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Review

Review of the background and application of triolein-containing semipermeable membrane devices in aquatic environmental study

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Abstract

This paper briefly reviews research on passive in situ samplers for aquatic environments but focuses on the development and application of the triolein-containing semipermeable membrane device in aquatic environmental monitoring. Special attention is paid to the calibration of the devices, quality control issues, and its potential uses in environmental assessments of aquatic contaminants. Also, the suitability of the technique for incorporation with selected bioassays is examined. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Review; Triolein-semipermeable membrane device; Calibration; QA/QC; Applications

1. Introduction

Chemicals listed by the US EPA as priority pollutants contribute little to broad environmental indices such as BOD, COD or TOC. Never the less, these contaminants can pose a major threat to ecosystem and human health. For example, many substances that cause cancer belong to persistent organic contaminants (POPs). In 1999, the China EPA designated 40-organic contaminants from US EPA's list of 2347 toxic chemicals as priority pollutants for water quality standards.

Nearly all-environmental samples require some type of preparation before analysis. Conventional solid phase extraction (SPE), such as XAD resin sorption, and liquid–liquid extraction are among the oldest and most frequently used sample preparation methods. However, use of these methods for monitoring ultra trace to trace-level (e.g. pg to ng/L) organic contaminants in water, may be problematic. More specifically, difficulties or limitations associated with the methods are often encountered when collecting and extracting large volumes of water needed for trace contaminant analysis. These include sampling and handling induced changes in some water quality parameters, and loss of analytes due to filtration,

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volatilization and sorption. Also, analysis of excised water reflects residue composition only at the moment of sampling and may fail to detect episodic contamination events (Huckins et al., 1990a, 1993). Therefore, the recent availability of SPE cartridges has facilitated the analysis of many environmental samples, but the method is generally more suitable for the analysis of samples with moderate (e.g. $\mu\text{g/L}$) to trace levels of target contaminants.

Because of the aforementioned difficulties in analyzing trace-level contaminants, the levels of POPs in water are often inferred from their equilibrium concentrations in the tissue of aquatic organisms. Weaknesses in this approach include possible metabolism and depuration of accumulated chemicals, prejudices in absorption, site-to-site variations in organism stress, and limited viability (Prest et al., 1995b), which affect equilibrium concentrations. Estimates of POP concentrations in water can also be made by measuring their concentrations in benthic sediments from rivers, lakes or seashores and then using equilibrium distribution coefficients (i.e. K_{oc} s) to derive levels of dissolved phase analytes (Gale et al., 1997). This approach is limited by the assumption of equilibrium between sediments and the water column, and the potential effects of organic carbon quality differences among sediments that are not accounted for in current equilibrium partition models.

Increasingly, the development of effective, economic and selective passive sampling techniques is becoming a widespread goal of environmental scientist. In particular there is a need for techniques, which fulfill the demands of monitoring trace or ultra-trace bioavailable organic contaminants in water and at the same time bridge the gaps between environmental analytical chemistry and ecotoxicology approaches. Among various passive sampling approaches for organic contaminants, the solid phase micro-extraction (SPME) fibers and semipermeable membrane devices (SPMDs) appear to show the most promise. SPME fibers are widely accepted as analytical tools for measuring semi-volatile contaminants (Pawliszyn, 1997), are very convenient to use, but are generally limited by small sample size/capacity.

Several passive samplers have been proposed based on the diffusion of hydrophobic substances from the water to membrane bags filled with lipophilic phases. Some of the early designs included dialysis bags made of regenerated cellulose tubing and polyethylene membrane bags filled with hexane (Sodergren, 1987, 1990; Johnson, 1991; Hasset et al., 1989). At about the same time, Zabik (1988) and Huckins (1988) evaluated polypropylene, polyvinyl chlorides, polyacetate, and silicone membranes for use in passive samplers. In other studies (Byrne and Aylott, 1980), vinyl chlorides, polyvinylidene fluoride, polytetrafluoro ethylene, acrylic copolymer and nylon membrane bags were used as semipermeable membranes for passive samplers. Also, polyethylene membranes were filled with XAD-4 and C_{18} , or common organic solvents such as 2,2,4-trimethylpentane, octanol, and hexane for environmental sampling (Zabik et al., 1992). Pekol and Cox (1995) described a system in which micellar Brij35 and Brij58 were used in combination with a cellulose ester dialysis membrane. The micellar media compared well with organic solvents as receivers for fugacity based membrane preconcentrators of hydrophobic compounds. In a comparative study (Macrae and Hall, 1998), triolein-containing semipermeable membrane device (triolein-SPMD), Tenax TA, and polyethylene tube dialysis (PTD) of sediment were used to estimate the available fraction of polycyclic aromatic hydrocarbons (PAHs) in marine sediment slurries. The results of this study suggested that PTD is useful for assessing chemical exposure from soils or sediments, while triolein-SPMD and Tenax TA are useful for estimation of the fraction of chemicals in sediments that would likely be biodegradable in reasonable length of time.

Recently a polar organic chemical integrative sampler (POCIS), consisting of a hydrophilic polyethersulfone membrane containing an admixture of a hyper-cross linked polystyrene-divinylbenzene SPE resin and S-X3 Biobeads coated with fine particles of dispersed Ambersorb[®] 1500, was designed (Alvarez et al., 2000). The polyethersulfone membrane was selected because of all the membranes studied; it exhibited the greatest up-

take of hydrophilic analytes and had the greatest membrane durability. Using POCIS samplers, linear uptake of polar analytes (e.g. atrazine) was observed through 28 days, and biofouling was minimal.

Besides SPME fibers, the most popular passive sampling configuration for aquatic environments is the triolein-containing SPMD developed by Huckins (1988) and Huckins et al. (1990a). Fig. 1 illustrates the principle of the triolein-SPMD. The following sections summarize the theory, practice, and applications of SPMDs as passive in situ samplers of aquatic environments.

2. Design and basis of triolein-SPMDs

2.1. Generic configuration

All triolein-SPMDs contain a thin film of lipid sealed within an additive free layflat polyethylene (LDPE) tube. LDPE employed in triolein-SPMDs is referred to as nonporous, although random

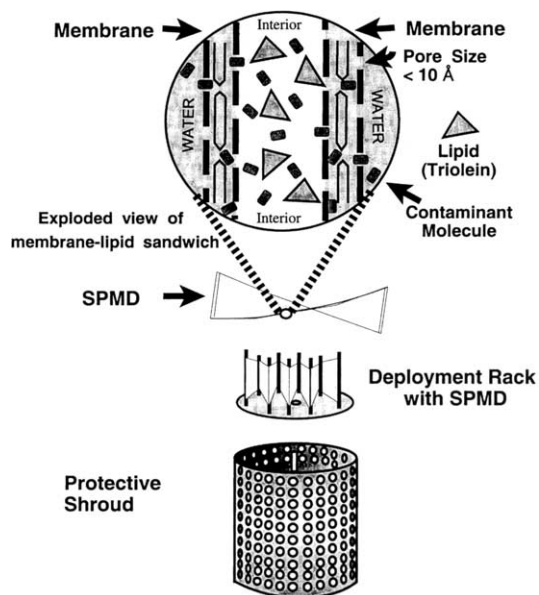


Fig. 1. Illustration of the principle of nonporous membrane size-exclusion phenomenon, which mediates the containment of triolein-SPMD lipid and allows the diffusive exchange of smaller analyte molecules. Also, a partial illustration of deployment apparatus is shown as well. Courtesy of Carl Crazier and Randal Clark, USGS, Columbia, MO, USA.

thermal motions of the polymer chains form transient cavities with maximum diameters of approximately 10 \AA (Huckins et al., 1990a). Because the cross-sectional diameters of most environmental contaminant molecules are nearly as large as LDPE cavities, only dissolved (i.e. readily bioavailable) organic contaminants can diffuse into the membrane and be concentrated in the membrane and triolein. The neutral-triglyceride triolein was selected for use in SPMDs for the following reasons: (1) it is a significant constituent of fish lipids; (2) Chiou (1985) has shown a good correlation between equilibrium triolein–water partition coefficients ($K_{tw,s}$) and widely available equilibrium octanol–water partition coefficients ($K_{ow,s}$); (3) the high molecular weight of triolein (i.e. $> 800 \text{ Da}$) greatly reduces LDPE membrane permeability even during organic solvent dialysis; and (4) triolein is commercially available in high purity forms (Huckins et al., 1990a, 1993, 1996).

Triolein-SPMDs were designed to mimic the bioconcentration of organic contaminants in fatty tissues of organisms, using a much more reproducible sampling matrix. Among the many potential environmental variables, uptake rates are only affected by temperature, flow velocity-turbulence, and biofouling. SPMDs can be used for in situ monitoring contaminants, estimating respiratory exposure, concentrating trace organic contaminants for assessing their toxicity, and the LDPE tubing can be used for analytical separations (Huckins et al., 1990a,b; Meadows et al., 1993; Strandberg, 1998; Bergqvist et al., 1998a). Huckins et al. (1990a, 1993, 1996, 1999, 2000) have delineated important considerations in the design, application, performance, and data comparability of SPMDs.

2.2. Models for estimation of ambient concentration

Procedures for the estimation of ambient water concentrations of contaminants from their concentrations in triolein-SPMDs are different from those used in active sampling strategies. In general, sample size and thus concentration factors are not predetermined for SPMD exposures, as is common in active sampling strategies. There are many mathematic models developed to estimate ambient

analyte concentration based on first-order exchange kinetics and equilibrium partitioning concepts (Booij et al., 1998; Huckins et al., 1993; Huckins et al., in press). Perhaps, the most simple and common approaches used are the equilibrium (Eq. (1)), linear uptake kinetics (Eq. (2)), and exponential accumulation (Eq. (3)) models given by Huckins et al. (1993).

$$\frac{C_t}{C_w} = K_{tw} \quad (1)$$

$$\frac{C_t}{C_w} = \frac{R_s t}{V_t} \quad (2)$$

$$\frac{C_t}{C_w} = K_{tw}(1 - e^{-k_u t}) \quad (3)$$

Eq. (1) describes the equilibrium partitioning of a pollutant between the triolein and water phases, where C_t is the concentration of the contaminant in the lipid (does not include membrane contribution), C_w is the water concentration, and K_{tw} was defined earlier. Eq. (2) is based on the assumption that C_t is linearly related to the sampling time, where R_s is the chemical-specific SPMD (triolein alone) sampling rate, expressed as the volume of water cleared of chemical per unit time (t), and V_t is the volume of the lipid in the device. The R_s values for chemicals of interest are independent of analyte concentration and are obtained through laboratory exposures under controlled conditions. Eq. (3) is based on the assumption that C_t is exponentially related to the exposure time, where k_u is defined as the overall uptake rate constant and is mathematically identical to the loss rate constant (k_e). Eq. (3) integrates all three phases of SPMD uptake (i.e. linear, curvilinear and equilibrium). Because triolein-SPMDs have a large capacity for hydrophobic contaminants, most lipophilic analytes will not achieve equilibrium within sampling periods of < 28 d.

A simple relationship between $\log K_{tw}$ and $\log K_{ow}$ can be applied (Chiou, 1985) for the derivation of K_{tw} , used in Eq. (1) and Eq. (3).

$$\log K_{tw} = \log K_{ow} + 0.105 \quad (4)$$

where K_{ow} was defined earlier and values are available for most of the priority contaminants.

Application of Eqs. (1)–(3) is also based on the

assumption that the chemicals accumulated by triolein-SPMDs are only in the triolein phase. However, the membrane is a functional constituent in the sampling process rather than simply a container for the triolein (Huckins et al., 1990a; Petty et al., 1994; Gale, 1998; Booij et al., 1998). Studies have indicated that the polyethylene membrane used in triolein-SPMD is a significant reservoir for hydrophobic residues and has a membrane/solute partitioning coefficients only a little less than the inner triolein reservoir ($K_{pw} \approx 0.1-0.5K_{tw}$, Gale, 1998). For example, a typical sampler has a total mass of about 4.5 g, which contains 0.91 g (1 ml) of triolein and represents a polyethylene to triolein ratio of about 4:1 (Huckins et al., 1996). This finding implies that about 33–71% of the total accumulated chemicals are in triolein phase at steady state.

If the lipid and membrane are analyzed together (e.g. organic solvent dialysis of intact SPMDs), a simple alternative to modeling lipid accumulation alone is to substitute V_{SPMD} for V_t and C_{SPMD} for C_t in Eq. (2) to obtain the empirical sampling rates for the whole device (Huckins et al., 1999):

$$\frac{C_{SPMD}}{C_w} = \frac{R'_s t}{V_{SPMD}} \quad (5)$$

where R'_s is the sampling rate for the whole device (i.e. polyethylene plus triolein), C_{SPMD} is the concentration in the whole device, and V_{SPMD} is the volume of the whole sampler.

A three-compartment (3C) differential equation model has been developed and used to describe the kinetics of the accumulation processes (Gale, 1998). Based on the 3C model, it was suggested that the accumulation of a chemical in a triolein-SPMD may be controlled by either: (1) polymer film diffusion for large molecules with low polymer diffusivity, where steady-state solute concentrations in polyethylene and water are reached before they attained in polyethylene and triolein; (2) aqueous film diffusion for highly polymer-diffusive molecules, where the ratio of the solute concentrations in triolein and polyethylene reaches steady state before the whole device approaches steady state with the water; (3) a combination of aqueous and polymer film diffusion where solute concentrations in polyethylene and

triolein reach a relatively constant ratio, but not necessarily the final steady-state value (i.e. equilibrium concentrations among the three compartments). By modeling potential variations in exposure conditions and the triolein-SPMD physical parameters, the overall accumulation by the whole device is predicted to remain under aqueous film control for high K_{ow} compounds. However, for very large molecules, accumulation in the triolein may be subject to polymer film control.

In the literature, most of the R_s (or R'_s) values were obtained under controlled laboratory conditions (Huckins et al., 1993, 1999; Huckins et al., in press, Rantalainen et al., 2000). When triolein-SPMDs are used in natural environments periphyton often attach to the exterior of the membrane and contribute to the total impedance to chemical uptake. Ellis et al. (1995) reported extensive biofouling of triolein-SPMD membranes during an exposure on the upper Mississippi River. Periphyton growth varies with environmental conditions under which the device was deployed, and it is difficult to correct for its influence. Huckins et al. (1993, 1996, 1997a) and Huckins et al. (1999) and Huckins et al. (2000) have proposed the use of permeability/performance reference compounds (PRCs; i.e. selected compounds spiked into SPMD triolein prior to deployment), which provide information that can be used to derive in situ triolein-SPMD sampling rates. Thus, laboratory-sampling rates (R_s) of triolein-SPMDs can be adjusted to reflect specific field sampling conditions, such as biofouling, by introducing a coefficient F_i , which is defined as one minus the fractional reduction in sampling rate due to biofouling (Petty et al., 2000):

$$R_{sc} = R_s F_i \quad (6)$$

where R_{sc} is the corrected sampling rate for a chemical and is obviously a conditional constant for a specific set of exposure conditions. Currently, the PRC approach has been extended to the effects of temperature and flow velocity-turbulence of the medium sampled (Huckins et al., in press), which permits the derivation of an exposure adjustment factor (EAF). The EAF accounts for the effects of all three environmental variables (i.e. flow-turbulence, temperature and biofouling) affecting triolein-SPMD sampling rates. Correct use of the

PRC approach should enable investigators to predict water concentrations with estimation errors of less than twofold (Huckins et al., in press).

2.3. Quality control

The level of quality control related to triolein-SPMD applications varies with project goals and the analytical procedures used. A typical analytical scheme for analyzing organic contaminants in triolein-SPMDs includes sample preparation, extraction, enrichment/purification, fractionation, and quantitative or qualitative analysis. For example, analysis of PAHs in triolein-SPMDs generally includes dialytic recovery of the PAHs from the intact device, cleanup the dialysate using size exclusion and adsorption chromatography, then analysis by gas chromatography (GC) with photoionization or mass spectrometric detection (Lebo et al., 1992, Orazio et al., 1995). More specifically, triolein-SPMDs are dialyzed in hexane to recover the analytes, followed by high performance size exclusion chromatography and potassium silicate enrichment procedures (Petty et al., 2000). The precision of this process, including sampling and analysis, is typically better than 20% RSD (Petty et al., 2000). In the case of triolein-SPMDs, used to preconcentrate water samples for bioassays or biomarker tests, cleanup is typically less rigorous than that described above. However, some potential lipid impurities may still interfere with the assay. This issue is subsequently discussed in more detail.

Devita and Crunkilton (1998) applied triolein-SPMDs to monitor PAHs in an urban stream. Relative percent differences (RPDs) were calculated to estimate precision in triolein-SPMD replicates and RPDs were found within 13.9–56.0% ($n = 14$). Variations in replicates encompassed triolein-SPMD preparation, deployment, exposure, retrieval and analysis, and the average percent recoveries were 52–82% ($n = 7$). The method detection limits (MDLs) were assessed by spiking each of 10 triolein-SPMDs with 0.200 mg PAHs per g triolein. After a 14-day exposure period, the MDLs for the PAHs studied corresponded to detectable water concentrations of 2.1–13 ng l⁻¹. These values were as much as 2000 times lower than MDLs derived from standard approach of

solvent extraction of water samples. In general, the quality control criteria used for GC-mass spectrometric identification of target chemicals in triolein-SPMDs is the same as other sampling strategies (Strandberg, 1998). Clearly, when inter-laboratory results are compared, there is a need for the standardization of triolein-SPMDs to ensure comparability of results.

3. Environmental monitoring and research applications

Since the beginning of the 1990s, triolein-SPMDs have received wide recognition, especially in the United States, as effective tools for environmental research and analysis. They have been successfully used for monitoring chemicals in aquatic environments (Huckins et al., 1990a; Huckins et al., 1997b; Petty et al., 1995, 1998; Ellis et al., 1995; Lebo et al., 1992, 1995; Bennett et al., 1996; Moring and Rose, 1997; Bergqvist et al., 1998a; Axelman et al., 1999; Zimmerman et al., 2000), and in air (Ockenden et al., 1998; Lohmann et al., 2001). Triolein-SPMDs have also been used for screening and preliminary identification of emission sources in wastewater systems and groundwater (Stuer-Lauridsen and Kjolholt, 2000; Granmo et al., 2000; Gustavson and Harkin, 2000), and appear to simulate the bioconcentration of dissolved chemicals by aquatic organisms (Huckins et al., 1996; Prest et al., 1992; Wood, 1994; Devita and Crunkilton, 1994; Herve et al., 1995; Peven et al., 1996; Hofelt and Shea, 1997). The procedure for dialytic recovery of analytes can be used separately to remove lipids and other interferences from environmental sample extracts (Huckins et al., 1990b; Meadows et al., 1993, 1996; Strandberg, 1998; Bergqvist et al., 1998b).

In general, triolein-SPMDs can be used for a wide range of organic contaminants. However, chemicals that are predominantly ionic at environmental pHs are not accumulated in triolein-SPMDs. In addition, chemicals with $\log K_{ow}s < 2.0$ are too polar or their fugacity from non-polar organic phases is too high to be sufficiently concentrated in triolein-SPMDs.

3.1. Comparisons to biomonitoring organisms

Triolein-SPMDs have been proposed as a mimetic (i.e. to mimic complex biological processes in simple media) supplement or replacement for biomonitoring organisms used in organic contaminant assessments (Herve et al., 1995; Prest et al., 1995a). Regardless of the issue of the appropriate application of triolein-SPMDs to biomonitoring programs, these authors found triolein-SPMDs to be very useful tools for assessing the presence of bioavailable organic contaminants.

The capacity of an organism to accumulate non-metabolized organic contaminant residues is mainly controlled by the lipophilicity (i.e. K_{ow}) of the compound and the lipid content of the organism. Usually, a correlation between bioconcentration factor (BCF) and the device (triolein-SPMD) concentration factor (DCF) is assumed, when triolein-SPMDs are substituted for organism in extreme environments. However, Huckins et al. (in press) has pointed out that organism uptake rate constants vary widely for the same chemical and unlike triolein-SPMDs their tissues levels may not be proportional to environmental concentrations. Thus, it is unlikely that correlation between BCFs and DCFs will always be found (Huckins et al., in press). A good correlation was shown between the $\log K_{ow}$ and \log BAF (bioaccumulation factor) in mussels and between the $\log K_{ow}$ and \log DCF (Sabaliunas et al., 1998). These findings are based on a continuous-flow laboratory exposure of triolein-SPMDs and lake mussels (*Anodonta piscinalis*) to four pesticides (Sabaliunas et al., 1998). The compositions and ratios of different pesticides in triolein-SPMDs and in mussels were also similar, which indicate that triolein-SPMDs serve as good surrogates for aquatic organisms with respect to the discriminatory uptake of these hydrophobic chemicals (Sabaliunas et al., 1998). When goldfish (*Crassius auratus*) and triolein-SPMD were simultaneously exposed to nine relatively hydrophilic chlorophenols in a laboratory continuous flow experiment, steady state concentrations were achieved after 12 h in triolein-SPMDs and in fish, and the partition coefficients ($\log K_{tw}$, \log BCF, and $\log K_{ow}$) were closely cor-

related each other (Wang et al., 1998). Similar results were obtained for nine weakly hydrophobic nitroaromatics (Wang et al., 1999a).

In field studies, the relationship between log DCFs and log BCFs often becomes more difficult to establish, mostly because of problems related to the measurement of free concentrations of contaminants in complex mixtures and the much longer times to equilibrium for SPMDs. For chemicals with high K_{ow} s, i.e. $\log K_{ow}s > 6.0$, attainment of equilibrium in standard triolein-SPMDs may require more than a year (Gale, 1998). However, similar concentrations of chemicals have been reported in side-by-side field exposures of triolein-SPMDs and biomonitoring organisms (Prest et al., 1998; Gale et al., 1997). Hofelt and Shea (1997) suggested that the correlation between SPMDs and monitoring organisms was improved when using a device with a smaller volume of triolein, a thinner LDPE membrane and a larger membrane surface area (25 μm thick and 900 cm^2 in area). The correlation coefficients (R^2) for triolein-SPMDs and caged mussels (*Mytilus edulis*) ranged from 0.57–0.85 for individual pesticides ($n = 16$) and from 0.81–0.96 for individual congeners of polychlorinated biphenyl (PCB, $n = 20$). However, based on the work of Booij et al. (1998) and Gale (1998), membrane thickness should have little to do with time to equilibrium of contaminants with $\log K_{ow}s$ greater than about 5.0. Also, when benthic organisms (i.e. *Lumbriculus variegates*) and triolein-SPMDs were exposed simultaneously to sediment-bound chemicals, such as polychlorinated diphenylethers (PCDEs), BCFs and DCFs were reasonable close (Kukkonen et al., 1998).

The propensity of some organisms to rapidly biotransform certain anthropogenic chemicals, such as PAHs (Buhler and Williams, 1989), through activation of the mixed function oxidases (MFOs), severely limits any correlation between concentrations in tissue concentrations and exposure concentrations. Because no biotransformation or metabolism of chemicals occurs in triolein-SPMDs (assuming photolysis is prevented), they can be used to determine the relative roles of uptake from water (the bioconcentration process) and by difference, the dietary route (the BAF reflects both routes of uptake).

Application of triolein-SPMDs with PRCs to monitoring programs could improve the inter-laboratory comparability of residue concentration data for many contaminants (Huckins et al., in press). Because a variety of SPMD designs have been employed for environmental assessments without PRCs or appropriate calibration data, the comparability of these data will be questionable. Even if PRCs are used, shortcomings will exist in the extrapolation of triolein-SPMD data to some organisms, such as the inability to directly predict (models are required for these estimates) contaminant transfer up through the food web, i.e. SPMD levels do not reflect the potential for biomagnification. Clearly, triolein-SPMDs can be applied to discriminate bioconcentration from bioaccumulation in field studies. In summary, even though several laboratory and field tests have shown that triolein-SPMD and test organism tissue concentrations are remarkably similar across a wide range of chemical hydrophobicities, it is unreasonable to expect SPMDs to closely mimic the accumulation of all organic contaminants by all biomonitoring test species (Huckins et al., 2000).

3.2. Use in chemical monitoring

Since their inception, triolein-SPMDs have been largely intended for passively monitoring chemical concentrations in different environmental media. There are several advantages in using SPMDs for monitoring priority organic pollutants, which include the following: (1) the non-mechanical or passive operation; (2) the ability to sample large sample volumes (i.e. volume of water or air extracted) and (3) the generally reduced effort required for triolein-SPMD deployment and analytical cleanup when compared to transplanted organisms.

The following studies are specific examples of triolein-SPMD use for environmental contaminant monitoring. Prior to and after an extensive Midwest (USA) flood of 1993, triolein-SPMDs were employed to detect the presence of bioavailable organochlorine pesticides (OCs), PCBs, and PAHs in the water of the main stem of the lower Missouri River, and its tributaries (Petty et al., 1995, 1998). Contaminant residues found at post-

flood sites were nearly all at higher concentrations than those found in the earlier pre-flood sampling. Dieldrin was found to range from a low of 110 ng sample⁻¹ in the Gasconade River to a high of 2000 ng sample⁻¹ at Glasgow, while in the pre-flood sampling, dieldrin ranged from a low of 64 ng sample⁻¹ at Sioux City to a high of 800 ng sample⁻¹ at Glasgow (Petty et al., 1998).

In a study on the temporal distribution patterns of different contaminants in flood-plume water along the Swedish Coast, DDTs, PCBs, and dieldrin showed elevated levels during the first and second sampling period (Bergqvist et al., 1998b). Then, a more stable, but lower contaminant level followed. Surprisingly, chlordanes and hexachlorocyclohexanes (HCHs) showed a more complex pattern with elevated levels at the beginning, followed by a temporary decrease and then a second rise in concentrations. Chlorobenzenes showed no measurable shift in concentrations during the total sampling period (Bergqvist et al., 1998b).

Ultra-trace organic contaminants can be detected by using triolein-SPMDs. Following dialysis, cleanup, and fractionation, concentrations of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) as low as 30 fg l⁻¹, were detected (Lebo et al., 1995) in aqueous exposures using a composite sample of four triolein-SPMDs (17 g, includes mass of membrane and triolein). Also, the average TCDD equivalents obtained from residue quantitation by GC/MS was generally similar to that measured by a H4IIE bioassay (Lebo et al., 1995).

Rantalainen et al. (1998) compared the levels and the congener profiles of PCDDs, PCDFs and non-*o,o'*-PCBs sampled by triolein-SPMDs in the water column and in the sediments of the lower Fraser River (Canada). Triolein-SPMD concentrations were compared to concentrations in resident benthic-feeding fish. SPMD derived concentration estimates of the water column were compared to measured values as determined by an active Infiltrax[®] sampler equipped with SPE columns. The results suggested that triolein-SPMDs are the most suitable for sampling water for contaminants such as PCDD/Fs and non-*o,o'*-PCBs, which are present at ultra-trace levels in the

environments of interest (Rantalainen et al., 1998). In another case, extracts from SPE of water samplers, triolein-SPMDs, fish and sediment were compared for their efficacy as monitors of prior pollutants in the Yanghe River, China. Triolein-SPMD appeared to be the most efficient approach (Wang et al., 1999b). The triolein-SPMD approach also has an advantage of being useable in extreme environmental and climatic conditions. For example, it was successfully deployed at McMurdo station in Antarctica in both the water column and sediments (Crockett, 1994).

Triolein-SPMDs have been shown to concentrate several other types of compounds of environmental concern, such as organometallics (Folsvik et al., 2000) and volatile olefinic and aromatic hydrocarbons. The latter hydrocarbons include monoterpenes, which are emitted from bark wounds as part of a tree defense mechanism and during wood processing (Strandberg, 1998). More specifically, triolein-SPMDs can be used to concentrate monoterpenes to adequate levels, so that the post identification and analysis is easier to perform.

Both Prest et al. (1998) have suggested that triolein-SPMDs are unsuitable for determining rapid or short-term temporal variability, since they are designed to integratively sample (i.e. they provide time weighted average [TWA] concentrations) over periods on the order of days or weeks not hours. Also, Gustafson suggested that triolein-SPMDs might be unsuitable for monitoring gas exchange of chemicals across the air–water interface, because flux is dependent upon instantaneous concentration gradients. In such circumstance, Prest et al. (1998) suggested that the simultaneous air and water sampling with SPEs and triolein-SPMDs is likely to be a powerful tool for assessing the net flux of chemicals between these compartments. His argument was based on the observation that thermodynamic relationships for air–water transport are formulated in terms of dissolved and vapor phase concentrations and the triolein-SPMD membrane inherently provides a level of discrimination against particle bound chemicals (Prest et al., 1995a,b; Ockenden et al., 1998; Booij et al., 1998). When triolein-SPMDs

are applied to soil ecosystem, they provide a simple and efficient in situ method for the concentration of pollutants in compost, as well as lipophilic vapors above the soil surface (Strandberg, 1998).

In principle, triolein-SPMDs were designed to sequester free concentrations (i.e. dissolved and vapor phases) of chemicals in waters. However, the fraction of free concentrations of very hydrophobic contaminants in natural waters and air may be small when compared to the total concentrations. For example, dissolved PCB congener concentrations in water samples from a contaminated spring were assessed with triolein-SPMDs and total water-borne PCB concentrations were determined separately with a conventional solvent extraction (i.e. liquid/liquid partitioning) approach (Meadows et al., 1998). Concentrations of dissolved hydrophobic chemicals in water (C_{wd}) were related to the TOC content of the water by the following equation (Meadows et al., 1998):

$$C_{wd} = \frac{m_{a(\text{tol})}}{m_w + M_{oc}K_{oc}} \quad (7)$$

where $m_{a(\text{tol})}$ is the total mass of analyte, m_w is the mass of water, K_{oc} is the compound's organic carbon sorption coefficient, and M_{oc} is the mass of organic carbon in the water. The results of this exercise show that the total organic carbon content of the water is critical in determining the amount of high K_{ow} compounds accumulated by triolein-SPMDs or biota, because of its impact on the fractional amount of the dissolved, or readily bioavailable residues in water. For example, assuming that $K_{oc} \approx K_{ow}$, dissolved concentration of PCBs with $\log K_{ow}$ greater than 7.0 are reduced by more than 80% when correcting for 0.5 mg l^{-1} TOC. However, aquatic organisms that ingest carbon rich particulates or prey organisms with very hydrophobic chemicals may accumulate a significant fraction of the residues by assimilation across the gut.

3.3. Preconcentration of samples for bioassays

There appears to be considerable need for rapid, easy to use, effective, and low-cost integrative methods that allow not only the direct moni-

toring of the fate and concentrations of trace-contaminant mixtures in the environment, but also an assessment of the potential hazards these chemicals pose to aquatic organisms and human health. Extracts of triolein-SPMDs can be examined with standard bioassays (Huckins et al., 1996; Sabaliunas and Sodergren, 1997). Often, risk assessment of organic contaminants in aquatic environments is based on the measurement of individual compound levels and comparison of each chemical's concentration to existing toxicity data. However, all chemicals exert their effects as components of complex environmental mixtures that are influenced by a number of factors. Clearly, it is the effects of the complex mixtures that must be considered in a comprehensive environmental risk assessment. When triolein-SPMDs are used as surrogates for or in conjunction with biomonitoring organisms, the sequestered contaminants are available for assessment with a wide array of biomarker and bioassay tests. For example, concentrations of the dialysates of triolein-SPMDs have been assayed with standard bioindicator screening tests, such as Microtox and Mutatox (Huckins et al., 1996), or the ethoxy resorufin-*o*-deethylase assay (Niewolny et al., 1995). Consequently, this triolein-SPMD-bioassay linkage provides a potential means of determining the relative biological significance of contaminants mixtures accumulated at study sites.

There have been numerous trials using triolein-SPMDs for ecotoxicology applications. Enriched extracts from triolein-SPMDs exposed to bleach Kraft mill effluents (Huckins et al., 1996) and surface water contaminated by trace levels of PCDDs and PCDFs (Huckins et al., 1996; Lebo et al., 1995) were found to induce cytochrome P450 activity in fish and rat cell lines. Purified dialysates from triolein-SPMDs, which were exposed to pesticides in a laboratory continuous-flow system or deployed in polluted water in Lithuania, were highly toxic to the luminescent bacteria *Vibrio fischeri* (Sabaliunas and Sodergren, 1997). It is noteworthy that these bioassays were performed with only a small portion of dialysate. However, sample clean-up procedures to remove oleic (an impurity is some triolein) may be required prior to toxicity testing for the estima-

tion of the true toxic potential of accumulated pollutants (Sabaliunas et al., 1999).

In freshwater microcosm studies that simulated a crude oil spill, triolein-SPMDs were used to concentrate the oil related pollutants in air, water columns and sediments. By using triolein-SPMDs the time-dependent changes in the acute toxicity (as assayed by Microtox[®]) and the genotoxicity (as assayed by Mutatox[®]) were successfully monitored (Johnson, 1995). The combination of the use of triolein-SPMDs for the preconcentration of certain trace contaminants (e.g. PAHs) and the subsequent assay of enriched dialysates by bioindicator tests appears to be an useful approach for screening the relative toxicity of bioavailable organic contaminants (Johnson et al., 2000). Triolein-SPMDs were deployed in the Athabasca River area to sequester any hydrophobic toxic compounds from different point sources along the river. The SPMD-extracts were assayed for MFO induction in a fish cell line (Parrott et al., 1995). Discharges from three pulp mills were found to have pollutants that strongly induced MFO activity in the cell line, when compared to the background river water.

Koistinen et al. (1998), used liquid–liquid extraction, SPE, and triolein-SPMDs to extract pollutants from the effluents and sludge of primary and secondary clarifiers of activated sludge treatment plants at a Finnish bleached-kraft pulp and paper mill, and then assessed the resulting extracts with two Hepa-1 mouse hepatoma cells bioassays. SPMDs were found to be particularly useful in accumulating non-polar inducers of MFO from the pulp mill effluents. Petty et al. (1998) exposed SPMDs to Missouri River water at several sites following the great flood of 1993 (Midwest USA). Enriched extracts of triolein-SPMD laboratory processing controls injected into rainbow trout (*Oncorhynchus Myriss*) showed no evidence of vitellogenin production (a bioindicator of the presence of estrogenic chemicals), whereas injection of extracts from SPMDs exposed at the Napoleon site on the river showed enhanced estrogenic activity in the trout. The authors suggest that these data indicate that long-term exposure of fish and wildlife to this type of contaminant mixture, may result in reproductive perturbations.

3.4. Overview of attributes and drawbacks

From the investigations summarized in this work, it is clear that triolein-SPMDs have considerable potential as monitors of environmental pollutants. However, all sampling or monitoring methods have strengths and weaknesses and triolein-SPMDs are no exception. Table 1 compares the attributes and drawbacks of triolein-SPMDs and two other common environmental monitoring approaches.

4. Conclusions

The most common applications of triolein-SPMDs appear to be the determination of the presence, source, and TWA concentrations of hydrophobic organic contaminants in aquatic environments and in the atmosphere. Also, triolein-SPMDs are often used as surrogates for, or additions to biomonitoring studies to improve estimates of exposure to waterborne organic contaminant mixtures, and in some cases, to predict tissue concentrations of specific contaminants in the tissues of organisms of concern (Petty et al., 1998). To reduce the magnitude of the error associated with a triolein-SPMD derived water concentration estimate, PRCs must be used to correct for site-specific environmental factors such as variations in temperature, membrane biofouling, and the flow-turbulence regime (Booij et al., 1998; Booij and Drooge, 2001; Huckins et al., 1997b, 1999, 2000; Huckins et al., in press). Standardization of the design of the triolein-SPMDs (e.g. membrane thickness and triolein to membrane mass ratios) is also needed to improve the comparability of triolein-SPMD data (Huckins et al., 1999).

The use of triolein-SPMDs as a tool for the assessment of the ecological consequences of chemical pollution is promising, particularly when the effects of long-term exposure to ultra-trace hydrophobic contaminants are a primary concern. Triolein-SPMDs can be used as a mimetic surrogate or as a compliment to biomonitoring organisms (Huckins et al., 2000) for the determination of bioavailable contaminants in aquatic environ-

Table 1
Summary of the attributes and drawbacks of three widely used methods for assessing exposure to environmental contaminants

Passive triolein-SPMDs	Biomonitoring organisms	Active SPE/Batch extraction
<i>Attributes</i>		
Non-mechanical, no maintenance required, limited historic data for some environments	The real thing, non-mechanical, historic data available for some environments	Historic data available for some environments
Can be used in multiple media, mimics respiratory uptake or bioconcentration	A number of available species are suitable for transplanting, detected residues often represent bioaccumulation	Direct measurement of particulate and dissolved/vapor phases (<0.7 µm)
Integrates a wide range of dissolved or vapor phase residues over extended time periods, reduces false negatives due to episodic events	Samples both organics and metals (i.e. ionic species), equilibrium is often achieved during longer exposures	Some SPE systems sample polar contaminants not concentrated by SPMDs or biota
Samples only readily bioavailable (solutes/vapors) residues, provides TWA concentrations of environmental media	Accumulated residues clearly bioavailable, assuming gut contents are removed	Mass and concentration of particulate phase known for estimates of bioavailability
Extremely low detection limits of hydrophobic compounds, high analytical precision	Bioaccumulation enables low detection limits of some compounds	Large volume systems often have low detection limits
Sampling not affected by most water quality parameters (e.g. DO, ammonia, and salinity), reproducible	Some organisms have low xenobiotic metabolism rates and relatively high tolerance to exposure conditions	Extraction efficiency unaffected by water quality, known volume of water extracted, reproducible
Provides mimetic extracts amenable to bioindicator/bioassay tests	Analysis of edible tissues is definitive test of human health risk	Extracts have been used with bioindicator tests
Analytical methods well developed, sample analysis generally easier than tissues	Analytical methods well developed	Sample analysis easier than tissues
<i>Drawbacks</i>		
Does not account for dietary route of uptake and biomagnification (relevant to persistent contaminants with $\log K_{ow,s} > 6.5$) and will not sample ionic chemical species	Many contaminants of concern are metabolized by commonly used biomonitoring organisms and bioavailable low K_{ow} compounds are often not detected	Large volume SPE sampling is labor intensive and costly, and results do not account for dietary uptake and biomagnification
In some cases, oleic acid and sulfur may have to be removed from sample extracts prior to bioindicator /bioassay tests	No survival at some sites and stress (e.g. salinity, ammonia levels, etc) can affect uptake, or cause non-contaminant related site to site variations in BAFs	Uncertainty about the bioavailability of detected residues and difficult to relate to adverse biological effects
In the case of aqueous exposures, care must be used to prevent vapor phase contamination of samplers and photodegradation of certain PRCs may be problematic without shading	Data do not represent integrative sampling for compounds that approach equilibrium, data scatter or variance is generally greater than that associated with SPE and SPMD analysis, and the ability to accurately estimate water concentrations from tissue levels has not been demonstrated	Values reflect only a small window of time (<1 d), unless intensive sampling through time is undertaken
Does not respond fast enough to track rapid changes in solute or vapor phase concentrations, and verification of estimates of ultra-trace levels of contaminants generally not feasible with other methods	Removal of gut contents (e.g. bivalve depuration) is required to ensure that residues are tissue incorporated	Direct assessment of analyte recoveries during in situ sampling in the field is not possible

Clearly, combinations of these methods are often complimentary but costs are the limiting factor. In general, passive samplers such as the triolein-SPMDs and SPMEs (not listed in Table 1) appear to be reasonably cost effective while providing environmentally relevant data.

ments. The mimetic nature of triolein-SPMDs, suggest that bioassays of SPMD extracts will be more representative of feral organism responses than a combination of active sampling traditionally used followed by bioassay of sample extracts. Although more research work is needed to fully develop the aforementioned applications, considerable progress has been made.

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