Science of the Total Environment xxx (2009) xxx–xxx

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

How useful are the "other" semipermeable membrane devices (SPMDs); the mini-unit (15.2 cm long)?

Steven L. Goodbred [a], Wade L. Bryant [b], Michael R. Rosen [c,*], David Alvarez [d], Terri Spencer [e]

[a] US Geological Survey, Modoc Hall-Suite 3005, 3020 State University Drive, East, Sacramento CA 95819, United States
[b] US Geological Survey, Spaulding Woods Office, Park, Suite 160, 3850 Holcomb Bridge Road, Norcross GA 30092, United States
[c] US Geological, Survey, 2730 North Deer Run Road, Carson City NV 89701, United States
[d] US Geological Survey, 4200 New Haven Road, Columbia MO 65201, United States
[e] Environmental Sampling, Technologies Laboratory, 502 Fifth Street, Saint Joseph MO 64501, United States

ARTICLE INFO

Article history:
Received 1 October 2008
Received in revised form 25 February 2009
Accepted 27 February 2009
Available online xxxx

Keywords:
Mini semipermeable membrane device
Urbanization
P450RGS assay
Fluoroscan
Hydrophobic organic compounds

ABSTRACT

Mini (15.2 cm) semipermeable membrane devices (SPMDs) were used successfully in 169 streams from six metropolitan areas of the US to sequester hydrophobic organic compounds (HOCs) that are indicative of urbanization. A microscale assay the P450RGS, which responds to compounds that bind to the aryl hydrocarbon receptor (AhR), and the Fluoroscan, a chemical screen for polycyclic aromatic hydrocarbons (PAHs), were performed on each mini SPMD extract. Results show both tests were sensitive enough to respond in streams with low urbanization and responded exponentially in a predictable way to a gradient of urbanization. Mini SPMDs had sufficient sampling rates to detect HOCs using gas chromatography with mass spectrometric detection (GC/MS) in streams with low levels of urbanization. The total number of HOCs in streams had a linear response to a gradient of urbanization, where 73 of 140 targeted compounds were detected. A diverse group of compounds was found in urban streams including, PAHs, insecticides, herbicides, musk fragrances, waste water treatment compounds and flame retardants. Pentachloroanisole (PCA), a breakdown product of pentachlorophenol (wood preservative), was the most ubiquitous HOC, and was detected in 71% of streams. An evaluation of mini SPMD performance showed they can detect concentrations in water below toxicity benchmarks for many HOCs with the exception of 2,3,7,8 tetrachlorodibenzo-*p*-dioxin. A comparison of mini SPMDs with full sized (91.4 cm) SPMDs showed they have several distinct advantages. The most notable advantages are their low cost, small size, and reduced chance of vandalism. The greatest limitation is the inability to detect compounds at low concentrations (pg/L). Mini SPMDs perform quite well in a wide array of environmental settings and applications and should be considered as an option in environmental studies.

Published by Elsevier B.V.

1. Introduction

Semipermeable membrane devices (SPMDs) consist of a thin film of the lipid triolein sealed inside a lay-flat thin-walled tube of low-density polyethylene and have been used for almost 2 decades to mimic hydrophobic organic contaminant (HOCs) exposure to and bioaccumulation in lipids of aquatic organisms (Huckins et al., 1990, 1993, 2006). SPMDs have been deployed in a wide variety of environmental settings to assess water quality in aquatic environments (Moring and Rose, 1997; Echols et al., 2000; Wang et al., 2001; Barber et al., 2003; Rowe et al., 2005; Rosen et al., 2006). A recent book by Huckins et al. (2006) provides a review of published studies and research on SPMDs.

The advantages of using SPMDs to monitor water quality are that results are reproducible, the equipment is durable in severe environments, and samples are not metabolized (Rosen et al., 2006). In addition SPMDs integrate HOCs over time increasing chances of detecting episodic releases and trace concentrations of HOCs present in many streams (Huckins et al., 2006). SPMDs sample nearly all nonionic HOCs with molecular weights ≤600 Da and log octanol–water partition coefficients (K_{ow})>3.0 (Huckins et al., 2006). General classes of hydrophobic compounds sampled by SPMDs include polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organochlorine pesticides, chlorinated dioxins and furans, pyrethroids, alkylphenols and certain heterocyclic aromatics.

SPMDs are commercially available from Environmental Sampling Technologies (EST) in Saint Joseph MO, USA (http://www.est-lab.com/spmd.php) and from two companies in Sweden, Exposmeter AB (http://www.mamut.net/exposmeter/) located in Taveljö, and ALS-Analytica AB in Täby (http://www.alsglobal.com/Environmental/

* Corresponding author. Tel.: +1 775 887 7683; fax: +1 775 887 7629.
E-mail address: mrosen@usgs.gov (M.R. Rosen).

0048-9697/$ – see front matter. Published by Elsevier B.V.
doi:10.1016/j.scitotenv.2009.02.037

ARTICLE IN PRESS

NewsContent.aspx?key=16). To insure comparability of SPMDs between studies, all SPMDs should have a surface area to volume ratio of about 460 cm^2 mL^{-1} of triolein, a 0.25 lipid-to-membrane-mass ratio, and a 70–95 µm wall thickness (Huckins et al., 2002, 2006). Typically SPMDs come in two lengths, mini (15.2 cm) and full sized (91.4 cm) with each size having a different carrier and deployment device (Fig. 1). However other SPMD sizes (10 cm–15.2 cm) have been used in the laboratory to determine efficiencies of PAH recovery after dialysis (Williamson et al., 2002), uptake of chlorophenols (Wang et al., 1998), and assessing different methods to reduce bioavailability of PCBs and PAHs in marine sediment (Zimmerman et al., 2004; Cho et al., 2007). However if choosing among smaller SPMD lengths, the advantage of using the mini SPMD is that they are available commercially along with a device to deploy them. Most published studies have used the full sized SPMD because it has proven adequate for sampling HOCs in water and air across a wide variety of environmental conditions (Huckins et al., 2006; and references therein). Often 5 or more full sized SPMDs are used to detect extremely low HOC concentrations (e.g. Alvarez et al., 2008). While the full sized SPMDs can theoretically sample approximately six times more water (or air) than the mini SPMD, mini SPMDs have certain advantages including lower cost, a reduced chance of vandalism, and the ability to be deployed in very shallow water.

The potential toxicity to aquatic organisms can currently be assessed using sensitive microscale/*in-vitro* assays and toxicity testing with SPMD extracts (Johnson, 1998). The advantages of using these microscale tests are they require very little sample (µL compared to mL L), cost less, and provide increased sensitivity which have been shown to be adequate for environmental studies using mini SPMDs. Assays that have been used on SPMD extracts include, Microtox®, Mutatox®, mixed function oxygenase (MFO) induction, ethoxyresorufin-*O*-deethylase (EROD) activity, sister chromatid exchange, vitellogenin induction, Daphtoxkit F®, Ames mutagenicity test, and yeast estrogen screen (YES) (Huckins et al., 2006). A more recent application of mini SPMDs has been to use an *in-vitro* assay, P450RGS, on extracts to assess potential toxicity of aryl hydrocarbon receptor (AhR) agonists like PAHs and PCBs. Rosen et al. (2006) were the first to use the P450RGS assay on extracts of mini SPMDs deployed along an urban gradient. They found potential toxicity was generally lower in the less urbanized Lake Tahoe watershed and greater along the Truckee River especially below the highly urbanized Reno/Sparks, NV area. Other applications of mini SPMDs and the P450RGS assay have shown strong correlations with degree of urbanization (Gregory and Calhoun 2007; Bryant and Goodbred, 2008), and have been used with stable isotopes to detect anthropogenic influences (Saito et al., 2008).

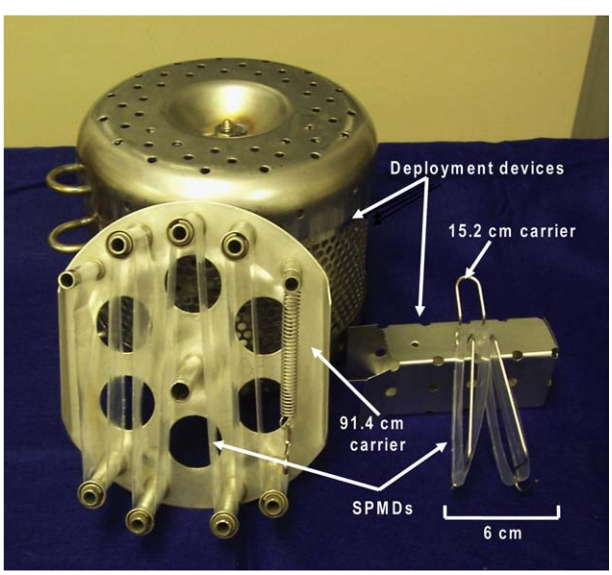

Fig. 1. Size comparison of the mini and full size SPMD showing the deployment devices, and the SPMDs wound around the carriers.

While a number of studies have assessed the health of ecological communities in urban streams (Cuffney et al., 2005), it is difficult for water quality managers and regulators to develop specific strategies for restoration because urbanization can affect streams by altering many factors including hydrology, geomorphology, nutrients, toxicity, temperature, and habitat (Coles et al., 2004). To help better identify which factors are more important in degrading urban streams the U.S. Geological Survey's National Water Quality Assessment (NAWQA) Program initiated a series of studies in 2000 that used an urban intensity index (UII) based on population density (McMahon and Cuffney, 2000) to select 30 sites in streams along an urban gradient. These 30 sites were centered around a major metropolitan area while efforts were made to minimize differences in natural basin characteristics to examine the regional effects of urbanization on aquatic communities (Tate et al., 2005). Once stream reaches were selected representing a gradient from low to high UII, the hydrology, temperature and water quality at each reach were characterized, and periphytic algae, benthic macroinvertebrates, and fish were sampled (Gregory and Bryant, 2003).

Results from three pilot studies in Boston, MA, Salt Lake City, UT, and Birmingham, AL (Brown et al., 2005) indicated that benthic macroinvertebrate communities were impaired at the lowest levels of urbanization and degraded linearly with increasing UII across a wide UII range in all three metropolitan areas (Cuffney et al., 2005). NAWQA followed up these pilot studies in six other metropolitan areas, Denver, CO, Atlanta, GA, and Raleigh, NC in 2003, and Millwaukee–Green Bay, WI, Portland, OR, and Dallas–Fort Worth, TX in 2004. (Fig. 2). Mini SPMDs were used in the 2003 and 2004 urban studies to characterize the HOCs present, and compare relative concentrations among sites. In addition, microscale assays were performed on SPMD extracts to screen for potential toxicity to aquatic organisms (Wells et al., 1998). Results showed that 30 endpoints measured in SPMD extracts (HOC concentrations or microscale assays) were significantly correlated to the percent of urban land use in streams from at least one of the six metropolitan areas studied (Bryant and Goodbred, 2008). The most consistent and significant correlations were for the P450RGS assay.

The objective of this study was to perform an evaluation of the utility of mini SPMDs in environmental studies by assessing their performance when deployed in streams along a gradient of urban land use. The evaluation was primarily based on chemical analysis and a microscale assay done on mini SPMD extracts in streams centered around six U.S. metropolitan areas (Fig. 2) based on the NAWQA study described in the previous paragraphs. Further evaluations were made with comparisons of minimal detectable water concentrations in mini SPMDs to toxicity benchmarks, and a comparison of cost and advantages with full sized SPMDs.

2. Materials and methods

2.1. Study design

A multimetric index was developed to select 30 stream basins along an *a priori* gradient of UII from low to high (McMahon and Cuffney, 2000) in six major metropolitan areas in the U.S. (Fig. 2). Development of an urban gradient and final site selection was an iterative process of sequentially reducing the number of 75 candidate index variables, which include land cover, infrastructure, and socio-economics of candidate basins (Coles et al., 2004) in each metropolitan area. Sampling sites were selected from wadeable third- to fifth-order magnitude streams with a basin size between 50–250 km^2. Basins were selected that did not contain known point source

Please cite this article as: Goodbred SL, et al, How useful are the "other" semipermeable membrane devices (SPMDs); the mini-unit (15.2 cm long)? Sci Total Environ (2009), doi:10.1016/j.scitotenv.2009.02.037

ARTICLE IN PRESS

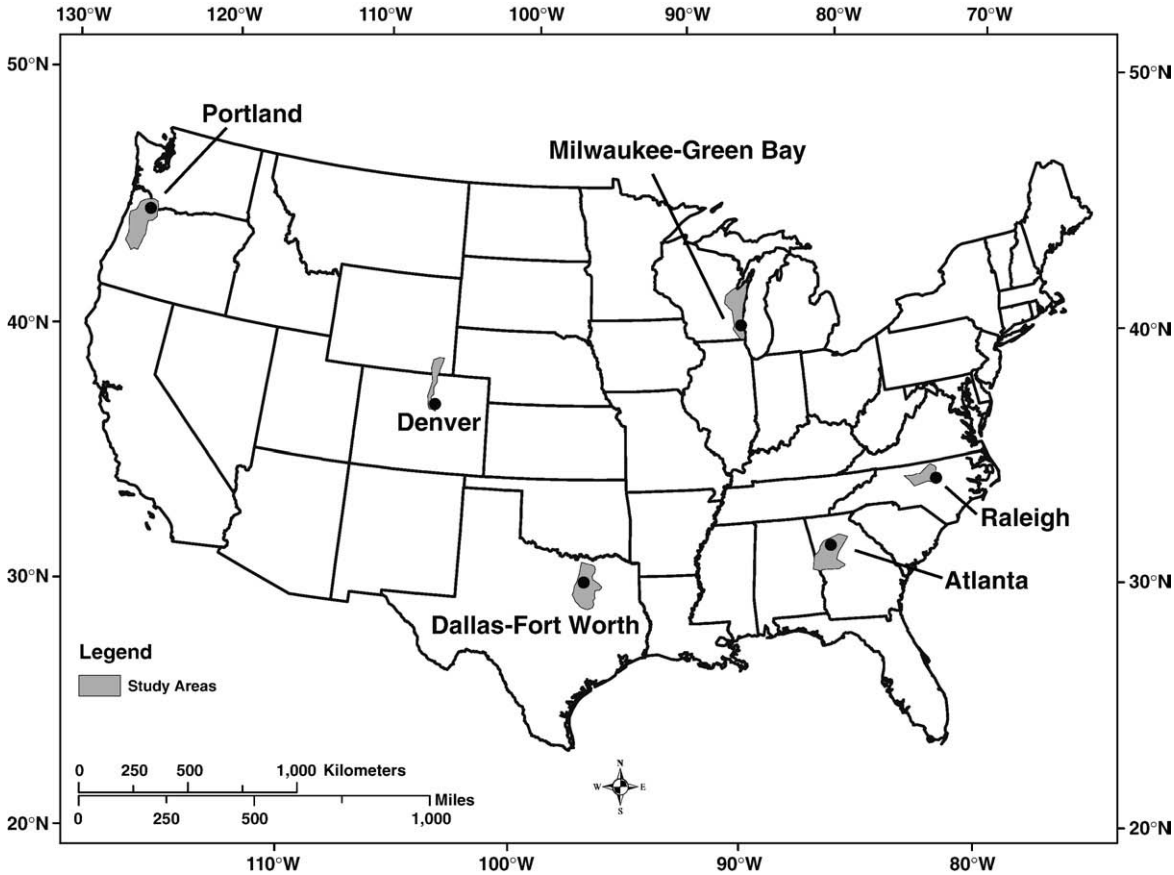

Fig. 2. Map showing locations of the six metropolitan urban study areas in the US.

discharges so that chemical and toxicological profiles reflected general effects of urbanization and not an effect of a specific discharge. Sites were chosen to minimize natural variability including ecoregion, slope, canopy closure, and bed substrate. Using this design one can predict responses like presence of HOCs or potential toxicity in SPMD extracts at various levels of urban intensity. This approach is known as "space for time" because sites are synoptically sampled at all levels of urban intensity. The other option is to select a stream in each metropolitan area with minimal urbanization and monitor water quality and aquatic communities over a long period of time as its watershed becomes more urbanized to determine how urbanization effects stream health. A detailed description of data sources and methods used to characterize degree of urbanization, comparisons of the environmental settings, and key features of urbanization can be found in Falcone et al. (2007). A list of streams sampled, their location, and other information including land use can be found in Bryant et al (2007).

2.2. SPMD deployment, retrieval, and dialysis

The mini SPMDs were supplied by EST. Two mini SPMDs were placed around a stainless steel carrier inside a protective metal deployment device, sealed in solvent rinsed, airtight cans over argon gas, and shipped overnight. The cans were kept at <0 °C until deployment and brought chilled to the field in coolers. Nitrile gloves were worn during both deployment and retrieval. The mini SPMDs were deployed where velocities were at least 3 cm/s but not so fast that floating debris could cause damage. Stream locations were selected to have sufficient depth so that during the deployment period the mini SPMD would remain submerged. Water depth and point velocity were measured using a wading staff and a pygmy flow meter at each mini SPMD location. An additional consideration in site selection was to minimize chances of vandalism. A field blank with two mini SPMDs was opened exposing them to the atmosphere as the mini SPMDs for deployment were taken out of the sealed container, placed quickly underwater, and attached to the 1 m lengths of 1 cm rebar with a plastic tie. Time of deployment was noted then the field blank can was resealed and stored in a freezer. Field water quality measurements of dissolved oxygen, pH, specific conductance and water temperature were made using hand-held and calibrated meters in the general location of the mini SPMDs. In addition within each stream reach where mini SPMDs were deployed a water quality probe continuously measured water temperature.

During retrieval, the mini SPMD field blank can was opened, while wire cutters were used to cut the plastic tie securing the deployment device to the rebar. The deployment device was removed, cleaned of sediment and debris, and quickly sealed in its original shipping can at the same time the can containing the blank SPMD was sealed. The cans were chilled in a cooler, brought back to the lab, and stored at <0 °C till shipment. Following the same protocol used during deployment, the point velocity, water depth, and field water quality parameters were measured at the time of SPMD retrieval.

SPMDs were shipped (overnight delivery) to EST for extraction. The SPMDs were removed from the carrier and trimmed of all non-lipid containing membrane before cleaning and dialysis. The lipid-containing membrane was then washed with tap water, cleaned with a soft bristled brush, rinsed in a beaker containing 1 N HCl for 30 s, rinsed with tap water followed by an acetone and an isopropyl alcohol rinse, then allowed to air dry. The SPMDs were then put in clean jars (two jars and two mini SPMDs per site) with at least 50 mL of hexane and incubated at 18 °C for 18 h. The hexane was then decanted into another jar and the now empty jar was refilled with hexane. Both jars

Please cite this article as: Goodbred SL, et al, How useful are the "other" semipermeable membrane devices (SPMDs); the mini-unit (15.2 cm long)? Sci Total Environ (2009), doi:10.1016/j.scitotenv.2009.02.037

were further incubated for 8 h after which the contents were combined into a Kuderna–Danish flask. The combined sample was concentrated by evaporation with ultra high purity N_2 to approximately 0.5 mL, and filtered through glass fiber filter paper (Fisher, G-6) using hexane as the transfer solvent. Half of the extract from the two mini SPMDs deployed at each site was evaporated with ultra high purity N_2 and exchanged into iso-octane, then quantitatively transferred to an amber ampoule for the P450RGS assay. The other half of the sample was used for Fluoroscan, and transferred to dimethyl sulphoxide (DMSO) in screw top vials. These were placed in a warm water bath and evaporated under N_2 for several hours to remove all traces of hexane. The final volume for each sample was adjusted to 1.0 ml with either iso-octane or DMSO and was the equivalent of one mini SPMD.

2.3. Microscale assay

The P450RGS *in-vitro* assay described in more detail in Ang et al. (2000), and Anderson et al. (2005), employs human hepatoma HepG2 cells (101L cells) that are stably transfected with a plasmid containing the human CYP1A promoter sequence fused to the firefly luciferase gene as a reporter. The induction of the CYP1A gene results in the production of luciferase and the light produced responds to the presence of compounds that bind to the AhR in a quantitative fashion. Results are reported in toxic equivalents (TEQ) which are the number of picograms of 2,3,7,8 TCDD in 1 ml of mini SPMD extract that would cause the same response as the sample. Samples were run in triplicate and quality control samples included standard reference material (bed sediment from New York Harbor; SRM NY/NJ1944) and solvent, dialysis, and field blanks.

2.4. Chemical analysis

The Fluoroscan, a screen for PAHs, was used to determine both the presence and relative concentration of PAH compounds from each site. A fluorometer (Idexx Laboratories, Inc., Westbrook, ME) was used to measure the fluorescence of the extract exposed to ultraviolet light at 280 nm and compared to a standard curve for a common PAH, pyrene (Johnson et al., 2004). The estimated PAH concentration for each site is reported as the equivalent number of μg of pyrene in 1 ml of the mini SPMD extract that would produce the same fluorescence and is reported as a pyrene index (PI). Samples were run in duplicate, and QC samples included solvent, dialysis and field blanks.

A portion of each SPMD extract in iso-octane solvent was analyzed for the identification and quantitation of HOCs. The extracts were concentrated to approximately 0.25 mL in the original ampoule and then transferred to amber glass vials while adjusting the final volume to 400 μL. Internal standards were added (spiked) to the dialysates just prior to gas chromatography/mass spectrometry (GC/MS) analysis. The extracts were analyzed by GC/MS using both electron-capture negative ionization (ECNI) and electron ionization (EI). Selected pesticides, PCBs, and brominated diphenyl ethers were measured by ECNI using a scan range of 35–600 Da, a scan cycle rate of 1.3 s, with methane as the modifying gas, and a source pressure was 4.2×10^{-4} Torr. Organic compounds related to wastewater discharges such as alkyl phenols, polycyclic musks, and plant and fecal steroids were determined using EI. The EI conditions included a scan range of 35–600 Da, a scan cycle rate of 1.3 s, and the source pressure set at 2×10^{-5} Torr. Mass spectra for individual target compounds and retention times from sample extracts were compared with authentic standards from the standard curve for identification. A six-point linear calibration curve was used for quantitation.

2.5. Quality assurance

Spike recoveries for GC/MS analysis ranged from 80.4 to 136%. Analysis of variance showed no difference in spike recoveries between metropolitan areas ($p<0.01$). Regression analysis showed no relationship ($p<0.01$) between percent recovery and the amount of urbanization in the basins (UII) in any metropolitan area. No corrections to data were made based on spike recoveries.

Duplicate SPMDs were analyzed at 3 sites per metropolitan area. Duplicate values differed by no more than 20% for any chemical concentration or assay. Since a few compounds were detected in only one of the duplicates, the maximum value for chemical concentration and microassays were used for all subsequent analysis.

Twenty-one compounds were detected in blanks. For the purposes of this study, all values of field samples were considered non-detects if less than the maximum value reported for any blank from that study area. Values of field samples greater than quality control samples were corrected by subtracting the value of the blank appropriate for that sample. The concentrations used for corrections and the percent of samples above the method detection limit prior to corrections but below the censoring value can be found in Bryant and Goodbred (2008).

2.6. Data analysis

Raw data from the Fluoroscan, and P450RGS assays were tested for normality using Kolmogorov–Smirnov and then range standardized for the number of days deployed compared to the site that was deployed the longest number of days. In addition results from the P450RGS assay were normalized by adjusting data within each metropolitan area to account for differences between the NY/NJ SRM sediment value of 250 ug/kg and the actual value obtained. Box plots showing the 75th and 25th percentile as well as the median and summary statistics were made using Origin 8.0 graphical and statistical program (OriginLab Corporation, Boston, MA.). Regression equations, adjusted R^2 and p values were done on deciles of UII versus median number of HOCs detected, TEQs and PIs also using Origin 8.0.

3. Results and discussion

3.1. Microscale assay

Results from the P450RGS assay expressed as TEQs on mini SPMD extracts in streams from all six metropolitan areas plotted by deciles of UII show a response at the lowest levels of urbanization (Fig. 3). A TEQ value could be calculated for all 160 streams although eight streams had at least one replicate less than the limit of quantitation (LOQ), and one stream, Bear Creek in southwest Wyoming (low UII reference site for Denver, CO), had a replicate that was less than the limit of detection (LOD). There was also a predictable (adjusted $R^2=0.99$, $p<0.0001$) exponential increase in median TEQ from a low of 286 pg/SPMD at 0–10 UII to a high of 2498 pg/SPMD at 90–100 UII. Some UII deciles had extreme outliers above the 95th percentile (not shown in box plots), although this is probably more a function of variability in the UII rather than performance of the mini SPMDs.

This exponential increase in P450RGS assay toxicity compared to UII is not unexpected because the P450RGS assay responds to many AhR agonists like PAHs and PCBs that are prevalent environmental contaminants in urban environments (Moring and Rose, 1997; Hwang and Foster, 2006; McCarthy, 2006). However some streams might have low enough urbanization in the watershed that AhR agonist levels would be too low to be detected in SPMD extracts with the P450RGS assay. Due to its larger size, sampling with the full sized SPMDs would have accumulated higher quantities of AhR agonists and be able to respond at lower levels of urbanization but mini SPMDs were sensitive enough to respond to low urbanized streams in this study. If necessary, the sensitivity of mini SPMDs can be increased if left in the field for a longer period of time (>30days). This approach however does increase chances of vandalism, biofouling, possible photodegradation of certain PAHs as well as possible equilibrium of less hydrophobic compounds (Huckins et al., 2006).

Please cite this article as: Goodbred SL, et al, How useful are the "other" semipermeable membrane devices (SPMDs); the mini-unit (15.2 cm long)? Sci Total Environ (2009), doi:10.1016/j.scitotenv.2009.02.037

ARTICLE IN PRESS

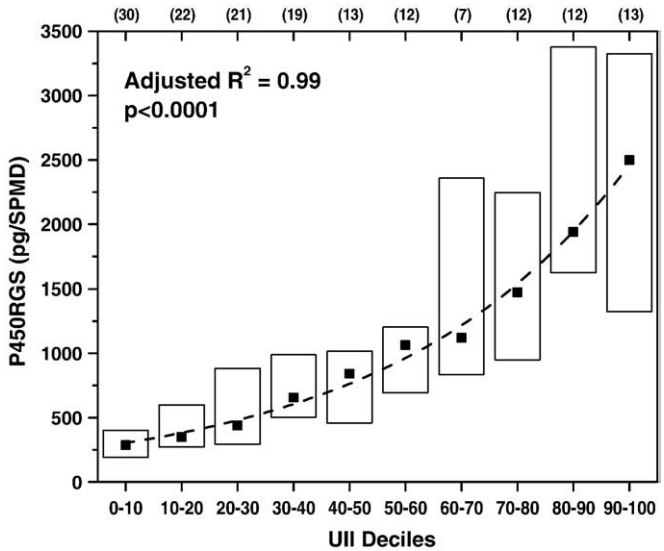

Fig. 3. Box plots of P450RGS assay results (TEQ) in SPMD extracts shown by deciles of urban intensity index (UII) in streams from six metropolitan areas of the US. Numbers in parentheses indicate the number of samples analyzed for each interval.

3.2. Chemical analysis

Results of the Fluoroscan from all six metropolitan areas by UII deciles also show a response at the lowest level of urbanization (Fig. 4). Out of 30 streams with a UII from 1–10 there were only two sites (7%) where the fluorescence was below the LOD (≈1 μg/L of pyrene). The response of median Fluoroscan values to an urban gradient best fit an exponential curve and had a relatively good correlation with UII (adjusted $R^2 = 0.85$, $p < 0.0001$). Because the Fluoroscan analysis primarily responds to PAHs (Johnson et al., 2004) this indicates that PAHs are present even in streams with very low urbanization at concentrations that can be detected by measuring fluorescence. The more mutagenic PAHs (≥4 rings) are more difficult to detect in water because of their low solubility requiring large volumes of water to be sampled (Lin et al., 1994). However, even in spite of the low solubility (<10 μg/L) of mutagenic PAHs, the sampling capabilities of the mini SPMD and the sensitivity of the Fluoroscan enabled the detection of PAHs even in streams with very low urban UII. Also, Fluoroscan has an advantage in assessing water quality along an urban gradient because it cumulatively responds to all fluorescent PAHs. However, the response is likely primarily due to the PAHs with lower log K_{ow}s (i.e., naphthalene, phenanthrene, fluoranthene, and pyrene) which are commonly present at the highest concentrations in the water column.

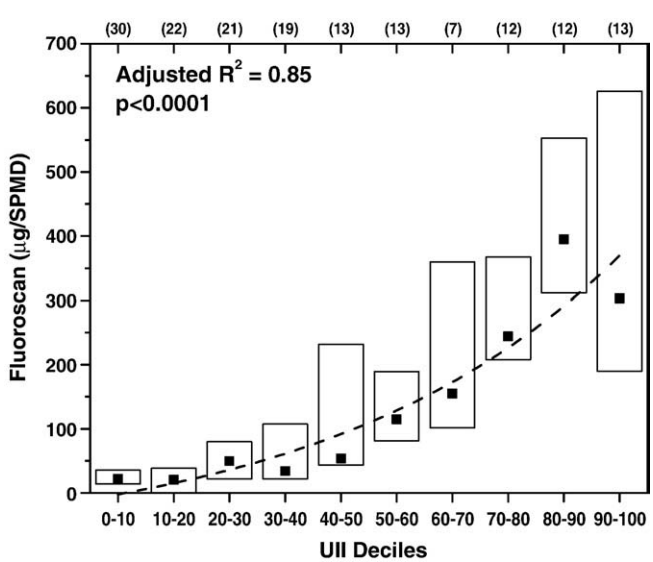

Fig. 4. Box plots of Fluoroscan results (Pyrene Index) in SPMD extracts shown by deciles of urban intensity index (UII) in streams from six metropolitan areas of the U.S. Numbers in parentheses indicate the number of samples analyzed for each interval.

PAHs are ubiquitous in the environment, found even in streams with very low urbanization because they occur from both natural sources (such as from volcanic activity, combustion of organic material during wildfires, and microbial, algal, and macrophyte synthesis) as well as anthropogenic sources (such as vehicle exhausts, oil spills, and fossil fuel power plants) (Eisler, 1987). So, even in streams with very little urbanization, automotive road and bridge crossings as well as railroad tracks can contribute PAHs from exhaust, and oil and petroleum leaks. Sealcoats used on driveways, roads, and parking lots are also a potential source of PAHs to streams (Mahler et al., 2005) and weren't able to be quantified in the UII calculation. Thus, between natural sources and anthropogenic sources the PAH concentration appears to be high enough in most streams that they can be detected by fluorescence in a mini SPMD extract. However the Fluoroscan method does not quantify and identify individual PAHs. Typically that would require more expensive and sophisticated methods such as high performance liquid chromatography coupled with programmable fluorescence detection (Williamson et al., 2002), gas chromatography coupled with a mass spectrometry flame ionization detector, or photoionization detection (Petty et al., 2000; Alvarez et al., 2008).

The total number of compounds detected in this study was 73 out of the 140 targeted (Table 1). A complete list of targeted compounds their LOQ, what compounds were detected in each streams and a discussion of these results can be found in Bryant and Goodbred (2008) and are only briefly discussed here. Twenty-four compounds were detected in at least 25% of streams. These include PCA, PAHs, insecticides, herbicides, musk fragrances, WWTP compounds, and flame retardants (Bryant and Goodbred, 2008). Many of these compounds are toxic to aquatic biota when concentrations exceed certain thresholds. This wide range of compounds detected in urban streams across the United States using mini SPMDs demonstrates their utility to help identify HOCs that could be of concern for water quality and aquatic biota.

There were only four streams, all in the Dallas–Fort Worth area, where none of the 140 target compounds were detected in mini-SPMD extracts. The rest of the streams ($N = 156$) had at least one of the targeted compounds detected. This shows that even in streams with minimal urbanization mini SPMDs were able to concentrate sufficient amounts of some compounds to be detected, although using full sized SPMDs may have resulted in a greater number of detections. Streams in the Raleigh area had the highest number of compounds detected (49) while streams in Dallas–Fort Worth TX and Portland OR had the lowest number of compounds detected (36 and 39, respectively), (Table 1). The total number of compounds detected in mini SPMD extracts in this study from six U.S. metropolitan areas (range 36–49) was comparable to a comprehensive study in the

Table 1
Number of hydrophobic organic compounds[a] detected in mini SPMD extracts from streams in six metropolitan areas of the U.S.

Metropolitan area	# Streams	Minimum	Median	Maximum	Total
Atlanta,GA	28	4	15	29	48
Raleigh, NC	30	2	19	32	49
Denver, CO	21	5	17	28	40
Dallas–Fort Worth, TX	24	0	5	24	36
Portland, OR	28	1	6	19	39
Millwaukee–Green Bay, WI	29	1	8	28	48
National	160	0	11	32	73

[a] Out of 140 target compounds.

Please cite this article as: Goodbred SL, et al, How useful are the "other" semipermeable membrane devices (SPMDs); the mini-unit (15.2 cm long)? Sci Total Environ (2009), doi:10.1016/j.scitotenv.2009.02.037

ARTICLE IN PRESS

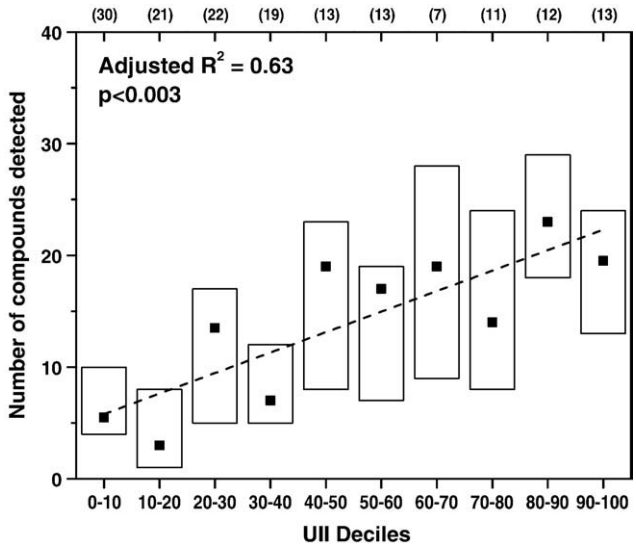

Fig. 5. Box plots of number of hydrophobic organic compounds (HOCs) detected in SPMD extracts shown by deciles of urban intensity index (UII) in streams from six metropolitan areas of the US. Numbers in parentheses indicate the number of samples analyzed for each interval.

Balkan region of Eastern Europe on Lake Shkodra/Skadar where 39 HOCs were found using full sized SPMDs (Rastall et al., 2004). Streams in the lowest UII decile (0–10) had a median of over 5 compounds detected while those in the highest UII decile (90–100) had a median of almost 20 compounds detected (Fig. 5). There was a significant linear correlation (adjusted $R^2 = 0.63$, $p > 0.003$) between the number of compounds detected in streams and UII deciles. This response was both different (linear and not exponential) and not as strong as that between urbanization and the P450RGS assay and the Fluoroscan.

There are several reasons to explain the different responses for the number of HOCs by analytical chemistry (linear) and P450RGS and Fluoroscan response (exponential) to urbanization. Analytical chemistry with GC/MS for 140 HOCs provides a more robust chance of responding directly to increases in urbanization since it measures a wider variety of compounds that are associated with urbanization. The P450RGS and Fluoroscan specifically respond to more hydrophobic (log $K_{ow} > 4$) compounds that can be effectively bound to soil in riparian areas of streams with lower urbanization therefore reducing the response. Also at low levels of urbanization loading of some compounds like PAHs to streams can be offset by photo and microbial degradation. At higher levels of urbanization there are less riparian areas to adsorb hydrophobic compounds so the P450RGS and the Fluoroscan respond exponentially after a threshold urbanization value is reached (Figs. 3 and 4). In contrast, the total number of compounds detected in SPMD extracts along an urban gradient includes HOCs with lower log K_{ow}s (<4) than PAHs and other AhR compounds. These more hydrophilic compounds have lower tendencies to bind to soil or sediment so that the amount of buffer area has less influence on concentrations in streams. Therefore, the total number of compounds tends to increase linearly with urbanization even at low levels (Fig. 5).

Table 2
Minimum quantifiable water concentrations for selected hydrophobic organic compounds assuming a 30 day deployment with mini SPMDs compared to toxicity benchmark values.

Compound	log K_{ow}	Sampling rate R_s (L/d)[a]	Minimum quantifiable concentration (ng/L)[b]	Aquatic health benchmark (ng/L)	Human health benchmark (ng/L)
Polycyclic aromatic hydrocarbons (PAHs)					
Anthracene	4.54	0.48	0.087	1.3[c]	200,000[d]
Benzo[*a*]anthracene	5.91	0.53	0.079	27[c]	200,000[d]
Benzo[*a*]pyrene	6.35	0.53	0.079	27[c]	200,000[d]
Fluoranthene	5.20	0.60	0.069	6160[c]	200,000[d]
Naphthalene	3.45	0.32	0.13	23,400[c]	200,000[d]
Phenanthrene	4.46	0.63	0.066	3230[c]	200,000[d]
Polychlorinated biphenyls (PCBs)					
PCB 77	6.36	0.42	0.099	14[e]	500[d]
PCB 78	6.35	0.63	0.066	14[e]	500[d]
PCB 79	6.42	0.73	0.064	14[e]	500[d]
PCB 81	6.36	0.53	0.079	14[e]	500[d]
PCB 126	6.89	0.32	0.13	14[e]	500[d]
PCB 127	6.95	0.23	0.18	14[e]	500[d]
PCB 169	7.42	0.30	0.14	14[e]	500[d]
Dioxins and furans					
2,3,7,8-TCDD	6.53	0.37	0.11	0.011[f]	0.03[d]
OCDF	7.97	0.07	0.60	20,400[c]	NA
Organochlorine pesticides					
trans-chlordane	5.38	0.40	0.19	4.3[e]	2,000[d]
Dieldrin	4.60	0.22	0.136	56[e]	2000[g]
p,p′-DDT	5.47	0.33	0.10	1[e]	100[g]
Endrin	4.63	0.38	0.11	36[e]	2000[d]
Lindane (γ-HCH)	3.71	0.12	0.35	80[c]	200[d]
Heptachlor epoxide	4.51	0.22	0.19	3.8[e]	200[d]

Bold compound has minimum detectable water concentrations using 30 day deployment of mini.
SPMDs higher than both aquatic and human health benchmarks/criteria.

[a] From Huckins et al. (2006); R_s divided by 6 to get sampling rate for mini SPMD; for PAHs and pesticides *R*s determined at 10 °C and flow of 0.004 cm/s and for PCBs, dioxins, and furans at 11 °C and 8 cm/s.

[b] Using modified equation from Huckins et al. (2006); $C_m = \mathrm{IQL}(V_i)/R_s t P_r E_t$ where IQL is instrument quantitative limit (1 ng/mL) V_i, injection volume of 0.001 mL C_m is minimal concentration (ng/L) detectable in a mini SPMD, R_s is sampling rate (L/d) adjusted for mini SPMD, t is time of deployment (30 days), P_r is overall method recovery (0.8), and E_t is the fraction of total sample extract injected into instrument for chemical analysis (0.001).

[c] Chronic freshwater quality benchmark (Suter, 1996).

[d] Maximum concentration level in drinking water (U.S. EPA, 2008).

[e] Chronic freshwater criteria (U.S. EPA, 2008).

[f] No effect level (Grimwood and Dobbs, 2006).

[g] Human health screening benchmarks (Toccalino et al., 2007).

Please cite this article as: Goodbred SL, et al, How useful are the "other" semipermeable membrane devices (SPMDs); the mini-unit (15.2 cm long)? Sci Total Environ (2009), doi:10.1016/j.scitotenv.2009.02.037

Table 3
Comparison of the relative costs[a] between mini SPMD and full sized SPMD.

	Mini (15.2 cm)	Full size (91.4 cm)
SPMD[b]	$15.00	$60.00
Deployment device	$8.00[c]	$100.00[d]
Dialysis	$75.00	$115.00
Sub-total	$98.00	$275.00
GPC cleanup[e]	$110.00	$150.00
Total	$208.00	$425.00

[a] July 2008 costs from EST (http://www.est-lab.com/spmd.php).
[b] Constructed with ultra high pure triolein.
[c] Deployment device is disposable.
[d] Rental for 1 month.
[e] Gel permeation chromatographic (GPC) cleanup commonly used with SPMDs prior to chemical analysis and/or microscale assays.

Pentachloroanisole (PCA), a breakdown product of the fungicide pentachlorophenol, was detected in mini SPMD extracts from 71% of all streams, and 50% of streams at the lowest UII deciles. Pentachlorophenol use is restricted and although not available to the public it is still used as a wood preservative in utility poles, railroad ties, and bridge pilings (Bryant et al., 2007). PCA was frequently detected in streams across the United States as reported by Gilliom et al. (2006) and has also been detected in SPMDs below a waste water treatment plant (WWTP) in Arizona (Barber et al., 2003).The prevalence of PCA in this study can be partially explained because of its widespread use and a very low LOD (2 ng/SPMD). Because PCA has a relatively low solubility in water (200 µg/L), a high log K_{ow} (5.7) and a very high bioconcentration factor (10^4) in fish it is usually monitored for in bed sediment and fish tissue (Nowell et al., 1999). Even so the mini SPMDs were sensitive enough in this study to detect this compound in water from most streams.

3.3. Assessing potential toxicity

One of the advantages of using passive samplers like SPMDs in environmental studies is that they have the ability to accumulate larger amounts of HOCs than traditional discrete water samples. This is particularly useful for HOCs that have lower water solubility or those that are toxic at very low concentrations. Because a mini SPMD has a theoretical water sampling rate about one-sixth that of a full sized SPMD, they could have a disadvantage in assessing potential toxicity of very toxic compounds at low concentrations. To evaluate how much of an issue this might be, a theoretical calculation was made for the minimum quantifiable concentration of selected HOCs from mini SPMDs deployed for 30 days (Table 2). These results showed only one compound, 2,3,7,8-TCDD, out of 21, had a minimum quantifiable concentration in water that was above both an aquatic and human health toxicity benchmark. Even though these results are based on theoretical calculations, and included several assumptions, they do demonstrate that mini SPMDs can detect HOCs at low enough concentrations to assess potential toxic concentrations of many compounds. Not only are the minimum quantifiable water concentrations for these 20 HOCs below screening toxicity benchmarks but in most cases they are at least one order of magnitude below.

When trying to determine the potential toxicity in a stream the selection of SPMD size depends on project objectives and consideration of other factors such as deployment time, temperature, and water flow. The two questions that should be answered are: (1) does the chemical of concern have a benchmark/threshold toxicity level or water quality criterion and if so has the lowest environmental concentration of concern been established, and (2) will SPMD sampling rates provide adequate mass of the target compound/s for analysis or toxicity assessment? Question 1 can be answered for 21 HOCs, where both toxicity benchmarks and sampling rates are available, using the information presented in Table 2. For 20 of these HOCs the answer to the second, more critical question is yes, based on comparing the minimal quantifiable water concentration of a mini SPMD deployed for 30 days to a toxicity benchmark. Generally a smaller SPMD will work in environmental conditions or with specific compounds that have higher sampling rates and with compounds that have higher toxicity benchmark concentrations. However, because many HOCs are not very water soluble and more of a concern in bed sediment or aquatic biota, only 3 (anthracene, dieldrin and diazinon) had concentrations that were potentially toxic to aquatic biota in streams from six metropolitan areas using mini SPMDs (Bryant et al., 2007). Therefore, to better assess potential toxicity of HOCs in streams, bed sediment and/or aquatic biota should be sampled along with using passive samplers.

3.4. General considerations

It is worthwhile to consider whether cost effective measures can be implemented while still achieving specific objectives of a study. Table 3 compares the cost of using a mini SPMD and a full sized SPMD. Assuming both dialysis and GPC cleanup are done when using the mini SPMD the cost is less than half of that when using a full sized SPMD. The savings are reduced if the deployment device for the full sized SPMD is purchased and reused; however even then the savings are still over 36% when using mini SPMDs. Beside cost there are several other advantages of using mini SPMDs compared to full sized SPMDs (Table 4). An obvious advantage of the mini SPMDs is their small size (Fig. 1) which enables them to be deployment in very shallow water (>0.25 m) typically found in small 1st or 2nd order streams. Their small size also makes them less conspicuous, and therefore less susceptible to possible vandalism, which is a very important consideration. Due to the low limit of quantification of many microscale assays, mini SPMDs are usually effective even though they will accumulate less total chemical mass than the full sized SPMD. However, the deployment devices for mini SPMDs are significantly less durable therefore increasing the possibility of damage or loss due to flooding and/or debris if they are deployed in an unprotected area. The full size SPMD are a better choice when a compound is present at a very low concentration (pg/L range) because the chance of detecting the compound is increased due to larger volumes of water sampled.

4. Conclusions

Mini SPMDs along with a microscale assay and chemical analysis were shown to be useful in environmental studies in urban streams from six metropolitan areas of the U.S. and for assessing the presence and potential toxicity of HOCs. This approach identified a wide variety of HOCs in urban streams and sampled sufficient volumes of water to find HOCs even in streams with low urbanization. PAHs and other AhR compounds were the most significant groups of HOCs identified in urban streams. A comparison with the larger full sized SPMDs showed that the mini SPMDs have several distinct advantages although limitations were also identified. The biggest advantages of mini SPMDs are their lower cost, smaller size, and reduced chance of vandalism. Mini SPMDs have an application in a wide array of environmental settings

Table 4
Comparison of advantages (denoted by X) of SPMD size in environmental studies.

Issue	Mini SPMD (15.2 cm)	Full size SPMD (91.4 cm)
Lower cost	X	
Shallow water (>0.25 m)[a]	X	
Minimize vandalism	X	
Contaminant gradient studies	X	X
Assessing contaminated sites	X	X
Compounds at very low levels		X
Conditions of low sampling rate (i.e. cold water temp)		X
Conditions of high sampling rate	X	X
Chance of detecting maximum number of compounds		X

[a] Using commercially available deployment devices.

Please cite this article as: Goodbred SL, et al, How useful are the "other" semipermeable membrane devices (SPMDs); the mini-unit (15.2 cm long)? Sci Total Environ (2009), doi:10.1016/j.scitotenv.2009.02.037

ARTICLE IN PRESS

and applications and perform quite well in urban settings. Environmental studies considering SPMDs should carefully evaluate the two commercially available sizes and select the one that best meets the planned goals and objectives of the study.

Acknowledgements

This study was a collaboration between two programs of the U.S. Geological Survey; the Contaminant Biology Program and the National Water Quality Assessment Program. Both the field and laboratory work involved many USGS biologists, chemists, hydrologists, and technicians and their dedication to this project is greatly appreciated. Reviews by Lari Knochenmus, Elena Nilsen, Jennifer Morace, Michael Lico and two anonymous journal reviewers improved the manuscript. Thanks to James Falcone for providing Fig. 2.

References

Alvarez DA, Cranor WL, Perkins SD, Clark RC, Smith SB. Chemical and toxicological assessment of organic contaminants in surface water using passive samplers. J Environ Qual 2008;37:1024–33.

Anderson JW, Hartwell SI, Hameedi MJ. Regional comparisons of coastal sediment contamination detected by a biomarker (P450RGS: EPA method 4425). Environ Sci Technol 2005;39:17–23.

Ang CY, Inouye LS, McCant DD, McFarland VA. Protocols for a rapid clean-up/extraction procedure and an improved P450RGS dioxin screening assay for sediments, 2007, DOER Technical Notes Collection (ERDC TN-DOER-C10). Vicksburg, MS: U.S. Army Engineer Research and Development Center; 2000. last accessed October 23, 2007 at http://www.wes.army.mil/el/dots/doer.

Barber LB, Steffanie HK, Brown KG, Taylor HE, Antweiler RC, Peart DB, et al. Organic and trace element contaminants in water, biota, sediment, and semipermeable membrane devices at the Tres Rios Treatment Wetlands, Phoenix, Arizona. Water-Resources Investigations Report 03-4129. Denver, CO: U.S. Geological Survey; 2003. p. 89. http://pubs.er.usgs.gov/usgspubs/wri/wri034129.

Brown LR, Gray RH, Hughes RM, Meador MR. Introduction to effects of urbanization on stream ecosystems. In: Brown LR, Gray RH, Hughes RM, Meador MR, editors. Effects of urbanization on stream ecosystems. SymposiumBethesda, MD: American Fisheries Society; 2005. p. 1–3.

Bryant WB, Goodbred SL. The response of hydrophobic organics and potential toxicity in streams to urbanization of watersheds in six metropolitan areas of the United States. Environ Monit Assess 2008;146.

Bryant WB, Goodbred SL, Leiker TJ, Inouye L, Johnson TB. Use of chemical analysis and assays of Semipermeable Membrane Devices extracts to assess the response of bioavailable organic pollutants in streams to urbanization in six metropolitan areas of the United States. Scientific Investigation Report 2007-5113. Denver, CO: U.S. Geological Survey; 2007. 46pp., 2app. http://pubs.usgs.gov/sir/2007/5113/.

Cho YM, Smithenry DW, Ghosh U, Kennedy AJ, Millward RN, Bridges TS, et al. Field methods for amending marine sediment with activated carbon and assessing treatment effectiveness. Mar Environ Res 2007;64:541–55.

Coles JF, Cuffney TF, McMahon G, Beaulieu KM. The effects of urbanization on the biological, physical, and chemical characteristics of coastal New England streams. Professional Paper 1695. Denver, CO: U.S. Geological Survey; 2004. 47pp. http://pubs.er.usgs.gov/usgspubs/pp/pp1695.

Cuffney TF, Zappia H, Giddings EMP, Coles JF. Effects of urbanization on benthic macroinvertebrate assemblages in contrasting environmental settings—Boston, Massachusetts; Birmingham, Alabama; and Salt Lake City, Utah. In: Brown LR, Gray RH, Hughes RM, Meador MR, editors. Effects of urbanization on stream ecosystems. SymposiumBethesda, Maryland: American Fisheries Society; 2005. p. 361–407.

Echols KR, Gale RW, Schwartz TR, Huckins JN, Wiliams LL, Meadows JC, et al. Comparing polychlorinated biphenyl concentrations and patterns in the Saginaw River using sediment, caged fish, and semipermeable membrane devices. Environ Sci Technol 2000;34:4095–102.

Eisler R. Polycyclic aromatic hydrocarbon hazards to fish, wildlife, and invertebrates—a synoptic review. Biological Report 85(1.11). Laurel, MD: U.S. Fish and Wildlife Service; 1987. 81 pp.

Falcone JA, Stewart JS, Sobieszcyk S, Dupree JA, McMahon G, Buell GR. A comparison of natural and urban characteristics and the development of urban intensity indices across six geographic settings. Scientific Investigations Report 2007-5123. U.S. Geological Survey; 2007. 133 pp. http://pubs.er.usgs.gov/usgspubs/sir/sir20075123.

Gilliom RJ, Barbash JE, Crawford CG, Hamilton PA, Martin JD, Nakagaki N, et al. The quality of our nation's waters-pesticides in the Nation's streams and ground water, 1992–2001. Circular 1291. Reston, VA: U.S. Geological Survey; 2006. 172 pp. http://pubs.er.usgs.gov/usgspubs/cir/cir1291.

Gregory MB, Bryant WL. Effects of urbanization on stream ecosystems in the piedmont ecoregion of Georgia and Albama—A study design: in Proceedings of the 2003 Georgia Water Resources Conference, Athens, Georgia; 2003. 5 pp.

Gregory MB, Calhoun DL. Physical, chemical, and biological responses of streams to increasing watershed urbanization in the piedmont ecoregion of Georgia and Alabama, 2003. Scientific Investigations Report 2006-5101B. Denver, CO: U.S. Geological Survey; 2007. 104 pp. http://pubs.er.usgs.gov/usgspubs/sir/sir20065101B.

Grimwood M, Dobbs T. A review of the aquatic ecotoxicity of polychlorinated dibenzo-*p*-dioxins and dibenzofurans. Environ Toxicol Water Qual 2006;10:57–75.

Huckins JN, Tubergen MW, Manuweera GK. Semipermeable membrane devices containing model lipid—a new approach to monitoring the bioavailability of lipophilic contaminants and estimating the bioconcentration potential. Chemosphere 1990;20:533–52.

Huckins JN, Manuweera GK, Petty JD, Macka D, Lebo JA. Lipid-containing semipermeable membrane devices for monitoring organic contaminants in water. Environ Sci Technol 1993;27:2489–96.

Huckins JN, Petty JD, Lebo JA, Almeida FV, Booij K, Alvarez DA, et al. Development of the permeability/performance reference compound approach for in situ calibration of semipermeable membrane devices. Environ Sci Technol 2002;36:85–91.

Huckins JN, Petty JD, Booij K. Monitors of Organic Chemicals in the Environment — Semipermeable Membrane Devices. New York: Springer; 2006. 223 pp.

Hwang H, Foster GD. Characterization of polycyclic hydrocarbons in urban storm water runoff flowing into the tidal Anacostia River, Washington, DC, USA. Environ Pollut 2006;140:416–26.

Johnson BT. Microtox toxicity test system—new developments and applications. In: Wells PG, Lee K, Blaise C, editors. Microscale testing in aquatic toxicology—Advances, techniques and practice. Boca Raton, FL: CRC Lewis; 1998. p. 201–18.

Johnson BT, Petty JD, Huckins JN, Lee K, Gauthier J. Hazard assessment of a simulated oil spill on intertidal areas of the St. Lawrence River with SPMD-TOX. Environ Toxicol 2004;19:329–35.

Lin ELC, Cormier SM, Racine RN. Synchronous fluorometric measurement of metabolites of polycyclic aromatic hydrocarbons in the bile of brown bullhead. Environ Toxic Chem 1994;13:707–15.

Mahler BJ, Van Metre PC, Bashara TJ, Wilson JT, Johns DA. Parking lot sealcoat—an unrecognized source of urban PAHs. Environ Sci Technol 2005;39:5560–6.

McCarthy K. Assessment of the usefulness of semipermeable membrane devices for long-term monitoring in an urban slough system. Environ Monit Assess 2006;118:293–318.

McMahon G, Cuffney TF. Quantifying urban intensity in drainage basins for assessing stream ecological conditions. J Am Water Res Assoc 2000;36:1247–61.

Moring JB, Rose DR. Occurrence and concentrations of polycyclic aromatic hydrocarbons in semipermeable membrane devices and clams in three urban streams of the Dallas–Fort Worth metropolitan area, Texas. Chemosphere 1997;34:551–66.

Nowell LH, Capel PD, Dileanis PD. Pesticides in stream sediment and aquatic biota, distribution, trends, and governing factors. New York: Lewis; 1999. 1001pp.

Petty JD, Orazio CE, Huckins JN, Gale RW, Lebo JA, Meadows JC, et al. Considerations involved with the use of semipermeable membrane devices for monitoring environmental contaminants. J Chromatogr 2000;879:83–95.

Rastall AC, Neziri A, Vukovic Z, Jung C, Mijovic S, Hollert H, et al. The identification of readily bioavailable pollutants in Lake Shkodra/Skadar using semipermeable membrane devices (SPMDs), bioassays and chemical analysis. Environ Sci Pollu Res 2004;44:1372–9.

Rosen MR, Rowe TG, Goodbred SL, Shipley DO, Arufe JA. Importance of land use, streamflow, and water quality on stream toxicity in the Lake Tahoe and Truckee River watersheds. In: Hughes RM, Wang L, Seelbach PM, editors. Landscape influences on stream habitats and biological assemblages. SymposiumBethesda, MD: American Fisheries Society; 2006. p. 129–49.

Rowe TG, Rosen MR, Goodbred SL, Shipley SL, Aruge JA. Relation between urbanization and relative toxicity of semipermeable membrane device extracts in the Lake Tahoe Basin and Truckee River watershed, Nevada and California. J Nev Water Res Assoc 2005;2:58–89.

Saito L, Rosen MR, Chandra S, Fritsen CH, Arufe JA, Redd C. Using semipermeable membrane devices and stable nitrogen isotopes to detect anthropogenic influences on the Truckee River, USA. Environ Eng Sci 2008;25:585–600.

Suter II GW. Toxicological benchmarks for screening contaminants of potential concern for effects on freshwater biota. Environ Toxic Chem 1996;15:1232–41.

Tate CM, Cuffney TF, McMahon G, Giddings EMP, Zappia H. Use of an urban intensity index to assess urban effects on streams in three contrasting environmental settings. In: Brown LR, Gray RH, Hughes RM, Meador MR, editors. Effects of urbanization on stream ecosystems. Symposium. Bethesda, MD: American Fisheries Society; 2005. p. 291–315.

Toccalino PL, Norman JE, Booth NL, Zogorski JS. Health-based screening levels: A tool for evaluating what water-quality data may mean to human health: U.S. Geological Survey, National Water-Quality Assessment Program, accessed November 21; 2007. http://water.usgs.gov/nawqa/HBSL/.

U.S. Environmental Protection Agency. Current National Recommended Water Quality Criteria, accessed February 18; 2008. http://www.epa.gov/waterscience/criteria/wqctable/index.html.

Wang Y, Wang C, Wang Z. Uptake of moderately hydrophobic chlorophenols from water by semipermeable membrane devices (SPMDs) and by goldfish (*Crassius auratus*). Chemosphere 1998;37:327–39.

Wang YZ, Wang M, Ma M, Wang C, Mo Z. Monitoring priority pollutants in a sewage treatment process by dichloromethane extractions and triolein-semipermeable membrane devices (SPMD). Chemosphere 2001;43:339–46.

Wells PG, Lee K, Blaise C. Microscale testing in Aquatic Toxicology: Advances, Techniques, and Practices. Boca Raton, FL: CRC; 1998. 642 pp.

Williamson KS, Petty JD, Huckins JN, Lebo JA, Kaiser EM. HPLC-PFD determination of priority pollutant PAHs in water, sediment, and semipermeable membrane devices. Chemosphere 2002;49:703–15.

Zimmerman JR, Ghosh U, Millward RN, Bridges TS, Luthy RG. Addition of carbon sorbents to reduce PCB and PAH bioavailability in marine sediments: physico-chemical tests. Environ Sci Technol 2004;38:5458–64.

Please cite this article as: Goodbred SL, et al, How useful are the "other" semipermeable membrane devices (SPMDs); the mini-unit (15.2 cm long)? Sci Total Environ (2009), doi:10.1016/j.scitotenv.2009.02.037