-Packard, Palo Alto, CA, USA) equipped with a 30 m×0.25 mm I.D. DB-5 capillary column (J&W Scientific, Folsom, CA, USA) and the following temperature program: inject at 60°C; hold for 2 min; then ramp at 4°C/min to 110°C; hold for 5 min; followed by 3°C/min ramp to 200°C; hold at 200°C for 10 min; then a 4°C/min ramp to 310°C. The PID system (HNU, Newton, MA, USA) has a 9.5-eV lamp operating at 270°C. The six-point standard curve is constructed using a 32-fold concentration range of the priority pollutant PAHs, with perdeuterated *p*-terphenyl as the instrumental internal standard.

Analysis of the SG-1 fraction (i.e., PCBs and non-polar OCPs) is performed using a DB-5 capillary (described earlier) with the following temperature program: inject at 90°C; then ramp at 15°C/min to 165°C; hold for 2 min; ramp at 3°C/min to 260°C; then ramp at 10°C/min to 320°C; and hold for 1 min. The ECD system is maintained at 330°C. The quantitation of total PCBs is performed using a six-point calibration curve employing solutions containing a 1:1:1:1 mixture of Aroclor 1242,1248,1254, and 1260 with octachloronaphthalene (OCN) as the instrumental internal standard. The PCB standards span a 40-fold concentration range, and the standards for the non-polar OCPs span an 80-fold range.

Analysis of the SG-2 fraction (OCPs is performed using a 30 m×0.25 mm DB-35MS capillary column (J&W Scientific) with the following temperature program: inject at 90°C; then ramp at 15°C/min to 180°C; hold for 2 min; then ramp at 5°C/min to 260°C; hold for 7 min; then 10°C/min to 320°C and hold for 1 min. The ECD system is maintained at 330°C. Quantitation of the analytes is performed using a six-point calibration curve with OCN as the internal standard. The OCP standards cover an 80-fold concentration range.

Mass spectrometric analyses of enriched sample extracts are conducted at the CERC using a Finnigan Voyager GC–MS system (Thermoquest, Manchester, UK) or a Micromass VG-70S high resolution GC–MS system (Fisions Instruments, Manchester, UK). Enriched SPMD extracts can be analyzed by GC–MS using any ionization technique including, electron impact [4], positive or negative chemical ionization [10], etc., in both high- and low-resolution modes.

When the levels of interferences for targeted analytes are low [4], dialysates from individual SPMDs can be combined to create composite samples in order to enhance the detection and quantitation of the contaminants of interest. Composite samples provide increased contaminant mass thereby allowing identification of unknown contaminants or facilitating use of the sequestered contaminant mixtures in toxicity identification evaluation (TIE) procedures. There are certain limitations to this approach, however, which are addressed in the following section.

3.4. Semipermeable membrane device-specific interferences

While the extracts of SPMDs are generally less difficult to purify than are extracts of tissue or sediment, certain specific interferences can be problematic. 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 and together are present at <50 mg per standard SPMD. Another potential interference encountered in environmentally exposed SPMDs is elemental sulfur. The polyethylene waxes and elemental sulfur are effectively and efficiently removed using the high resolution SEC procedure.

Unfortunately, oleic acid is generally present in the post-SEC-treated sample extracts, and is the

source of significant interference when the SPMD extract is evaluated by GC–MS. Fortunately, oleic acid can be effectively removed by using a small column of KS (5 g) and eluting with 50 ml of a mixture of hexane–dichloromethane (1:1, v/v). This simple procedure completely removes the residual oleic acid, facilitating the chromatographic analysis of the fully recovered neutral analytes. Another approach to remove residual oleic acid is to treat the extract by passing the post-SEC extract through a Florisil column as described in Section 3.2. We are currently characterizing both of these procedures to gain a better understanding of the variety of chemicals recoverable using each approach.

The removal of residual methyl oleate is more problematic. This material is generally a problem when SPMD field blanks, SPMD spikes, trip blanks, or day zero SPMDs are analyzed, since a large portion of this material (for field-deployed SPMDs) tends to diffuse to the SPMD membrane surface and be lost to the environment. While much methyl oleate is removed during the SEC treatment, a significant portion remains in the sample extract. Because the methyl oleate contains a polar functional group, it is found in our SG-2 fraction rather than SG-l. It causes little or no problem when the analysis is performed using GC–ECD or PID, however, it interferes with full scan GC–MS analyses. Complete removal of residual methyl oleate has not been achieved except when we have resorted to destructive techniques such as hydrolysis or cleanup by sulfuric acid impregnated silica gel. Obviously, many analytes of interest will not survive such drastic procedures. We are currently investigating modification of the SEC procedure to more effectively remove methyl oleate and the possibility of treating the triolein before preparation of SPMDs to remove both the oleic acid and methyl oleate before SPMD fabrication. The results of our research to improve SPMDs will be provided to the commercial vendor, Environmental Sampling Technologies.

3.5. Bioassay of semipermeable membrane device extracts

In addition to instrumental methods of analysis, the complex mixtures of chemicals sequestered by SPMDs can be examined by using a suite of bioindicator tests. These tests include, but are not limited to, determination of liver enzyme induction, inhibition of acetylcholinesterase activity, estrogenic activity, and the Microtox, Mutatox systems, etc. This aspect of the SPMD technology offers many avenues of investigation, all potentially providing information relating to the toxicological relevance of chemicals present in the environmental matrices sampled. Because most bioconcentratable contaminants are present in aquatic environments at trace to ultra-trace levels, a preconcentration method is required to permit the effective use of rapid bioindicator tests and immunoassay procedures. Several advantages of SPMDs over other potential preconcentration methods include: its mimetic design; that only readily bioavailable residues are sequestered; its statistical advantage of high reproducibility relative to biomonitors. Examples of the incorporation of bioassay assessment of environmentally relevant chemical mixtures have been described [7,4,16], and research continues in this aspect of the SPMD technology [18].

4. Samples from field exposures

The judicious choice of the appropriate sample processing and analysis techniques results in clean blanks and convenient chemical class fractions. Examples are presented in Figs. 2–6. Figs. 2–5 represent the SPMD control, the PAH fraction, the PCB fraction (SG- I) and the OCP fraction (SG-2) from SPMDs deployed for 29 days in the Nogales Wash, Nogales, AZ, USA to assess pollution in the Santa Cruz River.

Obviously, this source of water to the Santa Cruz River is potentially impacted by a wide variety of contaminants, and undoubtedly others not revealed by these analyses. The results of this research will be presented in detail elsewhere [19]. However, it is instructive to note that the GC–ECD chromatogram of the SPMD control is clean (the two peaks in the chromatogram at about 15.5 and 41 min are retention markers) and that the three fractions of the field-exposed SPMDs are representative of successful chemical class fractionation and analysis (example component peaks are identified in the figures).

Fig. 6 presents the GC–MS scans of SPMD

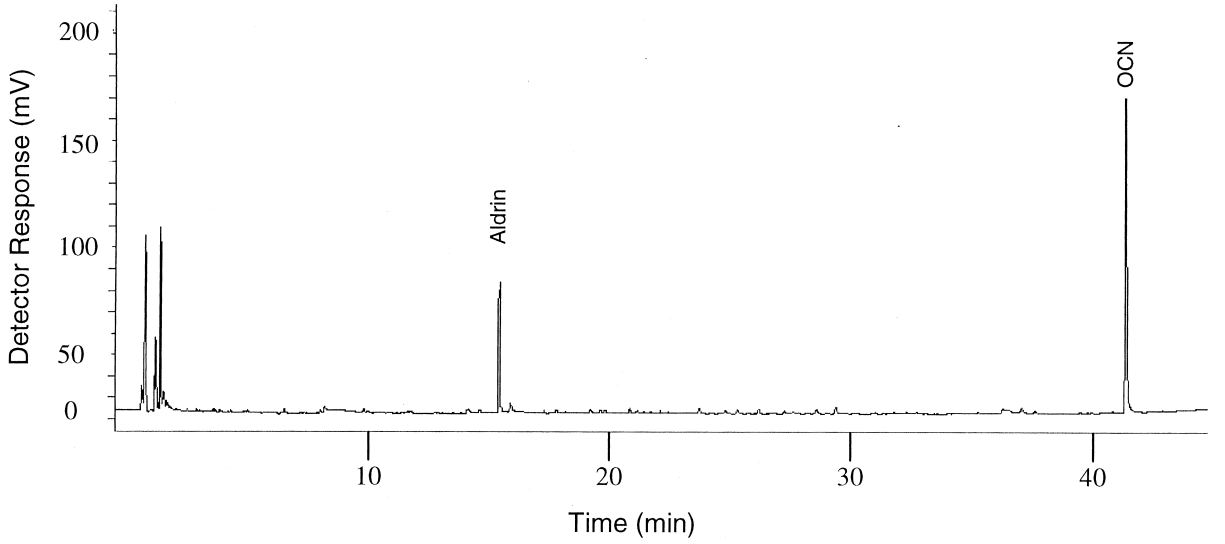

Fig. 2. Electron-capture detector response of SPMD control sample extract.

extracts analyzed after SEC only and after SEC then treatment with KS. The complete removal of the residual oleic acid allowed the determination of the priority pollutant PAHs in the samples.

4.1. Estimation of water concentrations

A detailed discussion of the models used in estimating ambient water concentrations from the concentrations in SPMDs has been presented [2], as have applications of these models to estimating waterborne concentrations of a variety of pollutants [3,4,6,7]. Briefly, the analyte sampling rate (R_S) or the uptake rate constant (k_1) for a given analyte is determined from laboratory or field exposures conducted under controlled conditions. Because field-

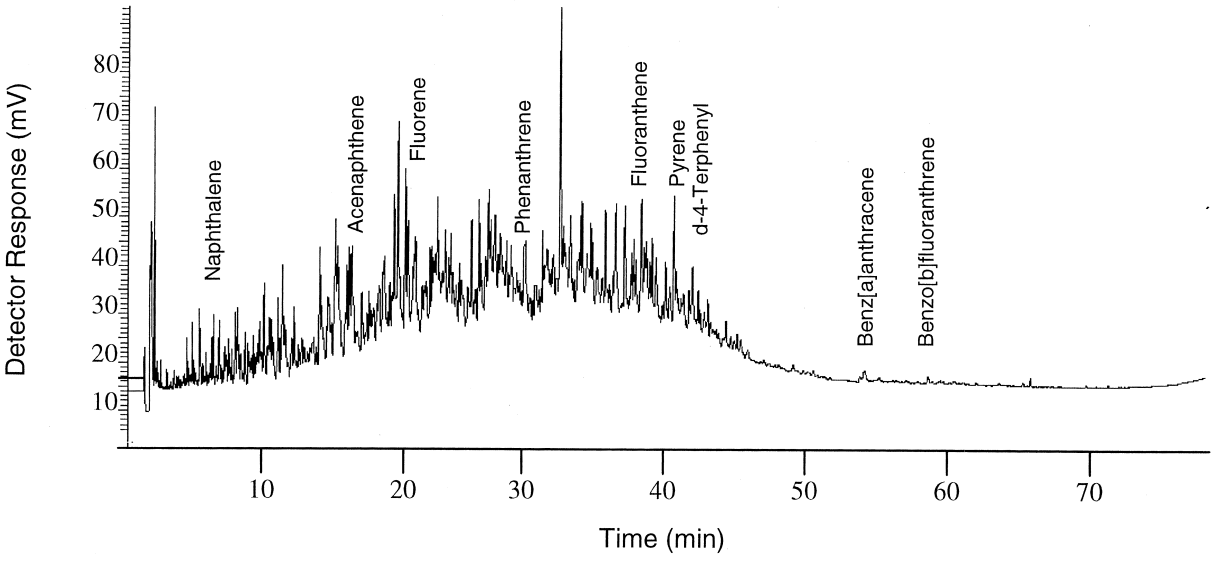

Fig. 3. Photoionization detector response (sample extract, 1-ml final volume) of PAHs from a composite sample of two standard SPMDs deployed in Nogales wash, Nogales, AZ, USA.

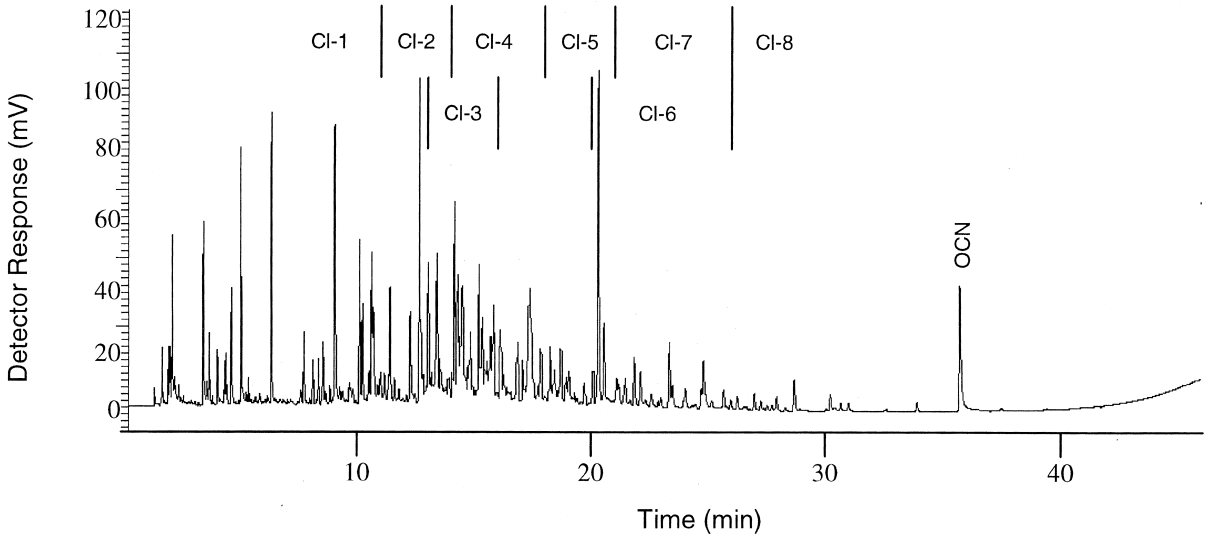

Fig. 4. Electron-capture detector response (sample extract, one ml final volume) of PCBs from a composite sample of two standard SPMDs deployed in Nogales wash, Nogales, AZ, USA.

deployed SPMDs often become biofouled, the potential impedance to analyte uptake due to aufwuchs layers needs to be accounted for, thus the environmental sampling rate (R_{SC}) is given by

$$R_{SC} = R_S F_I \quad (1)$$

where F_I is 1 minus the fractional reduction in uptake flux or sampling rate due to fouling. A visual examination of the deployed SPMDs is employed to estimate the extent of biofouling prior to initiation of sample processing procedures. Typically, for little or no biofouling, no correction is made. For mild

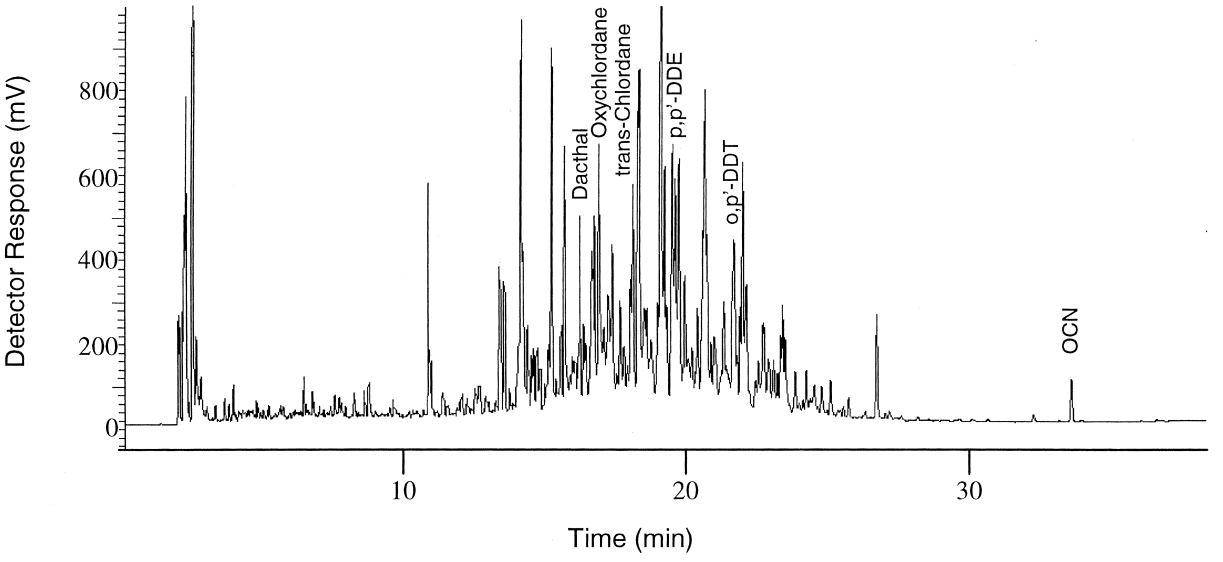

Fig. 5. Electron-capture detector response (sample extract, one ml final volume) of OCPs from a composite sample of two standard SPMDs deployed in Nogales wash, Nogales, AZ, USA.

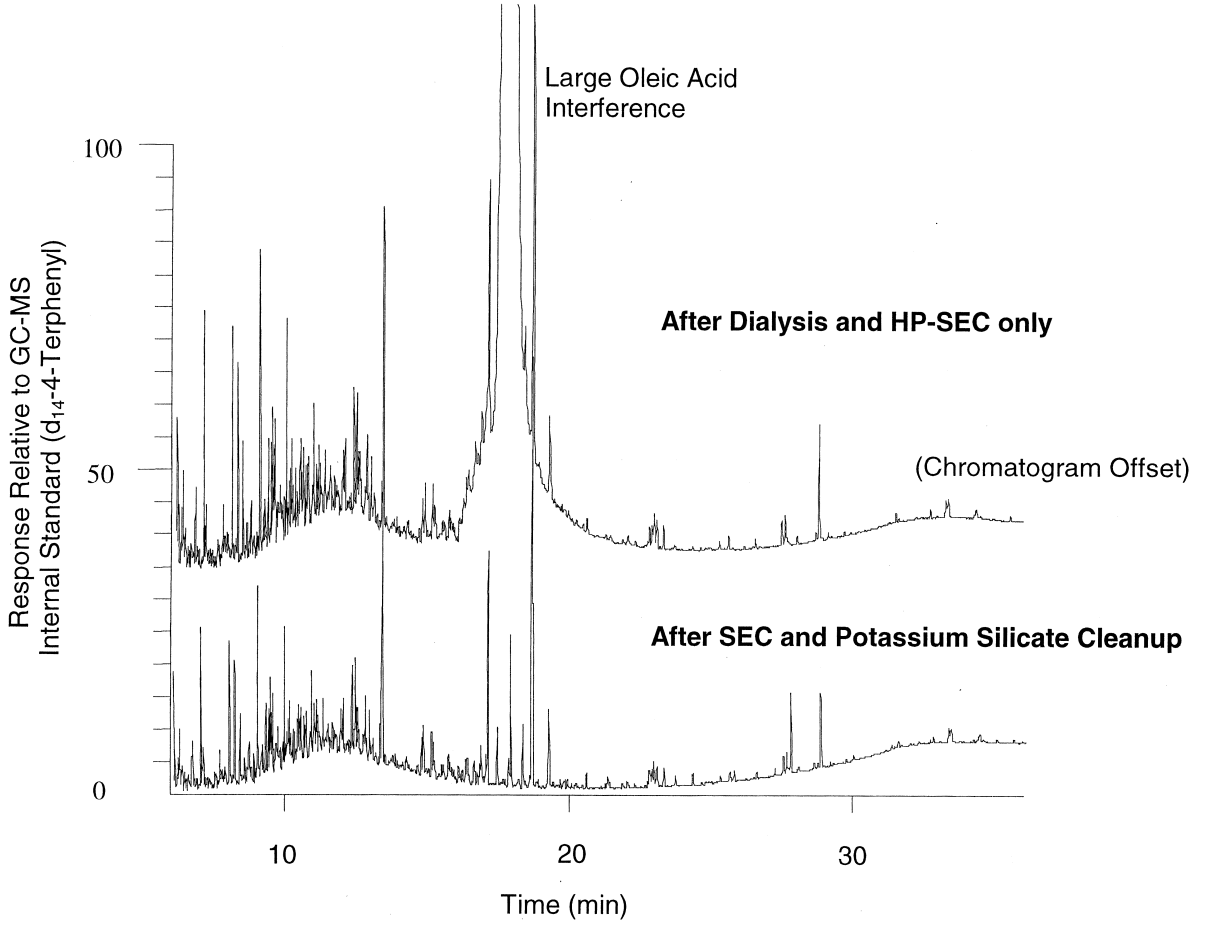

Fig. 6. GC–MS scan of a composite sample of three standard SPMDs (sample extract, 1-ml final volume) before and after removal of oleic acid.

biofouling, uptake impedance of 10% is assumed, for medium biofouling 30%, and for heavily biofouled SPMDs 50% impedance is assumed. These values are based on SPMD flow-through exposure studies conducted at CERC using heavily biofouled field deployed SPMDs and freshly prepared SPMDs [20].

Huckins et al. [2] derived several linear models used to calculate waterborne concentrations of very hydrophobic contaminants, including Eq. (2)

$$C_W = C_L V_L / R_{RSC} t \quad (2)$$

where C_W is the concentration of the analyte in water, C_L is the concentration of the analyte in the lipid, t is the exposure time in days, and V_L is the volume of lipid. However, since analytes present in the membrane are also recovered during the dialytic procedure, Eq. (2) can be rewritten as

$$C_W = C_{SPMD} M_{SPMD} / R_{SC} \quad (3)$$

where C_{SPMD} is defined as the concentration of the individual analyte in the SPMD and M_{SPMD} is the mass of the SPMD. R_{SC} is the corrected sampling rate in litres per day. Using the above approach and available R_{SC} values [12–14], the bioavailable waterborne concentrations of typical hydrophobic contaminants have been calculated for many field locations [3,4,6,7,18,19].

5. Conclusions

The SPMD technology is increasingly being applied to define the presence, concentrations, and potential effects of complex mixtures of chemical. In general, the mixtures of contaminants sequestered by SPMDs are amenable to analysis by any technique applicable to determining the identities and concentrations of those particular analytes in other environmental matrices. The judicious choice of techniques for sample processing, residue enrichment, and analysis has been demonstrated to provide data widely applicable to defining the consequences of pollution of a wide variety of environments. Problems stemming from SPMD-specific analytical interferences have been discussed and methods for minimizing or eliminating these materials have been developed. In summary, the SPMD technology is the subject of continuing research by environmental scientists worldwide and the application of this approach is expected to continue to expand.

Acknowledgements

We gratefully acknowledge the financial support of the US Fish and Wildlife Service, the US Bureau of Reclamation, the Department of Defence, and the Environmental Protection Agency for portions of this Research. We also thank David Alvarez and Randal Clark for technical assistance during the preparation of this manuscript.

References

[1] T. Colborn, F.S. vom Sall, A.M. Soto, Environ. Health Perspect. 101 (1993) 378.
[2] J.N. Huckins, G.K. Manuweera, J.D. Petty, D. MacKay, J.A. Lebo, Environ. Sci. Technol. 27 (1993) 2489.
[3] J.D. Petty, J.N. Huckins, C.E. Orazio, J.A. Lebo, B.C. Poulton, R.W. Gale et al., Environ. Sci. Technol. 29 (1995) 2561.
[4] J.A. Lebo, R.W. Gale, J.D. Petty, D.E. Tillitt, J.N. Huckins, J.C. Meadows et al., Environ. Sci. Technol. 29 (1995) 2886.
[5] J.D. Petty, J.N. Huckins, J.L. Zajicek, Chemosphere 27 (1993) 1609.
[6] J.A. Lebo, J.L. Zajicek, C.E. Orazio, J. D Petty, J.N. Huckins, Polyclic Arom. Comp. 8 (1996) 53.
[7] J.D. Petty, B.C. Poulton, C.S. Charbonneau, J.N. Huckins, S.B. Jones, J.T. Cameron et al., Environ. Sci. Technol. 32 (1998) 837.
[8] G.S. Ellis, J.N. Huckins, C.E. Rostad, C.E. Schmitt, J.D. Petty, J.D. MacCarthy, Environ. Toxicol. Chem. 14 (1995) 1875.
[9] A. Opperhuizen, E.W. Velde, F.A.P. Gobas, D.A.K. Leim, J.M.D. Steen, Chemosphere 14 (1985) 1871.
[10] T. Lieker, SGS National Water Quality Laboratory, Denver, CO, USA, personal communication.
[11] R.W. Gale, Environ. Sci. Technol. 32 (1998) 2292.
[12] J.N. Huckins, J.D. Petty, C.E. Orazio, J.A. Lebo, R.C. Clark, V.L. Gibson et al., Environ. Sci. Technol. 33 (1999) 3918.
[13] J.D. Petty, J.N. Huckins, C.E. Orazio, J.A. Lebo, R.C. Clark, V.L. Gibson, Evaluation of the Semipermeable Membrane Device (SPMD) as a Passive In Situ Concentrator of Military Organic Chemicals in Water, Final Report, US Army Medical Research and Material Command, Fort Detrick, MD, USA, approved for release, 11 September, 1997.
[14] J.C. Meadows, K.R. Echols, J.N. Huckins, F.A. Borsuk, R.F. Carline, D.E. Tillitt, Environ. Sci. Technol. 32 (1998) 1847.
[15] J. McKim, P. Schmieder, G. Veith, Toxicol. Appl. Pharmacol. 77 (1985) 1.
[16] J.N. Huckins, J.D. Petty, H.F. Prest, C.E. Orazio, R.C. Clark, A Guide for the Use of Semipermeable Membrane Devices (SPMDs) as Samplers of Waterborne Hydrophobic Organic chemicals, American Petroleum Institute, Washington DC, 2000, in press.
[17] W.M. De Vita, R.L. Crunkilton, in: E.E. Little, A.J. DeLonay, B.M. Greenburg (Eds.), Quality Control Associated with use of Semipermeable Membrane Devices, Environmental Toxicology and Risk Assessment, ASTM STP 1333, Vol. 7, American Society for Testing and Materials, 1998.
[18] K.S. Williamson, Ph.D. Thesis, University of Missouri-Columbia, Columbia, MO, USA, 1996.
[19] J.D. Petty, S.B. Jones, J.N. Huckins, W.L. Cranor, J.T. Parris, T.B. McTague et al., Chemosphere (2000) in press.
[20] J.N. Huckins, J.D. Petty, J.A. Lebo, C.E. Orazio, H.F. Prest, D.E. Tillitt et al., in: G.K. Ostrander (Ed.), Techniques in Aquatic Toxicology, CRC/Lewis Publishers, Boca Raton, FL, USA, 1996, p. 625.