Environ. Sci. Technol. **1998**, *32,* 1538−1543

Passive Air Sampling of PCBs: Field Calculation of Atmospheric Sampling Rates by Triolein-Containing Semipermeable Membrane Devices

WENDY A. OCKENDEN,*,† HARRY F. PREST,‡ GARETH O. THOMAS,† ANDY SWEETMAN,† AND KEVIN C. JONES†

Environmental Science Division, Institute of Environmental and Natural Sciences, Lancaster University, Lancaster, LA1 4YQ, U.K., and Long Marine Laboratory, University of California—Santa Cruz, 100 Shaffer Road, Santa Cruz, California 95060

Triolein-containing standard U.S. Geological Survey (USGS) designed semipermeable membrane devices (SPMDs) were deployed in the field alongside conventional active air sampling equipment for durations of up to 3 months. A high degree of reproducibility between duplicate samples and linear uptake of polychlorinated biphenyls (PCBs) by the USGS SPMDs were observed. USGS SPMD air sampling rates were calculated for a range of PCBs. Sampling rates were found to be higher in winter than in summer and in general increased with increasing chlorination and decreased with increasing ortho-substitution. The sampling rate for the sum of the ICES congeners (IUPAC congeners 28, 52, 101, 118, 138, 153, and 180) was found to be 1.9 m^3 day^{-1} $SPMD^{-1}$ in summer (mean temperature 18 °C) and 7.6 m^3 day^{-1} $SPMD^{-1}$ in winter (mean temperature 4 °C). In a separate study USGS SPMDs were deployed for 2 months, and sequestered concentrations and the aforementioned sampling rates were used to calculate atmospheric concentrations. Excellent agreement was found between air concentrations calculated from the SPMDs and active samplers. The immense potential of these lipid-containing USGS SPMDs for time-integrated passive atmospheric monitoring of gas-phase persistent organic pollutants (POPs), for example, in remote areas or for spatial mapping near potential sources, is confirmed.

Introduction

High-volume air samplers (HiVols) have been used for several years to monitor atmospheric concentrations of persistent organic pollutants (POPs). These systems use a pump to draw air through some form of filter (generally glass fiber) to collect particulate species followed by an absorbent trap where gaseous phase species are collected. Materials that have been used for the absorbent traps include polyurethane foam (PUF) plugs (*1*−*3*), XAD resins (*4*), and Tenax (*5*). There are several acknowledged artifacts with this form of air sampling. Such problems include volatilization of compounds from the particulate matter held on the filter (blow-off), "breakthrough" of analytes from the absorbent trap, and adsorption of vapor-phase species onto the filter material. In addition, requirements for remote atmospheric sampling stations are often compromised by the need for an electrical supply to operate HiVols and other active air sampling equipment, such as diffusion denuders. Development of passive air samplers would alleviate this latter major practical problem.

Passive air sampling techniques that have been developed include adsorption onto oil-covered plates and diffusion tubes and absorption of compounds by semipermeable membrane devices (SPMDs). The major drawback of the diffusion tubes and the plates is that they are unable to sample sufficient air for detection of compounds that are present in the atmosphere at low concentrations. The plates also sample wet deposition. Absorption techniques sample larger air volumes and concentrate target compounds, thereby permitting detection of trace level species. SPMDs consist of a sequestering solvent system enclosed by a polymeric membrane. One such system, which was developed by Huckins et al. (*6*) at the U.S. Geological Survey (USGS), Columbia, MO, uses a thin film of the synthetic neutral lipid triolein as the solvent system enclosed in a thin-walled (75−90 μm) polyethylene tubing. These USGS SPMDs were initially developed to monitor POP concentrations in water bodies, for which very high replicate reproducibility has been found and sampling rates using constant concentration water exposures have been calculated (*7*). Following the discovery of abnormally high concentrations in field and laboratory blanks, the potential of USGS SPMDs for use as passive air samplers was realized (*8*). In a laboratory study, it was found that under ambient conditions, a composite of three triolein-containing half-standard USGS SPMDs (total of 1.4 g of triolein) could sequester atmospheric polychlorinated biphenyls (PCBs) from 6.5 m^3 of air per day (*8*). In a separate study, Prest et al. (*9*) demonstrated the application of SPMDs for detection of POPs in the field by exposing USGS SPMDs to relatively clean coastal air. Atmospheric concentrations of HCHs, DDTs, and HCB were calculated using the sampling rates inferred from water exposures.

Despite the promising results reported by Prest et al. (*9*) and the numerous attractive qualities of USGS SPMDs (i.e., their long-term stability, low cost, and ease of deployment), there are only limited published data pertaining to the use of these passive sampling tools for field air monitoring. This could be because POP sampling rates have not been assessed in the field and comparison with more accepted air sampling methodologies has not been carried out. Therefore, the use of this technology is limited to giving qualitative/semiquantitative results. Data interpretation is limited to assessment of analyte profile differences between sites, and it is difficult to infer actual atmospheric concentrations.

Results are presented here from a study where USGS SPMDs were deployed alongside a conventional HiVol system in the field in the summer (temperature range 7−31 °C; mean 18 °C) and winter (temperature range −6−18 °C; mean 4 °C). Uptake kinetics for PCBs were assessed and effective air sampling rates calculated and reported. In a separate study, a third set of USGS SPMDs was deployed independently for 2 months. Results from the initial study were used to calculate atmospheric concentrations, and these estimated concentrations were compared with concentrations as measured by a HiVol.

---

* To whom correspondence should be addressed. Phone: (01524)-65201; fax: (01524)593985.

† Lancaster University.

‡ University of California—Santa Cruz.

S0013-936X(97)01020-1 CCC: $15.00

Methods

Triolein-Containing USGS SPMDs. Standard triolein-containing USGS SPMDs [80−90 cm by 2.5 cm, 75 μm membrane, each containing 1 mL (0.915 g) of triolein] were obtained from Environmental Sampling Technologies, St. Joseph, MO.

(A) Time-Course Study. In the summer of 1995, 12 standard USGS SPMDs were deployed at a semirural meteorological field station site near Lancaster University. The SPMDs were hung horizontally inside aluminum Stevenson Screens (aluminum boxes with louvered sides; internal measurements 30 cm × 30 cm × 30 cm) to protect them from wet deposition and sunlight while allowing movement of air across the samplers. A time-course experiment was established where two USGS SPMDs were collected after 15, 29, 45, 59, 71, and 88 days. The two triolein SPMDs collected on days 15, 29, and 45 were composited for these time intervals and subsequently treated as one sample to ensure that sequestered analytes would be above detection limits. Two field blank USGS SPMDs were also taken. Samples were frozen immediately on retrieval and stored in sealed, solvent-cleaned paint cans at −17 °C until extraction. Care was taken at all steps of deployment and collection to handle the SPMDs by the polyethylene endloops and thus ensure that the lipid-containing portion of the samplers was not touched.

A similar experiment was set up in the winter of 1995/1996 where 10 standard USGS SPMDs were deployed, with collection times of 14, 26, 39, 61, and 84 days. As above, to facilitate detection of analytes, duplicate samples were composited on the first three sampling occasions. Again, two field blanks were taken.

(B) Two-Month Deployment Study. Eight standard USGS SPMDs were deployed at the rural site for 8 weeks in the summer of 1996. The samples were housed in Stevenson Screens as described above. Four USGS SPMDs were taken as field blanks. Four of the exposed SPMDs were composited to make two replicates for the 56-day exposure, and similarly the four blanks were separately composited.

(C) Extraction and Cleanup. Exterior lipid, waxes, and any particulate matter were removed from the samples by adding 100 mL of hexane to the cans containing the USGS SPMDs. The can lid was replaced, and the sample was shaken vigorously for 20 s. This extract was separately analyzed and is subsequently referred to as the exterior fraction of the sample. The SPMD was removed, and the exterior fraction and the inside of the SPMD were spiked with a [$^{13}C_{12}$]PCB recovery standard in isooctane. The recovery standard contained [$^{13}C_{12}$]PCBs 28, 52, 101, 138, 153, 180, and 209 (IUPAC Nos. used throughout), and 2.5 ng of each congener was spiked into each sample. After spiking, the SPMD was resealed, and the sequestered analytes were extracted by dialysis in hexane. Dialysis was performed in 250-mL glass jars with aluminum foil-lined lids. Each SPMD was dialyzed in the dark for 24 h in 130 mL of hexane. The solvent was then refreshed and the sample dialyzed for a further 24 h. The dialysates were combined (referred to hereafter as USGS SPMD interior fraction). The volumes of the exterior and interior fractions were reduced using rotary evaporation to approximately 2 mL, and both fractions were cleaned up by silica chromatography followed by size exclusion chromatography and silica fractionation in modification of a method developed by Prest (*10*) for SPMD extracts.

Activated silica gel columns were prepared [25 mm i.d.; 15 g of silica gel (Merck grade 60) activated at 350 °C for 16 h] and rinsed with 100 mL of dichloromethane. Samples were quantitatively transferred to the column and eluted with 130 mL of dichloromethane. Eluent volume was reduced by rotary evaporation and blowdown under nitrogen to ca. 1 mL and ampuled.

Samples were transported to Long Marine Laboratory, University of California−Santa Cruz, where the waxes and other high molecular weight interferences common to SPMD extracts were removed by size exclusion chromatography using a modification of a method developed by Krahn et al. (*11*). An HPLC (Hewlett-Packard Co., Palo Alto CA, 1050 series) equipped with variable wavelength detector and a Phenomenex Phenogel column (Torrance CA, 5 μm, 100 Å, 21.2 mm × 350 mm) was used with dichloromethane mobile phase (5 mL min^{-1}). Collection windows were determined by the retention times of methoxychlor and sulfur. Approximately 50% of each sample was auto-injected with the fraction confirmed gravimetrically.

Samples were fractionated on silica gel columns [3 g of silica gel (Merck 60) activated at 350 °C for 16 h slurry packed into 9 mm i.d. glass chromatography column with hexane]. Two fractions were collected: the first (33.5 mL of hexane) containing PCBs. Volumes were reduced and solvent exchanged into the final solvent for analysis (50 μL of dodecane containing PCBs 6, 208, and [$^{13}C_{12}$]141 as GC internal standards).

Active Air Monitoring. Active air sampling was carried out at the meteorological station using a HiVol supplied by General Metal Works (model GPS1 PUF sampler). PCB and PAH monitoring data have been reported from this site previously (e.g., ref *12*). HiVol samples were collected weekly throughout the time-course experiments and the 2-month deployment study. Approximately 3.5 m^3 of air was sampled per hour (ca. 600 m^3 per sample). The particulate phase was nominally described as that retained by a Whatman 10 cm glass microfiber filter (GFF; grade GF/A) and the vapor phase by a PUF plug (length 8 cm, diameter 6.25 cm, density 0.035 g cm^{-3}). Prior to deployment, GFFs were fired at 450 °C for 16 h, and the PUF plugs were pre-extracted in dichloromethane for 16 h (solvent refreshed twice during this period) and dried under vacuum in a desiccator. PUF plugs were stored in solvent-cleaned glass jars with aluminum foil-lined lids and were used within 3 weeks of pre-extraction. After sample collection, PUF plugs and GFFs were stored frozen (−17 °C) in solvent-cleaned glass jars.

(A) Extraction and Cleanup. PUF plugs and GFFs were spiked prior to extraction with the [$^{13}C_{12}$]PCB recovery spike described above. Samples were extracted for 12 h on a Büchi Soxhlet extractor unit in hexane. Samples were cleaned up and fractionated using the silica gel fractionation method (3 g of activated silica) described earlier. PCB fractions were transferred to 500 μL of internal standard spiked dodecane.

Analysis. USGS SPMD, PUF, and GFF extracts were analyzed for PCBs by GC−MSD (Fisons MD-800), EI+ source in SIM mode. Two microliters of each sample was injected in the splitless mode on a 50 m × 0.18 mm CPSil-8 column. The oven temperature was as follows: 100 °C for 2 min, 20 °C min^{-1} to 140 °C, 4 °C min^{-1} to 200 °C, 200 °C for 13 min, 4 °C min^{-1} to 300 °C, and 300 °C for 10 min. The injector was set at 250 °C, source at 250 °C, and interface at 300 °C. Two masses were monitored per homologue group. A split seven-point calibration (two ranges) was carried out using an internal standard method. The following PCB congeners were screened: IUPAC Nos. 18, 28, 30, 31, 33, 37, 52, 54, 77, 81, 82, 101, 104, 105, 110, 114, 118, 119, 123, 126, 138, 149, 151, 153, 156, 157, 167, 169, 170, 180, 183, 185, 187, 188, 189, 191, 193, 194, 202, 204, 205, 206, and 209. Congeners 6, 208, and [$^{13}C_{12}$]141 were used as injection internal standards.

QA/QC. The routine quality assurance and quality control procedures employed by our laboratory were practiced during this study. Procedures adopted include the incorporation of procedural (laboratory) blanks at a minimum inclusion rate of 5%. For the HiVol samples, one field blank was collected for every five samples. Reference materials were

TABLE 1. Average Recoveries of [$^{13}C_{12}$]PCBs in USGS SPMDs, PUF Plugs, and GFFs[a]

	recovery (%)			
	USGS SPMD sample		HiVol sample	
congener	exterior	interior	PUF	GFF
[$^{13}C_{12}$]28	89 (11)	113 (15)	122 (7)	112 (15)
[$^{13}C_{12}$]52	66 (10)	72 (8)	88 (5)	87 (9)
[$^{13}C_{12}$]101	80 (10)	84 (7)	89 (4)	89 (5)
[$^{13}C_{12}$]138	92 (9)	96 (6)	93 (3)	99 (9)
[$^{13}C_{12}$]153	86 (10)	89 (6)	93 (3)	100 (9)
[$^{13}C_{12}$]180	93 (9)	97 (7)	106 (3)	113 (5)
[$^{13}C_{12}$]209	103 (12)	105 (12)	89 (4)	93 (4)

[a] Standard deviation in parentheses.

routinely Soxhlet extracted alongside the HiVol samples, with concentrations required to fall inside certified ranges. All samples were spiked with a [$^{13}C_{12}$]PCB recovery standard prior to extraction. Mean recoveries of this standard are presented in Table 1. Results are not corrected for recovery. Limits of quantification for PCBs are conservatively taken to be 1 pg on column. Concentrations less than this are reported as non-quantified. Although concentrations found in all blanks are relatively small, all reported data are blank corrected. As mentioned above, waxes, lipids, and any particulate matter that had collected on the outside of the SPMDs (exterior fraction) were extracted and analyzed. Due to the way in which this fraction is collected (20 s shake in solvent), errors in the actual contact time between the triolein SPMD and the solvent is likely to cause variations in apparent concentrations. In addition, if the sample was touched during sample handling, then contamination of or losses from this fraction may have occurred. This fraction is therefore included in analysis merely as a method check, which can be turned to in case there are discrepancies in concentrations found in interior fractions.

Results and Discussion

Due to the quantity of data obtained, results reported here for PCBs will be limited to the seven ICES (International Council for the Exploration of the Seas) congeners (PCBs 28, 52, 101, 118, 138, 153, and 180) and sums of the homologue groups. Data on an individual congener basis are available from the authors on request.

Time-Course Experiments. During the summer part of the time-course experiment, the temperature ranged from 7 to 31 °C (mean 18 °C) and in winter ranged from −6 to 18 °C (mean 4 °C).

Linear uptake by the USGS SPMDs was noted for all congeners over the time periods in which the experiments were conducted. Figure 1, panels a and b, shows uptake of PCB congeners 101 and 138, respectively, as examples. Table 2 presents gradients (equivalent to uptake rate in pg day^{-1} SPMD^{-1}) and regression coefficients for the plots for the ICES congeners and the homologue groups in both summer and winter (regressions were linear with forced origin).

Although SPMDs effectively only sample compounds that are in the vapor phase, it is possible that there may have been uptake of PCBs from particles that had stuck to the lipid and waxes which would have diffused to the exterior of the SPMD. Results from the HiVol air sampler showed that, in all samples, the nominally ascribed "vapor phase" constituted greater than 96% of PCBs sampled. Due to the possibility of SPMD uptake from the particles, however, it was decided to sum the HiVol-derived vapor and particulate phases in this study. Table 3 presents mean PCB concentrations obtained from the HiVol for both parts of the time-course experiment. Concentration ranges are also presented.

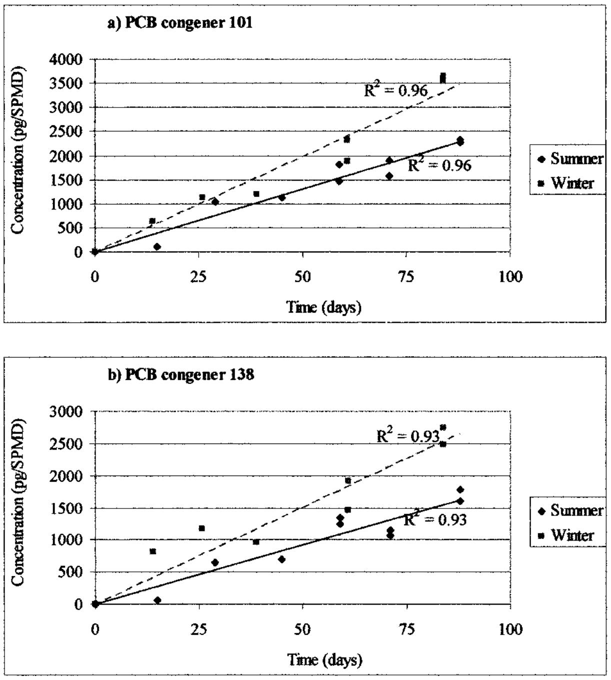

FIGURE 1. Temporal uptake of (a) PCB 101 and (b) PCB 138.

TABLE 2. Uptake Rate (pg day^{-1} SPMD^{-1}) of PCBs by Standard USGS SPMDs in Summer and Winter[a]

	uptake rate in pg per day per SPMD	
PCB	summer	winter
28 (2,4,4′)	32 (0.44)	70 (0.93)
52 (2,2′,5,5′)	19 (0.88)	43 (0.98)
101 (2,2′,4,5,5′)	26 (0.96)	40 (0.97)
118 (2,3′,4,4′,5)	23 (0.88)	21 (0.97)
153 (2,2′,4,4′,5,5′)	26 (0.96)	37 (0.92)
138 (2,2′,3,4,4′,5′)	19 (0.93)	30 (0.93)
180 (2,2′,3,4,4′,5,5′)	5 (0.89)	11 (0.91)
ΣICES	150 (0.95)	250 (0.97)
tri-CB	61 (0.67)	190 (0.94)
tetra-CB	19 (0.88)	43 (0.98)
penta-CB	67 (0.97)	86 (0.95)
hexa-CB	81 (0.96)	110 (0.95)
hepta-CB	18 (0.94)	34 (0.89)
8- & 9-CB	nq	nq
ΣPCB	250 (0.94)	470 (0.96)

[a] All plots are forced through the origin. R^2 values are shown in parentheses. nq Implies below Limit of Quantification. Tri-CB sum of congeners 18, 28, 30, 31, 33, and 37. Tetra-CB, sum of congeners 52, 54, 77, and 81. Penta-CB, sum of congeners 82, 101, 104, 105, 110, 114, 118, 119, 123, and 126. Hexa-CB, sum of congeners 138, 149, 151, 153, 156, 157, 167, and 169. Hepta-CB, sum of congeners 170, 180, 183, 185, 187, 188, 189, 191, and 193. 8- and 9-CB, sum of congeners 194, 202, 204, 205, and 206; ΣPCB, sum of all of these congeners. Congeners 54, 81, and 77 are below the limit of quantification; therefore, results for tetra-CB will be identical to those for PCB 52.

Atmospheric PCB concentrations are found to be greater in summer than in winter. This seasonal concentration difference is more pronounced for the lighter, more volatile PCBs. This observation is in accordance with that reported in the literature (*2, 13, 14*).

Results presented in Tables 2 and 3 can be used to calculate the average volume of air sampled per day by a standard triolein USGS SPMD. These rates are presented in Table 4. It can be seen that the volume of air sampled by an SPMD in winter is greater than that in summer when the temperature is higher. Compared with summer months, a decrease in temperature in the winter will cause the lipid−air partition

TABLE 3. Atmospheric Concentrations of PCBs As Determined by HiVol Sampler during USGS SPMD Uptake Experiments

	atmospheric concentration (pg m^{-3})					
	summer			winter		
PCB	mean	max	min	mean	max	min
28	41	74	19	16	28	2.1
52	15	26	8.9	6.9	9.6	4.0
101	7.9	14	3.9	3.7	6.0	1.8
118	3.3	7.6	1.6	1.5	2.2	0.7
153	5.9	11	3.0	2.4	3.7	1.5
138	4.3	7.3	1.8	1.7	2.6	0.8
180	1.1	2.0	0.4	0.8	1.2	0.4
ΣICES	78	130	41	33	53	18
tri-CB	130	240	58	55	81	43
tetra-CB	15	26	8.9	6.9	9.6	4.0
penta-CB	19	37	9.0	8.1	12	4.5
hexa-CB	19	31	8.4	7.7	11	4.8
hepta-CB	3.7	6.2	1.5	1.8	2.8	1.2
8- & 9-CB	nq[a]	nq	nq	nq	nq	nq
ΣPCB	190	330	86	80	120	58

[a] nq implies below quantification limit.

TABLE 4. Uptake Rates of PCBs by USGS SPMDs—Rates Based on Standard Triolein USGS SPMD (See Text for Details)

	uptake rate, m^3 day^{-1} SPMD^{-1}		
PCB	summer	winter	mean
28	*a*	4.5	4.5[b]
52	1.3	6.2	3.8
101	3.3	11	6.9
118	6.9	14	10
153	4.5	15	9.9
138	4.3	18	11
180	4.9	13	9.0
ΣICES	1.9	7.6	4.8
tri-CB	*a*	3.5	3.5[b]
tetra-CB	1.3	6.2	3.8
penta-CB	3.6	11	7.1
hexa-CB	4.2	15	9.4
hepta-CB	4.9	19	12
8- & 9-CB	*c*	*c*	*c*
ΣPCB	1.3	5.8	3.6

[a] No value given due to poor regression of uptake. [b] Value for winter only taken. [c] Atmospheric concentration below limit of quantification.

coefficient to favor accumulation in the lipid. This is primarily because there is a greater relative increase in the lipid and membrane compartment capacity for POPs than in that of the air compartment. The flux and the time for exposure determine the total amount accumulated inside an SPMD. Water sampling studies have shown that in general transport through the membrane decreases with decreasing temperature (*15*), as there will be reduced polymer chain movement within the membrane. The wax-point of triolein is approximately 0 °C (*16*), and triolein as a wax will lack crystalline regions. It is suggested therefore that, at low temperatures, compounds will accumulate at a greater rate in the exterior surface layer of lipid and the outer portion of the membrane, while diffusivity in the membrane is reduced. This results in an increased driving force or concentration gradient across the membrane. Membrane permeation will therefore remain the rate-limiting step.

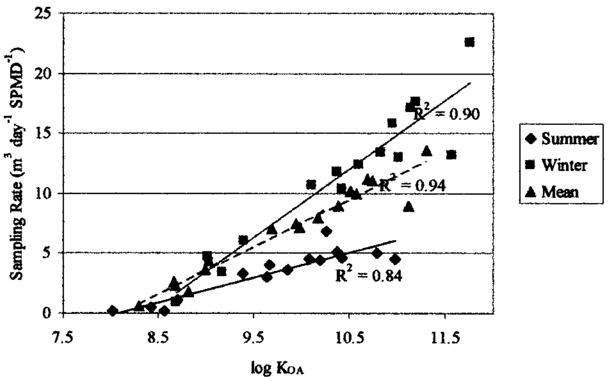

FIGURE 2. Uptake rate against log K_{OA} for summer and winter sampling. Mean uptake rate is also given. Log K_{OA} has been calculated for mean temperatures experienced by the samples during deployments (18 °C summer; 4 °C winter; 12 °C mean) using equations by Harner and Bidleman (*18*) and liquid-phase vapor pressures from Falconer and Bidleman (*19*).

Seasonal differences in wind speed during the SPMD exposures may also slightly affect the USGS SPMD air sampling rate. Higher wind speeds in winter (average of 4.6; cf. 2.7 m s^{-1}) may mean that the SPMDs experienced a larger volume of air—the 'run of wind' at the field station averaged 236 km day^{-1} during the summer sampling and 364 km day^{-1} in the winter exposure. The design of the Stevenson Screens housing the SPMDs may have partially buffered the effect of variations in wind speed. Therefore, the boundary layer thickness changes are likely to be small, and in view of the high diffusion rates in air relative to the permeation rates in the polyethylene, the membrane permeation and polyethylene sticking coefficients are likely to regulate uptake unless extreme conditions are encountered.

During both time periods, apparent sampling rates increase with increasing degree of chlorination. Chiou (*17*) has demonstrated that triolein–water and octanol–water partition coefficients (K_{TW} and K_{OW}, respectively) are related, and one would therefore expect the K_{OA} (octanol–air partition coefficient) and K_{TA} (triolein–air partition coefficient) to also be linearly proportional. In the absence of measured values for K_{TA}, K_{OA} values have therefore been used as a surrogate to plot the relationship between sampling rate and log K_{OA} for all congeners analyzed (Figure 2). In Figure 2, plots are shown for summer and winter deployments; a plot for the mean of the sampling rates is also shown. The log K_{OA} values in Figure 2 have been calculated and corrected for the average exposure temperatures using the equations given by Harner and Bidleman (*18*) and the vapor pressures given by Falconer and Bidleman (*19*). Good linear fits are seen for all three plots. Compounds with higher K_{OA} values (in general, compounds with increased chlorination have higher log K_{OA} values) are seen to have increased sampling rates—accumulation in the lipid/membrane is favored. Straight-line plots for sampling rate against log K_{OA} are indicative of linear uptake over the sampling period. The lighter compounds typically have lower K_{OA} (K_{TA}) values and would be expected to reach equilibrium more quickly than heavier less volatile species. If equilibrium were being approached during the period of exposure, a plot of sampling rate against log K_{OA} would presumably have become curvilinear. This does not happen (Figure 2), suggesting that the SPMDs have a capacity to continue linear uptake beyond the 3 months tested here.

The permeation rate of the membrane is compound specific, and substitution patterns are found to affect sampling rates. An increase in the number of ortho-substituted chlorines for the same degree of chlorination gives rise to a decrease in the sampling rate. For example, it was found that for a standard USGS SPMD the uptake rate (average summer and winter) of the mono-ortho-substituted congener 118 was 10 m^3 day^{-1} while for PCB 101 (di-ortho) it was found to be 7.0 m^3 day^{-1}. A similar observation has been noted by Huckins et al. (*20*). It is suggested that this

TABLE 5. Estimation of Time Required for Equilibrium between USGS SPMD and Atmosphere Using Average Sampling Rates (See Text for Details of Calculation)[a]

PCB	years to equilibrium
28	2.4
52	2.9
101	6.8
118	34
153	28
138	34
180	140
tri-CB	3.0
tetra-CB	2.9
penta-CB	18
hexa-CB	24
hepta-CB	100

[a] K_{OA} value used for estimation calculated at 12 °C (average temperature during summer and winter exposures).

difference in sampling rate results from changes in rotational freedom of the PCB molecules.

Petty et al. (*8*) report a sampling rate of 6.5 m^3 day^{-1} for three half USGS SPMDs (total 1.4 g of lipid) for PCBs from laboratory air. In this study, we found that, in the field, a single standard USGS SPMD (0.9 g of lipid) extracted PCBs from an average of 3.6 m^3 of air per day (mean result for ΣPCB, see Table 4). Huckins and co-workers (*20*) have measured air sampling rates for 1 g USGS SPMDs. On an individual congener basis, they calculated a sampling rate from air of 3.0 m^3 day^{-1} for PCB 52, 5.4 m^3 day^{-1} for PCB 101, 7.0 m^3 day^{-1} for PCB 153, and 7.1 m^3 day^{-1} for PCB 138. It can be seen that, on a unit sampler basis, there is good comparison between the results from these studies.

Approach to Equilibrium. SPMDs will clearly have a finite capacity for taking up POPs from the atmosphere. Equilibrium will be reached between the gas-phase component in the atmosphere and the SPMD-associated component. The length of time to equilibrium (t) for a standard triolein USGS SPMD for a particular compound at a specified temperature can be estimated from K_{OA}, the average air concentration (C_{AIR}), the equilibrium SPMD concentration (C_{SPMD}), and the dissipation constant (k, which can be calculated from the sampling rate and K_{OA}) using

$$C_{SPMD} = K_{OA}C_{AIR}(1 - e^{-kt})$$

Calculations have been carried out to estimate the length of time required to reach 95% of the K_{OA} implied equilibrium SPMD concentration using a mean of the summer and the winter sampling rates determined in this study for the ICES-7 PCBs, and the results are reported in Table 5. Results are also shown for the average times to equilibrium for different homologue groups. It is calculated that, for tri- and tetra-CBs, a standard USGS SPMD may equilibrate with the atmosphere in less than 3 years; for penta- and hexa-CBs, equilibration time may be closer to 20 years; for PCBs with 7 or more chlorines, equilibration time could be in excess of 100 years. However, it should be noted that (i) the above calculations ignore the capacity of the SPMD membrane for POPs, leading to an underestimation of the time required to reach equilibrium but (ii) for higher chlorinated congeners there is increased deviation between K_{TW} and K_{OW} (*17*), and presumably therefore also between K_{TA} and K_{OA}, leading to an overestimation of the time to equilibrium for these congeners.

Two Month Deployment Study. During the 2-month deployment study, temperatures at the field site ranged from 3 to 25 °C. Sequestered PCB concentrations by the USGS SPMDs are shown in Table 6. Since the temperature range encountered during this study did not fall entirely into the range of either part of the time-course study, a mean sampling rate was applied to these results, and atmospheric concentrations (C_{air}, pg m^{-3}) were calculated using

$$C_{air} = C_{SPMD}/(R_{air}t)$$

where C_{SPMD} is the concentration sequestered by a standard USGS SPMD (pg $SPMD^{-1}$), R_{air} is the mean air sampling rate (m^3 day^{-1} $SPMD^{-1}$; Table 4), and t is the duration of exposure (days). Table 7 shows the USGS SPMD-derived atmospheric concentrations and the mean atmospheric PCB concentrations determined from the HiVol samples during the deployment period. Excellent agreement is seen between derived and actual concentrations, with calculated concentrations for all ICES congeners and homologue groups falling within (or very close to) the observed concentration ranges. It can also be observed from the results in Table 7 that there is a very high degree of reproducibility between USGS SPMD duplicates.

TABLE 6. Amounts of PCBs Sequestered by USGS SPMDs in 2-Month Deployment Study[a]

	sequestered concentration (pg $SPMD^{-1}$)			
	sample 1		sample 2	
PCB	exterior	interior	exterior	interior
28	370	2500	480	3200
52	300	1700	350	1700
101	450	1700	510	1700
118	230	810	250	1000
153	220	1100	240	1100
138	180	820	200	870
180	32	260	33	290
ΣICES	1800	8900	2100	9800
tri-CB	920	8600	1100	8800
tetra-CB	300	1700	350	1700
penta-CB	830	3600	970	3900
hexa-CB	740	3300	810	3400
hepta-CB	120	830	130	900
8- & 9-CB	nq[b]	nq	nq	nq
ΣPCB	2900	18000	3400	19000

[a] Each sample is the composite of four USGS SPMDs. [b] nq implies below quantification limit.

TABLE 7. Atmospheric Concentrations during 2-Month Deployment Study[a]

	atmospheric concentration (pg m^{-3})					
	actual (HiVol)			calculated (USGS SPMD)		
PCB	mean	min	max	sample 1	sample 2	mean
28	18	6.0	30	10	13	12
52	6.7	3.9	8.5	8.1	7.9	8.0
101	4.2	3.1	4.9	4.3	4.4	4.3
118	1.9	1.5	2.2	1.4	1.7	1.6
153	3.1	1.7	4.1	2.0	2.0	2.0
138	2.1	1.3	3.3	1.3	1.4	1.4
180	0.7	0.6	0.8	0.5	0.6	0.5
ΣICES	37	21	50	33	37	35
tri-CB	65	20	94	45	46	45
tetra-CB	6.9	4.7	8.7	8.1	7.9	8.0
penta-CB	11	8.4	13	9.1	9.9	9.5
hexa-CB	8.6	4.5	12	6.3	6.5	6.4
hepta-CB	1.8	1.1	2.2	1.3	1.4	1.3
8- & 9-CB	nq[b]	nq	nq	nq	nq	nq
ΣPCB	93	41	120	90	94	92

[a] Actual (as determined by HiVol) and calculated (from USGS SPMDs, interior). [b] nq implies below quantification limit.

In summary, USGS SPMDs show great potential for measuring time-integrated atmospheric vapor-phase concentrations of persistent organic pollutants. Over 3 months, linear uptake of PCBs has been observed for USGS SPMDs deployed in the field. Simultaneous active air sampling was undertaken, allowing USGS SPMD uptake rates to be calculated. These rates have been applied to independently deployed USGS SPMDs, and atmospheric concentrations were derived. Excellent agreement is noted between these calculated concentrations and actual concentrations as measured by a conventional HiVol sampler, and very high reproducibility was seen between replicate SPMD samples. The time required to reach 95% equilibrium have been estimated, on the basis of the observed linear uptake rates and K_{OA} values, with the assumptions that the membrane has no capacity to retain PCBs and that triolein behaves identically to octanol. There is need, however, to carry out studies to ascertain the true capacity of USGS SPMDs for different compounds, allowing issues of approach to equilibrium and desorption to be properly addressed. Although USGS SPMDs have been used for sampling PAHs in water, assessment needs to be carried out for their use as atmospheric samplers for compounds such as PAHs, which are principally in the particulate phase. It should also be noted that SPMDs give no information on gas-particle partitioning, and ideally they will therefore be deployed alongside passive sampling devices to measure dry deposition.

The results from this study should allow the use of USGS SPMDs as air monitoring tools to become more widespread, particularly where medium to long-term time integrated data would be valuable. There is potential for global deployment of these samplers, permitting atmospheric concentrations to be derived in remote areas where it is either impossible to install active air monitoring equipment or where requirements for electrical supply for such technologies will compromise the integrity of remote samples. In addition, the results from this study combined with those where the water sampling rates by USGS SPMDs have been established (*7*) should allow USGS SPMDs to be used to shed considerable light on the dynamics of POPs at the air−water interface.

Acknowledgments

We gratefully acknowledge Dave Baldwin of George Whitehouse Ltd. and Roger Ockenden for the donation of the Stevenson Screens. W.A.O. was supported in part by a SETAC/Taylor & Francis Advanced Training Fellowship (received in the name Wendy A. Lead). We are also grateful to J. N. Huckins and J. D. Petty of USGS for many useful discussions regarding the use of SPMDs as environmental samplers.

Literature Cited

(1) Halsall, C. J.; Coleman, P. J.; Davis, B.; Burnett, V.; Waterhouse, K.; Harding-Jones, P.; Jones, K. C. *Environ. Sci. Technol.* **1994**, *28*, 2380.
(2) Halsall, C. J.; Lee, R. G. M.; Coleman, P. J.; Burnett, V.; Harding-Jones, P.; Jones, K. C. *Environ. Sci. Technol.* **1995**, *29*, 2368.
(3) Bidleman, T. F.; Walla, M. N.; Roura, R.; Carr, E.; Schmidt, S. *Mar. Pollut. Bull.* **1993**, *26*, 258.
(4) Alfheim, I.; Jebens, A.; Johansen, S. *Environ. Int.* **1985**, *11*, 111.
(5) Hart, K. M.; Isabelle, L. M.; Pankow, J. F. *Environ. Sci. Technol.* **1992**, *26*, 1048.
(6) Huckins, J. N.; Tubergen, M. W.; Manuweera, G. K. *Chemosphere* **1990**, *20*, 533.
(7) Huckins, J. N. In *Second International SPMD Workshop* May 10−11, 1994; Midwest Science Center: Columbia, MO, 1994.
(8) Petty, J. D.; Zajicek, J. L.; Huckins, J. N. *Chemosphere* **1993**, *27*, 1609.
(9) Prest, H. F.; Jacobson, L. A.; Huckins, J. N. *Chemosphere* **1995**, *30*, 1351.
(10) Prest, H. F. LML/UCSC, Santa Cruz, CA, Personal communication, 1997.
(11) Krahn, M. M.; Wigren, C. A.; Pearce, R. W.; Moore, L. K.; Bogar, R. G.; MacLeod, W. D.; Chan, S.-L.; Brown, D. W. *NOAA Technical Memorandum NMFS F/NWC-153*; 1988.
(12) Lee, R. G. M.; Jones, K. C. *Organohalogen Compd.* **1997**, *33*, 275−279.
(13) Manchester-Neesvig, J. B.; Andren, A. W. *Environ. Sci. Technol.* **1989**, *23*, 1138.
(14) Hoff, R. M.; Muir, D. C. G.; Grift, N. P. *Environ. Sci. Technol.* **1992**, *26*, 266.
(15) Manuweera, G. K. University of Missouri, Columbia, Personal Communication, 1992.
(16) Huckins, J. N. USGS/Environmental & Contaminants Research Center, Columbia, MO, Personal communication, 1998.
(17) Chiou, C. T. *Environ. Sci. Technol.* **1985**, *19*, 57.
(18) Harner, T.; Bidleman, T. F. J. *Chem. Eng. Data* **1996**, *41*, 895.
(19) Falconer, R. L.; Bidleman, T. F. *Atmos. Environ.* **1994**, *28*, 547.
(20) Huckins, J. N.; Petty, J. D.; Orazio, C. E.; Zajicek, J. L.; Gibson, V. L.; Clark, R. C.; Echols, D. R. *Abstracts of 15th Annual Meeting SETAC*, Denver, CO, November 1994; SETAC: 1994; Paper MB 01, p 106.

Received for review November 21, 1997. Revised manuscript received February 11, 1998. Accepted February 17, 1998.

ES971020C