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Toward an Understanding of the Global Atmospheric Distribution of Persistent Organic Pollutants: The Use of Semipermeable Membrane Devices as Time-Integrated Passive Samplers

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Triolein-containing semipermeable membrane devices (SPMDs) were deployed as passive air samplers alongside conventional air samplers at two sites, and derived atmospheric concentrations from each were compared. Excellent comparability was noted between sampling systems. SPMDs were also deployed for 2 years at 10 sites across a latitudinal transect from the south of the U.K. (ca. 50° N) to the north of Norway (ca. 70° N) to passively sample air. Time-integrated, simultaneous data were obtained, which were used to test the global fractionation hypothesis in the Northern Hemisphere. Extracts were analyzed for a suite of PCB congeners and α - and γ -HCH. A latitudinal change in PCB profiles was seen. The absolute atmospheric concentration of the tetra-chlorinated PCBs was relatively uniform over the study area (ca. 1.9 pg m⁻³), but their relative concentration increased with increasing latitude or decreasing temperature (12% of total PCB concentrations in the south of the U.K. as compared with 35% at the northern-most station). The concentration of the penta-chlorinated PCBs decreased from 6 pg m⁻³ at the southern U.K. site to 1.5 pg m⁻³ in the north of Norway, but their relative concentration was uniform (33% total PCB) over the transect. Absolute and relative concentrations of heavier PCBs decreased with increasing latitude and decreasing temperature. These data indicate that a temperature-controlled fractionation of PCBs is occurring in the atmosphere. Data were available for soil PCB concentrations at or near seven of the air sampling sites. Fugacity quotients suggested that across the study area the air/soil system is at or near to equilibrium for PCBs. Concentrations of the α -HCH isomer sequestered by the SPMDs increased from south to north while the sequestered γ -HCH concentrations decreased. The ratio of α/γ -HCH increased by a factor of approximately 20 from the south to the north of the study area. These data are consistent with the selective weathering of these

compounds during their long-range atmospheric transport from southerly source regions to remote northern locations.

Introduction

The hypotheses of global distillation and fractionation have been put forward in an attempt to explain the occurrence of persistent organic pollutants (POPs) in polar regions (e.g., refs 1–3). These theories suggest that not only are the majority of these pollutants reaching polar environments as a result of long-range atmospheric transport but also that during this process compounds become separated (fractionated) with latitude because of differences in their physico-chemical properties and ambient temperature. As a result, heavy relatively nonvolatile compounds would be deposited and accumulate close to their source, while more volatile compounds would undergo long-range atmospheric transport before deposition/temperature-controlled partitioning to terrestrial/aquatic surfaces in colder (e.g., polar) regions.

It has been suggested that compounds that may be susceptible to global fractionation include polychlorinated biphenyls (PCBs), organochlorine (OC) pesticides such as hexachlorocyclohexanes (HCHs), dieldrin, and DDT and its metabolites, and polyaromatic hydrocarbons (PAHs) with three or less rings (4). The fact that production and use of these compounds spanned several decades, and in some cases (e.g., HCH and PAHs) is still occurring, makes the finding of definitive evidence for their global fractionation extremely problematic.

To try to find evidence for or against this hypothesis, it is necessary to assess the global distribution of POPs, particularly in the atmosphere. Ideally atmospheric sampling should be carried out simultaneously at as many remote sites of different latitude as possible. To ensure direct comparability of data, all analyses should be performed either by one laboratory or by several with extremely rigorous interlaboratory comparison protocols. Additionally, due to varying air concentrations, either long-term or time-integrated sampling should be conducted. It is essential that sites chosen for monitoring studies are remote and far removed from potential source areas. In the Canadian Arctic, for example, fingerprints of PCB contamination from distant early warning (DEW-line) sites have been found in vegetation and soils up to 20 km from the original area of PCB usage (5). Conventionally, sampling of POPs in the atmosphere has been carried out using either high-volume air samplers (HiVols) (e.g., refs 6–8) or, rarely, diffusion denuders (e.g., ref 9). A drawback of these techniques, however, is that they require electrical supply. Sampling at truly remote sites is therefore not possible without the use of a generator, the inherent pollution from which may affect the integrity of the sample.

Triolein-containing semipermeable membrane devices (SPMDs) as designed by the U.S. Geological Survey (USGS) have shown immense potential for use as passive samplers for atmospheric pollutants (principally vapor phase) (10–12). USGS SPMDs consist of a thin-walled polyethylene membrane (75–90 μ m) containing a thin film of the neutral synthetic lipid triolein (13). Compounds are absorbed

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through the membrane and concentrate in the lipid. Detection of trace level species is therefore possible. Despite their potential, to date there are only limited studies where USGS SPMDs have been utilized as atmospheric monitoring tools. It is suggested that one of the main reasons for this is that rigorous studies have not been carried out comparing accepted active sampling methods with these passive sampling systems and until recently data have not been available on their atmospheric sampling rates (12). It should be noted that although USGS SPMDs effectively only sample vapor-phase compounds, it is possible that there may have been uptake of pollutants from particles that had stuck to the lipid and waxes that would have diffused to the exterior of the sampler (12). For this reason, PCB atmospheric sampling rates by USGS SPMDs were calculated using total (vapor plus particulate phases) atmospheric concentrations (12).

Results are reported here from a study where USGS SPMDs were used to assess atmospheric concentrations at 10 remote sites along a latitudinal transect from the south of the U.K. (ca. 50° N) to the north of Norway (ca. 70° N). At one of the U.K. sites and at an 11th site on the Svalbard Archipelago (ca. 80° N), HiVols were deployed alongside USGS SPMDs in order that derived atmospheric concentrations from each method could be compared in temperate and polar environments. The study has focused on polychlorinated biphenyls (PCBs) because, although they were widely used in the past, contemporary air concentrations are governed by temperature-controlled air/surface exchange processes (e.g., refs 14 and 15). Also, data are available on USGS SPMD atmospheric sampling rates of these compounds (12) and, as mentioned above, the physicochemical properties of PCBs make them a group of compounds that should be susceptible to global fractionation. For example, the log of their octanol/air partition coefficients (K_{OA}) ranges from 6 to 12 (16) and their sub/cooled liquid vapor pressures (P_L) from 0.00001 to 1 Pa (17). Wania and Mackay (4) predict that compounds with $P_L < 0.0001$ should be deposited close to source regions; compounds with $0.01 > P_L > 0.0001$ will be deposited at midlatitudes and compounds with $P_L > 0.01$ will reach polar regions before net deposition occurs. PCBs have been widely used in the U.K. in the past, in amounts and over a time frame that are typical of other industrialized countries from temperate latitudes (18). Norway has a low population density, with the majority of its peoples living in the south of the country, and long-range atmospheric transport has previously been shown to be the major contributor to the nation's pollutant burden (19). A transect from the south of the U.K. to the north of Norway is therefore ideal for studies of this type, particularly as sites remote from potential local sources can be chosen on the western seaboard where winds will predominate from the Atlantic.

HCH isomers are also prone to global redistribution and atmospheric fractionation (4). Differences in absolute concentrations and ratios of the α - and γ -HCH isomers yield information on distance from source regions and may be suggestive of long-range atmospheric transport (20, 21). Although the focus of this study was on PCBs, concentrations of α - and γ -HCH sequestered by the SPMDs are also reported. All data are discussed with reference to global cycling and the cold condensation and global fractionation hypotheses.

Methods

USGS SPMDs. Standard triolein-containing USGS SPMDs (80–90 cm \times 2.5 cm; 75 μ m polymer thickness; 1 mL triolein) obtained from Environmental Sampling Technologies, St. Joseph, MO, were used throughout this study.

In the summer of 1994, two USGS SPMDs were deployed at each of 10 sample sites from the south of the U.K. to the north of Norway (Figure 1, sites A–J). Sites chosen were as remote as possible from potential sources but were at or

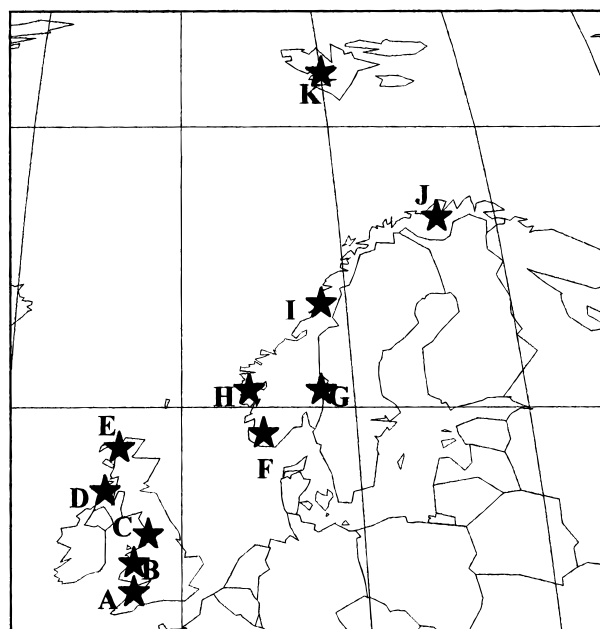


FIGURE 1. Location of atmospheric sampling sites.

TABLE 1. Locations and Temperatures of USGS SPMD Atmospheric Monitoring Stations

site ref	latitude	longitude	mean annual temp. (°C)	deployment temp range (°C)	
				min	max
A	50°45' N	03°54' W	9.6	–7	32
B	52°26' N	04°01' W	7.7	–11	33
C	54°03' N	02°48' W	7.2	–6	31
D	56°05' N	06°10' W	8.9	–4	32
E	58°03' N	05°01' W	7.0	–7	30
F	58°33' N	06°21' E	6.4	–14	31
G	61°15' N	11°53' E	2.2	–31	26
H	61°17' N	05°02' E	7.6	–12	28
I	64°59' N	13°36' E	1.1	–28	28
J	69°54' N	25°02' E	0.1	–31	26
K	78°55' N	11°56' E	–5.8	–33	16

near meteorological monitoring stations in order that temperature information would be available throughout the deployment period. Mean annual temperatures, temperature ranges during deployments, and site latitudes and longitudes are shown in Table 1.

The USGS SPMDs were hung horizontally inside aluminum Stevenson screen boxes. The boxes were to protect the samples from sunlight and direct wet deposition, but the louvered sides would still allow air to pass freely across the samples. Also, it is likely that the screens would have partially buffered the effect of varying wind speed between sites and would have minimized differences in boundary layer thickness, both of which may have affected uptake rates. All samples remained in the field for 2 years. Two USGS SPMD field blanks were also collected for each site—these were exposed briefly during sample deployment and retrieval and were stored in sealed cans within the Stevenson screen boxes throughout the deployment. Following collection, samples were transported at <4 °C and frozen as soon as possible until required for extraction.

USGS SPMD atmospheric sampling rates (in m³ of air per day per standard USGS SPMD) have been calculated in a previous study (12). These rates were calculated at site C in this study (Figure 1, Table 1). The mean annual temperature at this site is 7.2 °C. It was not clear whether it would be justifiable to apply these rates to sites where mean annual

temperatures are much lower—e.g., site J has a mean annual temperature of 0.1 °C. Three USGS SPMDs were therefore deployed at an 11th site (site K, Figure 1, Table 1) in the summer of 1996 for 1 year. These SPMDs were composited to form one sample. The mean annual temperature at site K is −5.8 °C, and during deployment, temperature ranged from −33 to +16 °C. Results have been published previously for a year-round atmospheric monitoring study that was carried out in 1993 approximately 2 km from site K (22). Comparison between the published results (22), which were obtained using conventional HiVol sampling methodology, and the USGS SPMD-derived atmospheric concentrations will give an indication of the reliability of applying the sampling rates obtained at site C to sites where annual temperatures are lower. It should be noted, however, that site K is not a truly remote site—the USGS SPMDs were deployed on the roof of a building in the research village of Ny-Ålesund. Until 1962, coal mining was carried out near the village, and discarded mining equipment are still visible in the area. Local pollution, though probably small, is possible. The results from this site are therefore not included in the latitudinal study.

Extraction and Cleanup. Methods for the extraction and cleanup of USGS SPMDs have been described in full elsewhere (12). Briefly, exterior lipid, waxes, and particulate matter were removed from the SPMDs by a 20-s shake in hexane. The interiors of the SPMDs were spiked with a [¹³C₁₂]-PCB recovery standard containing ¹³C₁₂ congeners 28, 52, 101, 138, 153, 180, and 209 (2.5 ng of each congener). Sequestered analytes were extracted from the interior of the samples by 2 × 24 h dialyses in hexane. Dialysates were cleaned up by activated silica chromatography followed by size exclusion chromatography. Prior to analysis, extracts were fractionated on silica gel columns into 2 fractions: *F*₁ containing PCBs and *F*₂ containing the HCHs.

HiVol Air Monitoring. Active air monitoring was carried out at site C using a General Metal Works HiVol model GPS1 PUF sampler. Samples were collected either weekly or biweekly throughout the USGS SPMD deployment, with approximately 600 m³ of air being collected per sample. The particulate phase was mechanically described as that being retained by a Whatman glass microfiber filter (grade GF/A), and the vapor phase was described as that retained by a polyurethane (PUF) plug (8 cm length × 6.25 cm diameter; density 0.035 g cm^{−3}). Prior to deployment, filters were fired at 450 °C for 16 h, and PUFs were preextracted in Soxhlet apparatus in dichloromethane for 16 h (12). After collection, samples were stored frozen until extraction and analysis (PCBs only).

As mentioned above, a year-round atmospheric monitoring study was carried out at site K in 1993 (22). To ascertain that the published atmospheric concentrations were comparable to those experienced during the SPMD deployment at the site, active air monitoring was carried out using a HiVol in September 1996. Sampling was carried out daily on nine separate occasions, with approximately 600 m³ of air constituting a sample. Filters and PUFs were precleaned as above and after collection were stored frozen.

Extraction and Cleanup. Prior to a 12-h Soxhlet extraction in hexane, PUFs and GFFs were spiked with the [¹³C₁₂]-PCB recovery standard. Extracts were cleaned up and fractionated on silica columns as described elsewhere (12).

Analysis. PCBs. All PCB fractions were analyzed by GC-MSD (Fisons MD-800), EI+ source in SIM mode. Instrument and calibration setup was identical to that described by Ockenden et al. (12), with congeners 6, 208, and [¹³C₁₂]PCB 141 being used as injection internal standards. The following PCB congeners (IUPAC numbering used throughout) were screened: 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,

TABLE 2. Mean Recovery of ¹³C₁₂ Spike for USGS SPMDs and PUF/GFF

congener	recovery (%)	
	USGS SPMD	PUF/GFF
[¹³ C ₁₂]PCB 28	89	117
[¹³ C ₁₂]PCB 52	66	88
[¹³ C ₁₂]PCB 101	80	89
[¹³ C ₁₂]PCB 153	92	96
[¹³ C ₁₂]PCB 138	86	97
[¹³ C ₁₂]PCB 180	93	109
[¹³ C ₁₂]PCB 209	103	91

167, 169, 170, 180, 183, 185, 187, 188, 189, 191, 193, 194, 202, 204, 205, 206, and 209.

α- & γ-HCH. USGS SPMD extracts were analyzed for HCHs by GC (Hewlett-Packard 5890) with dual ECD detection using HP-5MS and HP-50+ columns (both 60 m × 0.25 mm; 0.25 μm phase thickness). N₂ was the makeup gas, and He was the carrier gas with electronic pressure control being used to maintain flow at 1.9 mL min^{−1}. Temperature conditions were 100 °C for 2 min, 30 °C min^{−1} to 130 °C, 2 °C min^{−1} to 250 °C, 4 °C min^{−1} to 290 °C, 290 °C for 10 min. The injector was set at 250 °C, and detectors were set at 300 °C. A six-point calibration was used with acquisition and analysis being performed using HP ChemStation software. Tetrachloro-*meta*-xylene was used as injection internal standard.

QA/QC. Inclusion rates for blanks were as follows: 5% for procedural/laboratory blanks, 20% for HiVol field blanks, and 100% for USGS SPMD field blanks. All data are blank corrected. Reference materials were routinely Soxhlet extracted alongside the HiVol samples, with analyzed concentrations required to fall within the certified ranges. Prior to extraction, all samples were spiked with a [¹³C₁₂]PCB recovery standard, which contained congeners 28, 52, 101, 138, 153, 180, and 209. Mean recoveries are shown in Table 2. Results have not been corrected for recovery, but any sample with recovery found to be outside a range of mean ± 15% was rejected. Limits of quantification for both PCBs and HCHs were conservatively taken to be 1 pg on column.

Results and Discussion

PCBs. Of the suite of congeners screened, PCBs 18, 28, 31, 33, 52, 101, 110, 118, 138, 149, 151, 153, 170, 180, 183, and 187 were detectable in all samples. Results will be presented for the seven ICES PCB congeners (28, 52, 101, 118, 138, 153, and 180) and for sums of homologue groups (defined in Figure 2). Results for individual congeners are available from the authors on request.

Comparison between USGS SPMDs and HiVol Sampler.

(a) *Site C.* Results have previously been reported for atmospheric sampling rates of PCBs by USGS SPMDs at site C (12). These sampling rates assume linear uptake of PCBs by the SPMDs throughout the exposure time. The atmospheric concentration, *C*_{air} (pg m^{−3}), can be calculated from the sampling rate (*R*_{air}, m³ day^{−1} SPMD^{−1}), the concentrations sequestered by a USGS SPMD (*C*_{SPMD}, pg SPMD^{−1}) and the exposure time (*t*, days) using:

$$C_{\text{air}} = C_{\text{SPMD}} / (R_{\text{air}} t) \quad (1)$$

In this manner, atmospheric concentrations have been calculated for site C from the USGS SPMD sequestered concentrations for the 2-year exposure. The mean concentrations for the ICES congeners and the sums of the homologue groups are shown in Figure 2, panels a and b, respectively, with the error bars indicating the range of values. Very good reproducibility between USGS SPMD samples is

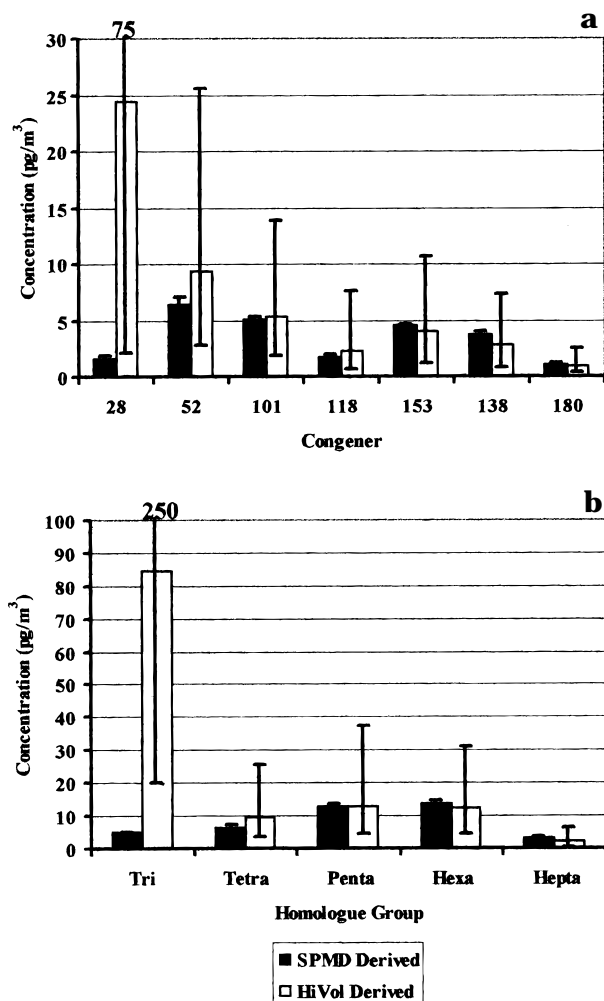


FIGURE 2. HiVol/USGS SPMD comparison at site C: (a) ICES congeners and (b) sum of homologue groups. Tri-CB, sum of congeners 18, 28, 30, 31, 33, and 37; tetra-CB, sum of congeners 52, 54, 77, and 81; penta-CB, sum of congeners 82, 101, 104, 105, 110, 114, 118, 119, 123, and 126; hexa-CB, sum of congeners 138, 149, 151, 153, 156, 157, 167, and 169; hepta-CB, sum of congeners 170, 180, 183, 185, 187, 188, 189, 191, and 193.

seen. Figure 2 also shows the mean atmospheric concentrations for the exposure period as determined by the HiVol sampler. Error bars show the range of measured concentrations during the sampling period. Excellent agreement is found between the atmospheric concentrations derived by the USGS SPMDs and the HiVol for PCBs with four or more chlorines. There is an obvious disparity between the concentrations for PCB 28 and for trichlorinated biphenyls in general. It has been calculated that, for trichlorinated biphenyls, USGS SPMDs are likely to approach equilibrium with the atmosphere in 2–3 years (12). Within the 2-year deployment, therefore, their uptake will undoubtedly have departed from linearity, which is being assumed in the above calculation to determine atmospheric concentrations. This will lead to an underestimation of the air concentrations. It should be possible to correct for nonlinearity by using

$$C_{\text{air}} = C_{\text{SPMD}} / \{K_{\text{SPMD-A}}(1 - e^{-kt})\} \quad (2)$$

to calculate the atmospheric concentration. ($K_{\text{SPMD-A}}$ is the USGS SPMD air partition coefficient and k is the dissipation rate constant, which can be calculated from the sampling rate, R_{air} , and $K_{\text{SPMD-A}}$.) Measured values for $K_{\text{SPMD-A}}$, however, are not available. It has been shown that the triolein/water

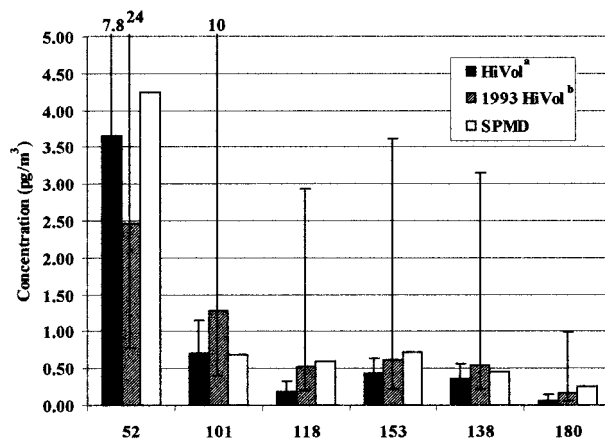


FIGURE 3. HiVol/USGS SPMD comparison at site K. Footnote a: Data from high volume deployed September 1996; this study. Footnote b: Data published by Oehme et al. (22) for 1993.

TABLE 3. Mean USGS SPMD Derived Atmospheric PCB Concentrations at Sites A–J

PCB	mean atmospheric concentration (pg m ⁻³)									
	A	B	C	D	E	F	G	H	I	J
52	1.9	2.5	6.5	1.9	1.7	2.7	1.4	1.6	2.0	1.6
101	2.4	2.6	5.0	1.6	1.4	2.2	0.80	1.12	1.1	0.75
118	0.80	0.94	1.8	0.43	0.28	0.51	0.23	0.36	0.18	0.15
153	2.4	2.3	4.5	1.3	0.89	1.6	0.47	0.92	0.63	0.40
138	2.0	2.0	3.7	1.1	0.67	1.4	0.48	0.65	0.55	0.31
180	0.53	0.57	1.0	0.23	0.17	0.31	0.09	0.14	0.10	0.06

partition coefficient (K_{TW}) and the octanol/water partition coefficient (K_{OW}) are proportional (23). It therefore seems probable that $K_{\text{SPMD-A}}$ would be related to K_{OA} since the USGS SPMD is a composite of triolein and a nonpolar membrane that also has a lipophilic nature. In the above equation, $K_{\text{SPMD-A}}$ can thus be replaced with K_{OA} , which can be corrected for the average temperature during the exposure using equations by Harner and Bidleman (16) and liquid-phase vapor pressures from Falconer and Bidleman (17). If eq 2 is applied to sequestered concentrations of PCB 28 and the sum of the trichlorinated congeners and only the triolein compartment of the SPMD considered, atmospheric concentrations of 17 and 42 pg m⁻³, respectively, are calculated. Although these values are much closer to the concentrations determined by the HiVol, there is still some discrepancy—mean atmospheric concentrations measured by the HiVol were 24 pg m⁻³ for PCB 28 and 85 pg m⁻³ for the sum of tri-CBs. It is suggested that the difference may be due to the fact that the membrane sequesters a significant portion of the residues. In addition, K_{OA} and $K_{\text{SPMD-A}}$ will not be equal. Both of these factors will lead to errors in calculations using eq 2. The following results, therefore, only deal with PCBs with four or more chlorines for which uptake is expected to remain in the linear region of the SPMD sequestering kinetics. This allows use of eq 1 to calculate atmospheric concentrations, and problems with estimating magnitude of membrane sequestration and $K_{\text{SPMD-A}}$ will be negated.

(b) Site K. The sampling rates from site C were applied to the SPMD results from site K in order to determine atmospheric concentrations, and the results for the ICES congeners (excluding congener 28) are shown in Figure 3. The mean and ranges in concentrations reported by Oehme et al. (22) for the all-year study near site K in 1993 are also shown in Figure 3, as are the mean and ranges as measured by the HiVol in this study in September 1996. The concentrations measured in this study were within the range of

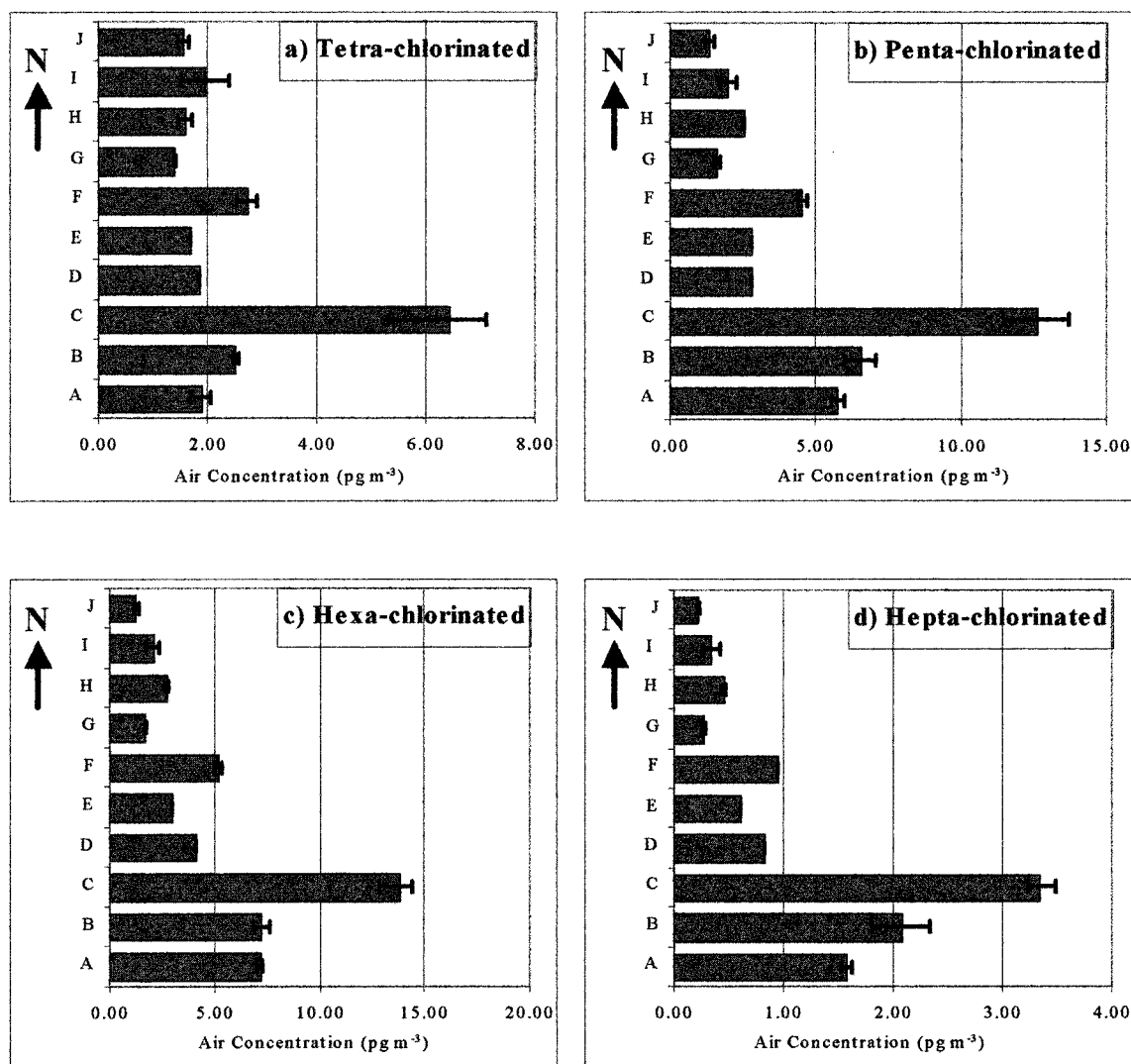


FIGURE 4. Atmospheric concentrations of PCB homologue groups at sample sites. [Sites shown according to latitude—it should be noted that site G is inland and therefore has a relatively low mean annual temperature (Table 1).]

published values, indicating that it is reasonable to use the data of Oehme et al. to evaluate the use of the USGS SPMD sampling rates from C at site K. Good agreement was seen between the concentrations determined by the HiVols and the USGS SPMDs. Despite the low temperatures at site K, it would therefore appear that we are justified to apply the sampling rates determined at site C to the passive samplers deployed at site K and therefore also to all of the other sites in this study.

Latitudinal Survey. (a) *Absolute Concentrations.* Table 3 shows USGS SPMD-derived atmospheric concentrations (pg m⁻³) for the ICES congeners. Figure 4, panels a–d, shows plots of changes in atmospheric concentration with sample site for PCB homologue groups. (Data for SPMD sequestered concentrations are available as Supporting Information.)

It is evident from Table 3 and Figure 4 that site C has much higher PCB concentrations than any of the other sites. A large database has been obtained on atmospheric PCB concentrations at site C, which is consistent with the values reported here as averages for 1994–1996 (e.g., ref 25). Site C is approximately 80 km north of the urban areas of Manchester and Liverpool. Several other small towns and cities are within tens of km. It is therefore believed that the site is affected by outgassing of PCBs from these urban centers (6) and that it is not as remote as the other locations.

With the exception of site C, the atmospheric concentration of tetra-CB is relatively uniform across the study area at approximately 1.9 pg m⁻³ (Figure 4a). (As congeners 54, 77, and 81 were below limits of quantification, the concentration of tetra-CB reported here is the same as that for PCB 52.) It would appear that lighter PCBs are well mixed in the atmosphere across the study area. It can be seen in Figure 4 that, for heavier compounds, there is a general decrease in atmospheric concentration with increasing latitude, with the south–north concentration gradient increasing with increasing chlorination. Between the southern- and northern-most sampling sites pentachlorinated CBs, for example, decrease by a factor of approximately 3, and hepta-CBs decrease by a factor of 7.

(b) *PCB Profiles.* Differences in profiles between sample sites are shown in Figure 5, panels a and b. Plots of the contribution of tetra-, penta-, hexa-, and heptachlorinated biphenyls to total PCB concentrations against latitude are shown in Figure 5a and against mean annual temperature of the sample site are shown in Figure 5b. There is an increase in the relative importance of tetra-CBs with increasing latitude or decreasing temperature, with percentage contribution ranging from about 12% at the southern-most site to 35% at the northern-most site. The relative contribution of penta-CBs to total PCB is fairly uniform across the sample area at

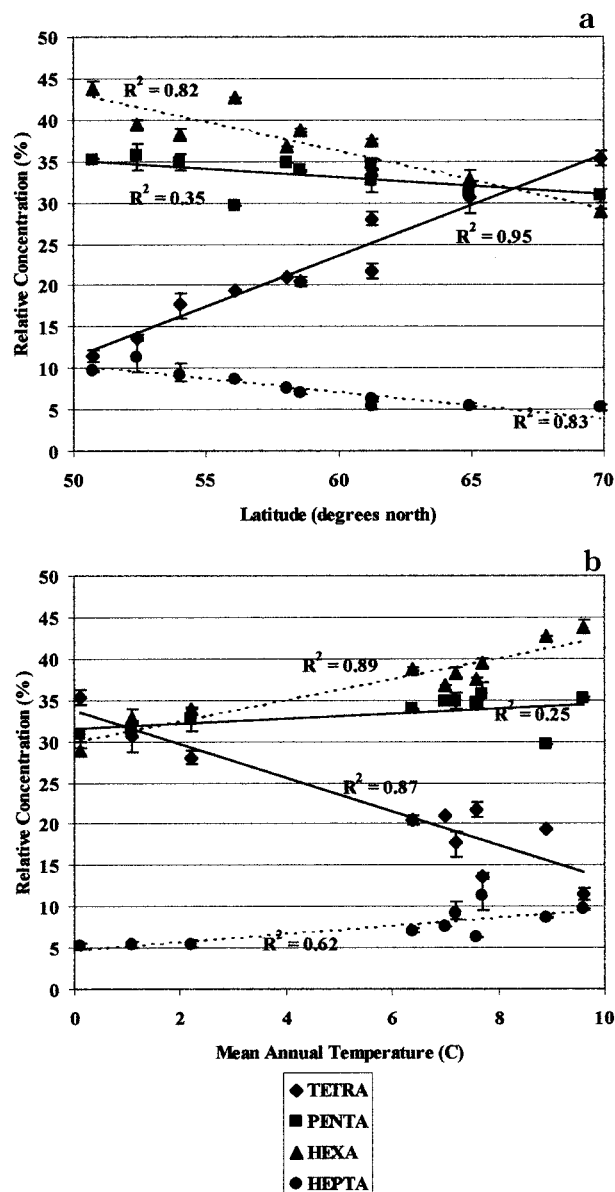


FIGURE 5. a) Latitudinal and b) temperature dependence of atmospheric PCB profile. Concentrations shown as percentage of sum of PCBs, excluding tri-CBs.

between 30 and 35% (mean 33%). The proportions of hexa- and hepta-CBs decrease with increasing latitude and decreasing temperature, with relative concentration of hexa-CBs ranging from 28 to 45% and hepta-CBs from 5 to 10%. It is interesting to note that although the actual concentrations at site C far exceed those at the other sites, when the profiles are examined, the site fits with the general picture.

A fractionation of PCBs is therefore being seen. Concentrations of the more volatile compounds are relatively uniform across the sample area, but their relative importance increases with decreasing temperature. There is little change in the relative importance of midvolatility PCBs with five chlorines across the latitudinal range examined, while the least volatile compounds are more important in the warmer southern-most sites than they are further north. In other words, the heavier, less volatile congeners do not appear to be being transported to the same extent as the more volatile congeners, perhaps due to differences in the air/surface partitioning at different temperatures. These results are in accordance with the volatility/mobility predictions for global fractionation as conjectured by Wania and Mackay (4).

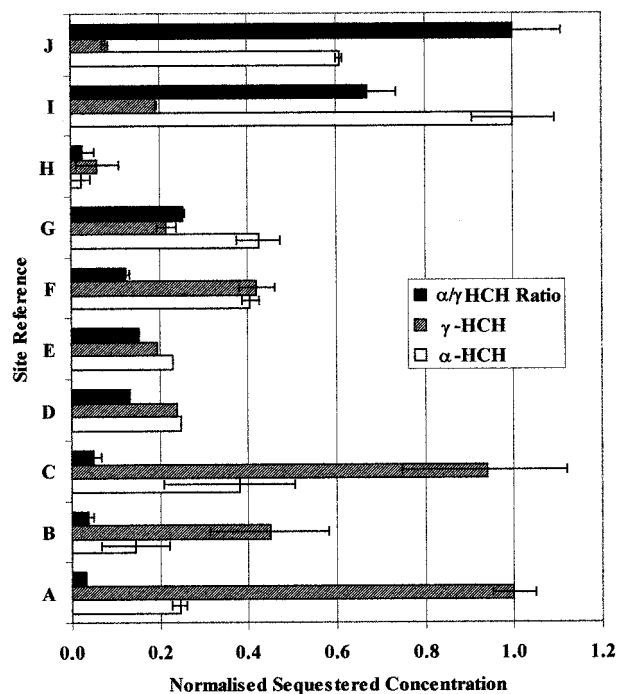


FIGURE 6. Normalized concentrations of α - and γ -HCH and normalized α/γ ratio. (Sites shown according to latitude—see Figure 4 comment.)

TABLE 4. Soil/Air Fugacity Quotients, Calculated As Described in the Text

PCB	site						
	A	B	C	E	F	I	J
52	4.1	0.70	1.7	6.8	4.8	2.7	1.5
101	2.5	3.1	2.6	4.0	4.6	2.6	1.8
118	17	0.49	2.7	1.0	2.6	2.0	1.1
153	1.2	2.5	0.79	1.6	4.0	3.0	1.5
138	0.34	0.45	0.18	0.73	0.57	0.37	0.31
180	0.17	0.57	0.11	0.39	0.03	0.21	0.09

Anderson and Hites (26) have recently investigated OH radical reactions as removal pathways for PCBs from the atmosphere. Lower chlorinated PCBs will have shorter half-lives than higher chlorinated compounds. This removal pathway will therefore cause a 'concentration gradient' of PCBs in the global atmosphere with higher concentrations of the least reactive species being favored. Other removal pathways from the environment, such as biodegradation, also favor selective removal of lighter compounds. It is suggested that these effects will enhance those of temperature-dependent partitioning processes, with all accumulating to create a global fractionation.

α - & γ -HCH. Atmospheric sampling rates by the USGS SPMDs are not available for HCHs. It is possible, however, to compare sequestered USGS SPMD concentrations of these compounds between sites to get an indication of relative atmospheric concentrations. Although α - and γ -HCH sampling rates may be different, assuming that the sampling rates are the same at all sites, the ratio of the two isomers should be proportional to the ratio in air. Figure 6 shows normalized sequestered concentrations of α - and γ -HCH against latitude (each compound is normalized to the highest measured concentration). Sequestered γ -HCH concentrations decrease with decreasing temperature, while the converse is true for sequestered concentrations of α -HCH. The normalized ratio of α - to γ -HCH is also shown in Figure 6. It is seen that the ratio increases by a factor of ap-

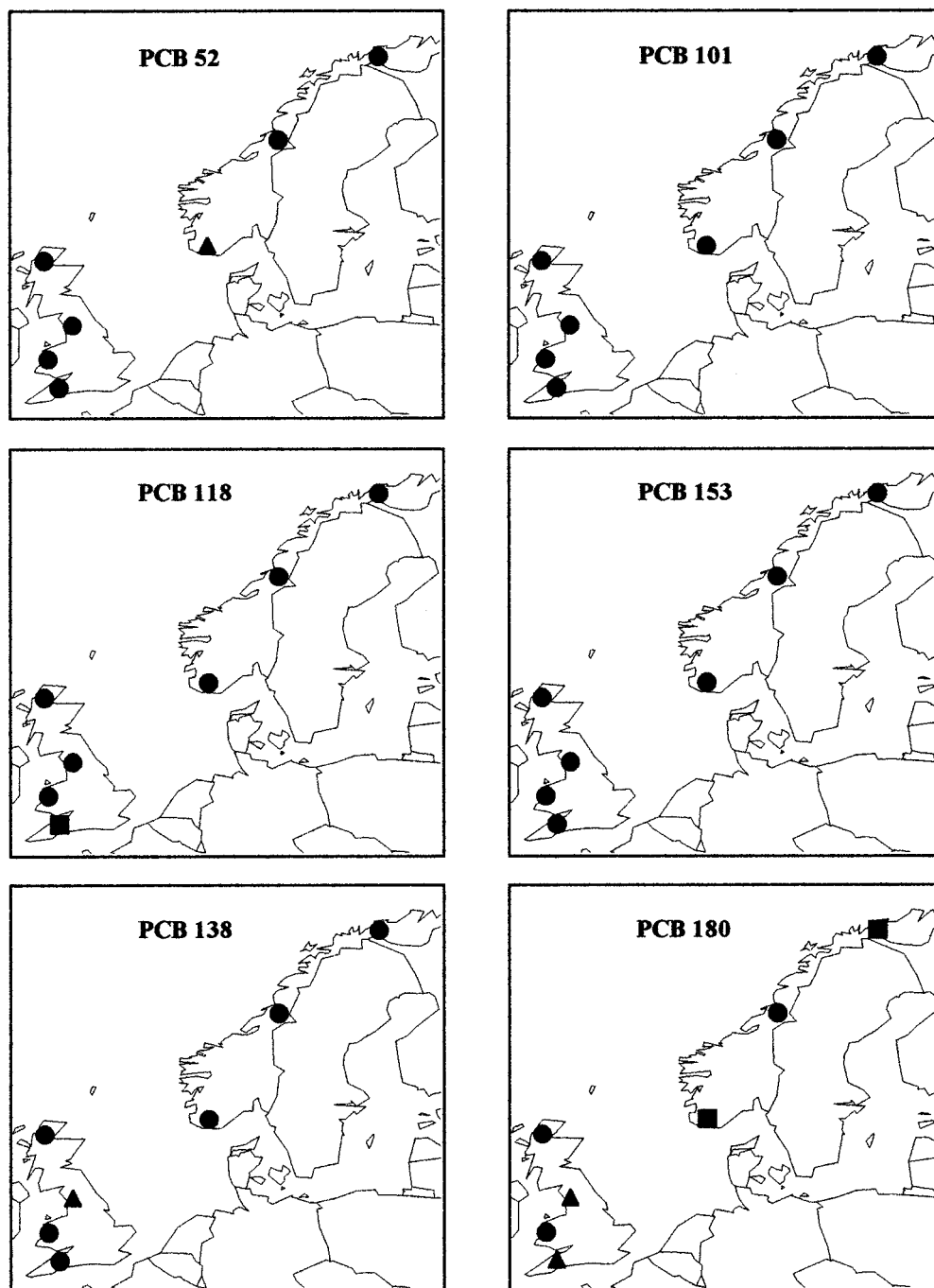


FIGURE 7. Air/soil equilibrium. Circle indicates $0.2 < f_{\text{soil}}/f_{\text{air}} < 5$; triangle indicates $0.1 < f_{\text{soil}}/f_{\text{air}} < 10$; square indicates $0.1 > f_{\text{soil}}/f_{\text{air}} > 10$.

proximately 20 from the south to the north of the study area. HCHs were available commercially as either lindane (the purified γ -isomer) or as technical HCH (60–70% α -, 5–12% β -, and 10–15% γ -HCH) (20), with lindane still being used in much of the world (27). α -HCH has a higher Henry's law constant and vapor pressure than the α - or β -isomers, indicating a greater tendency for atmospheric transport (20). In addition, it has been suggested that the γ -HCH isomer may be photolytically degraded to the α -isomer (21). Concentrations of HCH have been shown to be higher in northern than in southern oceans (28). Recent simultaneous air and water sampling has shown that since 1988 the air/water flux of α -HCH in the Bering and Chukchi Seas has reversed, so that there is currently net movement from the ocean to the atmosphere (29). All of these factors would give rise to increasing α/γ ratios of HCH with latitude and would

suggest that increased ratios are indicative of increasing distance from current source regions and long-range atmospheric transport. An unusually low α/γ ratio is observed at site H (Figure 6), and it is suggested that this is due to the site's high mean annual temperature (Table 1) in effect causing the site to appear as though it were more southerly.

Air/Soil Equilibrium Issues. It is informative to consider partitioning and flux directions between the air and depositional media. Seven of the air sampling sites (A, B, C, E, F, I, and J) were situated very near to sites where soil has been sampled in 1993 (U.K. sites) or 1990 (Norwegian sites). The soils have been analyzed for PCBs (30) (see Supporting Information).

To assess the net flux of PCBs between soil and air at each of the sites, fugacity quotients (ratio of the fugacity in the soil to the fugacity in the overlying air) were calculated using the

air and the soil concentration data. Although the use of quotients can be an oversimplification of a complex system, they provide a useful indication of the degree of departure from equilibrium. The fugacity (f) within a particular compartment is defined as the concentration of chemical in that compartment (C , mol m⁻³) divided by the fugacity capacity (Z) of that compartment, i.e.

$$f_{\text{air}} = C_{\text{air}}/Z_{\text{air}} \quad (3)$$

and

$$f_{\text{soil}} = C_{\text{soil}}/Z_{\text{soil}} \quad (4)$$

The fugacity capacity of the air (Z_{air}) and the soil (Z_{soil}) can be calculated using

$$Z_{\text{air}} = 1/(RT) \quad (5)$$

and

$$Z_{\text{soil}} = (f_{\text{OC}}\rho K_{\text{OC}})/H \quad (6)$$

where R is the gas constant (8.314 J mol⁻¹ K⁻¹), T is the temperature (K, taken to be site mean annual temperature), H is Henry's law constant (Pa m³ mol⁻¹), f_{OC} is the fraction of soil organic carbon, ρ is the soil bulk density (assumed to be 1.5 g cm⁻³), and K_{OC} is the soil organic carbon/water partition coefficient. K_{OC} was calculated from published values of K_{OW} (31) using Karickhoff's equation (32):

$$K_{\text{OC}} = 0.41K_{\text{OW}} \quad (7)$$

Values for H at 25 °C were taken from Mackay et al. (33) and were corrected for mean annual site temperature using their equations. The f_{OC} was calculated from the fraction of the soil organic matter (f_{OM} , Table 4) using

$$f_{\text{OC}} = f_{\text{OM}}/1.724 \quad (8)$$

The fugacity quotient can be cautiously interpreted as an indication of the air/soil equilibrium status. A ratio of 1 indicates equilibrium; a ratio <1 indicates net movement from air to soil, and a ratio >1 indicates net movement from soil to air. It is important to realize, however, that there are relatively large errors involved in the calculation of fugacity values (34). For example, there is still considerable discrepancy in the literature values for the physicochemical properties and also in how to correct these constants for temperature. It is perhaps reasonable to estimate that there could be at least a factor of 5 error in the calculation of fugacity values.

Table 4 shows the soil/air fugacity quotients calculated using the above approach. In nearly all cases for PCBs 52, 101, 118, and 153, movement is predicted to be from soil to air. These data can be interpreted as showing that soils have a tendency to outgas the lighter compounds (i.e., those with lower air/soil partition coefficients) at the present time. This implies that contemporary air concentrations are lower than in the past; in other words, in the past deposition was greater than volatilization. As primary sources of PCBs have been controlled there has been a reversal of the net soil/air flux (35). In contrast, for PCBs 138 and 180 net movement is predicted to be from air to soil (Table 4). One interpretation of this observation is that the soil has not scavenged sufficient quantities of these heavier PCBs from the air in the past for equilibrium to have been achieved. Soils have a greater fugacity capacity for the heavier congeners and hold them more strongly. Recent studies in the U.K. have shown a decrease in the PCB burden of U.K. soils, with the change

in concentrations being greatest for the lightest, most volatile congeners (30, 36).

Figure 7 shows the sites where air and soil were sampled and the predicted equilibrium position of the soil/air system. In Figure 7, circles indicate that the site is predicted to be close to equilibrium ($0.2 < f_{\text{soil}}/f_{\text{air}} < 5$); triangles show an order of magnitude difference in the soil and air fugacities (i.e., $0.1 < f_{\text{soil}}/f_{\text{air}} < 10$), and squares indicate that there is greater than 1 order of magnitude difference between the soil and air fugacities. It can be seen from Figure 7 that in all but three of the cases, soil/air fugacities are within a factor of 10 of being at equilibrium. There does not appear to be any trend between these three sites and latitude. It should also be noted that the quotients indicate that for most sites and PCB congeners the air and the soil fugacities are within a factor of 5. This implies that across the study area the air/soil system is approaching equilibrium for PCBs. It is suggested that atmospheric PCB concentrations are principally being maintained by recycling between environmental compartments rather than by fresh primary releases to air.

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Supporting Information Available

Two tables showing the mean sequestered amounts of PCB per SPMD and published soil concentrations (2 pages). Ordering information is given on any current masthead page.

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