PCB and PAH dynamics in a small rural lake

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PCB and PAH Dynamics in a Small Rural Lake

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Sediment traps were deployed for periods of 4−5 weeks between May 1990 and September 1991 at depths of 6.5 and 12.5 m in a 15 m deep, rural U.K. lake. Trap material was quantitatively analyzed for 14 PAH compounds, 43 PCB congeners, particle mass, and C and N contents. Derived depositional fluxes of total PAHs (11.7 mg m^{-2} yr^{-1}) and total PCBs (289 and 463 μg m^{-2} yr^{-1} at 6.5 and 12.5 m, respectively) are at the upper ends of the ranges reported in other comparable studies. The annual fluxes of individual PAH compounds are generally similar to accumulation rates determined for surface sediments at the same location, indicating the absence of significant recycling. The ratios of annual depositional fluxes to surface sediment accumulation rates are substantially greater than 1 in the case of phenanthrene (2.5) and PCBs (6.5−23). These relatively elevated fluxes combined with a consideration of particle dynamics in the lake suggest significant recycling between the sediments and water column, involving remobilization into solution accompanied by diffusive release. Recycling of PCBs tends to increase with increasing aqueous solubility. The depositional fluxes of PAHs and particle mass showed a similar seasonal dependence with the highest fluxes occurring in winter, when the water column was well-mixed. The high winter fluxes appear to be due to combination of high catchment-derived inputs (PAHs and particle mass) and atmospheric inputs (PAHs) and to sediment resuspension.

Introduction

Aquatic systems and their sediments represent important reservoirs in the global cycling of hydrophobic organic compounds (HOCs), such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). Exchanges across the air−water and sediment−water interfaces play a crucial role in the mass balance and

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dynamics of HOCs. As fresh sources of PCBs and to a lesser extent PAHs to the environment have diminished, there has been growing interest in the possibility that previously deposited compounds may be released back to the atmosphere from contaminated sediments and waters, i.e., that aquatic systems become an important secondary source of these compounds in the environment (*1*). Various workers have sought to assess the fluxes of HOCs across the air−water interface, either by direct measurement or indirectly by theoretical considerations of compound physicochemical properties (*2−4*). Comparatively little attention has been paid to cycling in the water column and across the sediment−water interface. Laboratory and field experiments have shown that recycling (release into solution) of PCBs occurs from spiked sediments (*2*, *5*), while recent sediment trap studies have provided compelling evidence that large-scale recycling of PCBs and low molecular weight PAHs can also occur under natural conditions in both freshwater (*6*) and marine (PAHs only) (*7*) environments. Earlier field studies (e.g., ref 8) also suggested the possibility of recycling, but interpretation was more uncertain because of the possible effects of confounding processes, such as sediment resuspension. Currently, the environmental extent of recycling in sediments and waters and the range of conditions under which recycling may occur are unknown.

This paper reports on monthly depositional flux (sediment trap) measurements of a range of PCB and PAH compounds in Esthwaite Water, a well-studied lake in the English Lake District (54°21′ N, 3°00′ W) (e.g., ref 9). Significantly, the lake has a number of contrasting characteristics relative to Lake Superior, where the recycling of PCBs and PAHs has been reported previously (*6*). Esthwaite Water is a seasonally anoxic, eutrophic lake with a surface area of 1.0 km^2 and a mean depth of 6.4 m. The relatively high catchment area:lake area ratio is of particular interest (17:1, cf. 0.6:1 in Lake Superior) as it may result in a greater catchment (e.g., river discharge) influence on HOC dynamics than is evident in Lake Superior (cf. ref 10). Previous studies on Esthwaite Water have estimated PAH concentrations in the overlying air and atmospheric deposition to surrogate surfaces at the lakeside (*11*, *12*) and also net sedimentation rates of PAHs and PCBs based on sediment core measurements (*13*, *14*). A quantitative comparison between the various flux measurements therefore makes an important contribution to our understanding of the general cycling of PAHs and PCBs in lakes.

Materials and Methods

Sampling and Initial Sample Treatment. Two sets of trapping apparatus were deployed for 4−5-week intervals close to the deepest point (15.5 m) of Esthwaite Water at depths of 6.5 and 12.5 m between April 1990 and September 1991. A water depth of 6.5 m lies within the metalimnion (i.e., below the well-mixed layer) during summer stratification (Institute of Freshwater Ecology, unpublished data). Each trapping configuration consisted of a set of four radially distributed collar-type traps and, during the early stages of the study, a separate baffled funnel trap. The collar trap comprised a PVC cylinder (cross-sectional area of 11.3 cm^2 and a height:diameter or aspect ratio of 2.7) fused into a

Perspex jar. Although the optimum trap design is now considered to be a simple cylinder with an aspect ratio $\geq 5{:}1$ and it is known that collar-type designs tend to overtrap (15, 16), we used the same traps that were employed in previous sedimentation studies in Cumbrian lakes (17–19). Representative sampling by these traps has been confirmed by controlled field experiments (20). Large quantities of particulate material for PAH and PCB determination were initially collected by means of a polyethylene funnel having a cross-sectional area of 1134 cm² and fitted with a polystyrene baffle comprising cells with an aspect ratio of 3. Although formerly regarded as an acceptable design (21, 22), baffled funnel traps are no longer recommended (15). Initially the collar traps were used only to obtain fluxes of particle mass, C, and N. PAH and PCB concentrations were measured in the funnel-trap material, and their fluxes were calculated as the product of the appropriate compound concentrations and the particle mass flux. Fresh mercuric red (HgI_2) was added to the traps to restrict microbial alteration of the sample during collection (15, 18). Uncertainty still exists over the ideal strategy for preserving the integrity of trap material during deployment (15). Zooplankton and other mobile plankton were not removed following retrieval of the traps in our study, possibly introducing some error into the measured trap fluxes (15). The active range of zooplankton in Esthwaite Water, however, rarely extends as deep as 12.5 m, and previous trap studies have shown negligible zooplankton material in traps at this depth (C. S. Reynolds, personal communication).

The first sample (May 1990) was obtained from only one set of traps moored at a depth of 11.5 m. Over a fortnight covering the end of January/beginning of February 1991, the surface of Esthwaite Water froze. During the subsequent thaw, one funnel trap was lost and both sets of collar traps beached on the shore of the lake. As a result, no 6.5- and 12.5-m samples were obtained over 37- and 83-day periods, respectively, in early 1991. Subsequent PAH and PCB analysis of the 12.5-m trap samples was restricted to material accumulated in the collar traps, facilitated by improved analytical sensitivity. Cumulative annual depositional fluxes at 6.5 m were calculated by (i) summing the measured fluxes between May 5, 1990, and May 16, 1991 (340 days taking into account the missing samples), and (ii) adding in an extra 25 days deposition with a flux equivalent to the mean for the periods immediately before and after the missing samples. The fluxes at 12.5 m were calculated in the same way but used the 6.5-m fluxes for the additional missing period of 46 days.

Trap contents were stored at 5 °C immediately on returning to the laboratory. Trap particles were isolated either by settlement or by filtration through 0.45-μm Millipore HA membrane filters and then air-dried and milled to a homogeneous fine powder. Total mass was determined gravimetrically. Total C and N contents were determined on a weighed subsample of powdered trap material using a Carlo Erba EA-1108 CHNS elemental analyzer. Because of the limited available material, no C and N data are available for the 12.5-m trap following the loss of the funnel trap. No correction was applied for carbonate-C because of the lack of carbonate rocks in the catchment (23), the soft-water nature of Esthwaite Water, and the absence of any reported carbonate precipitation in the lake (e.g., ref 9).

Extraction and Analysis of PAHs and PCBs. Samples were weighed into pre-extracted Whatman cellulose extraction thimbles and Soxhlet extracted for a minimum of 9 h with 200 mL of dichloromethane (DCM) on a Buchi 810 fat extraction system. Copper turnings were incorporated during extraction to remove any elemental S. The DCM extract was concentrated to 6 mL, and the sample was split in a 2:1 ratio for PCB and PAH analysis. Samples were extracted in duplicate where sufficient trapped material was available.

The PCB fraction was solvent exchanged into hexane, cleaned up on a 6-g column (i.d. 15 mm) of 1.25% H_2O-deactivated Florisil, and eluted with 40 mL of pesticide grade hexane. The eluent was spiked with a known quantity of congeners 30 and 209, which act as retention time reference standards, before reducing to 250 or 500 μL prior to analysis. Sample extracts were analyzed for PCBs on a Hewlett Packard HP5890 Series II gas chromatograph by electron capture detection (ECD). Instrumental conditions and parameters are described in Sanders et al. (13). Identification and quantification of PCBs were achieved by overlaying the chromatogram of a standard mix containing 51 congeners onto the sample chromatogram. Peaks were matched and named by retention time. Of the 51 congeners screened, the following 43 were quantified: 6, 10, 14, 18, 28, 40, 44, 52, 54, 61/74 (co-elute), 66, 77/110, 82/151, 99, 101, 104, 105, 118, 119, 128, 138, 149, 153, 155, 156, 170, 180, 183, 185, 187, 188, 189, 194/205, 198, 201, 202, 204, 206, and 208. Although congeners 77 and 110 could not be separately identified by ECD, congener 110 is known to constitute more than 90% of the combined peak from GC/MS analyses undertaken in our own laboratory. The average external recovery of all quantified congeners was 92%, determined by spiking of sediment trap material. On-column instrumental detection limits were ≤ 0.5 pg, based on three times the baseline noise. System blanks were continuously screened and typically gave peaks <10% of those for samples. In the case of samples with the lowest ΣPCB contents, blanks gave a maximum of 35% of the sample response. All sample peaks were blank corrected. It is clear that in some cases, most notably for the lower molecular weight congeners, samples were near detection limits. Subsequent studies in this laboratory have highlighted that air-drying of samples can be a source of contamination, particularly for lighter congeners (24). The trap samples were stored wet, air-dried, and extracted in two batches. While advocating wet extraction in the future, we are confident that the values and trends observed in this study provide a true reflection of in situ variability and behavior, based on more recent analyses of surface sediments using wet extraction.

The PAH fraction was cleaned up on a 1-g microcolumn (i.d. 5 mm) of activated Florisil and eluted with 15 mL of double-distilled DCM. The samples were then concentrated to between 100 and 1000 μL (dependent upon mass extracted), and the following 14 unsubstituted PAH compounds were quantified by high-performance liquid chromatography with fluorescence detection: naphthalene, acenaphthene/fluorene (co-elute), phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene/chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, 1,2,5,6-dibenz[ah]anthracene, and benzo[ghi]perylene. Extracts of 2 μL were injected onto a 25-cm Lichrocart RP-18 reverse-phase column via a Rheodyne valve. Solvent was delivered by a Perkin Elmer LC250 binary

pump, programed with the following acetonitrile (A)/water (B) gradient elution; 0–10 min, 65% A, increasing to 100% A at 15 min, maintaining this pattern until 25 min, followed by a constant reduction to 65% A at 30 min. PAHs were detected on a Perkin Elmer LS40 programmed fluorescence detector employing the following excitation (Ex)/emission (Em) pattern: 0 min, Ex 280 nm/Em 340 nm; 10 min, Ex 240 nm/Em 400 nm; 13 min, Ex 305 nm/Em 430 nm. All analysis information was acquired, stored, and processed on a VG Minichrom data handling package. PAH recoveries, determined by spiking of sediment trap material, were in excess of 85% for all compounds of three rings and greater, with anthracene giving the poorest reproducibility ($\pm15.3\%$, $n = 3$). The most volatile species, naphthalene and acenaphthene/fluorene, gave significantly lower recoveries (61 and 67%, respectively). System blanks were routinely screened and samples blank corrected. On-column instrumental detection limits were 4–80 pg, based on three times the baseline noise.

Results and Discussion

Sediment Deposition Characteristics in Esthwaite Water. The annual depositional flux calculated from the 12.5-m trap data is 1700 g m^{-2} yr^{-1} compared to 2030 g m^{-2} yr^{-1} measured in 1987–1988 (*25*). Present-day sedimentation rates, based on sediment dating, were recently measured both at the trap site (1680–1980 g m^{-2} yr^{-1}) (*26*) and in a water depth of 11 m approximately 200 m from the trap site (704 g m^{-2} yr^{-1}) (*14*). This disparity agrees with a third sediment study, which showed that the deep-water sedimentation rate in the vicinity of the trap site varies by a factor of ~2 (*27*). Based on a more extensive coring program, Hilton et al. (*28*) showed that approximately 60% of the observed variance in the sedimentation rate in Esthwaite Water as a whole was explained by a linear relationship with increasing water depth, attributed to resuspension and sediment focusing. In an early study, Pennington (*29*) reported that the trap flux to sedimentation rate in the deep-water region of Esthwaite Water was ~2.6 and attributed this to local resuspension, especially following autumn overturn of the water column. Consideration of all the data now available, however, indicates that while sediment focusing is an important process in the lake, sediment resuspension does not necessarily extend to its deepest waters.

The total mass flux over the single 58-day sampling period between November 29, 1990, and January 25, 1991, was more than double that during any other individual period throughout the study (Figure 1). More generally, the mass fluxes tended to be greater during the period of complete water column mixing between October 9, 1990, and May 14, 1991 (unpublished data, Institute of Freshwater Ecology). Similar seasonal variations in monthly flux data were previously observed at the same site in Esthwaite Water for the period April 1987–March 1988, although fluxes of ~10 g m^{-2} d^{-1} were evident then over a more extended period from mid-October to mid-February (*25*). Resuspension during complete mixing and a seasonal increase in catchment inputs probably both contribute to the enhanced depositional fluxes in winter. In a study of the neighboring Windermere catchment (*30*), a significant (*p* < 0.05) relationship was found between hydraulic discharge to the lake and the associated riverine concentrations of various allochthonous components (e.g., particulate Al).
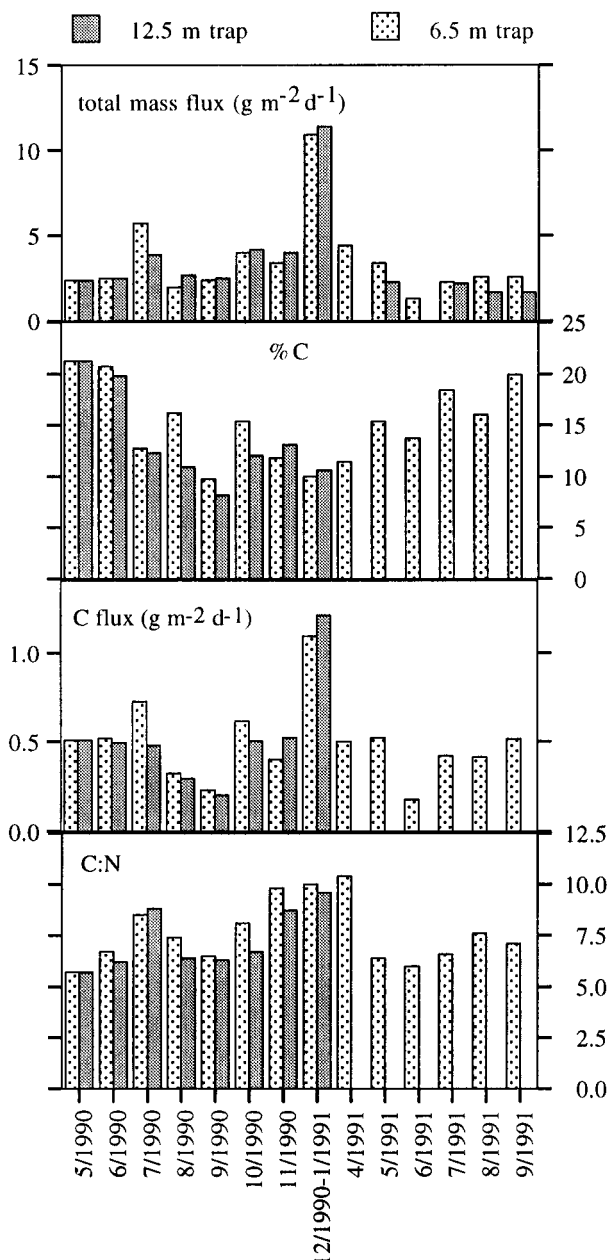

FIGURE 1. Characteristics of sediment trap material collected in Esthwaite Water between May 1990 and September 1991, including C content in wt % and the mass ratio of C:N.

Long-term rainfall records for the area indicate that the wettest months (August–January) have approximately twice the rainfall of the driest months (February–July) (*31*). It follows that sediment discharge to Esthwaite Water from rivers probably has a distinct seasonality with the highest inputs during the wettest months. For monthly variations in trap fluxes to be attributable to river inputs, the residence time of particles in the lake must be of a similarly short (i.e., $\sim$monthly) time scale and much less than the 2.5 yr estimated in Lake Superior (*6*). Independent estimates of particle residence time (*t*) can be made at the deepest point in Esthwaite Water, based on the estimated particle settling velocity ($S = 0.75$ m d^{-1}) (*32*) and on the typical wintertime suspended particle concentration ($C = 2$ g m^{-3}) (*33*) in the lake:

$$t = CZ/J = Z/S$$

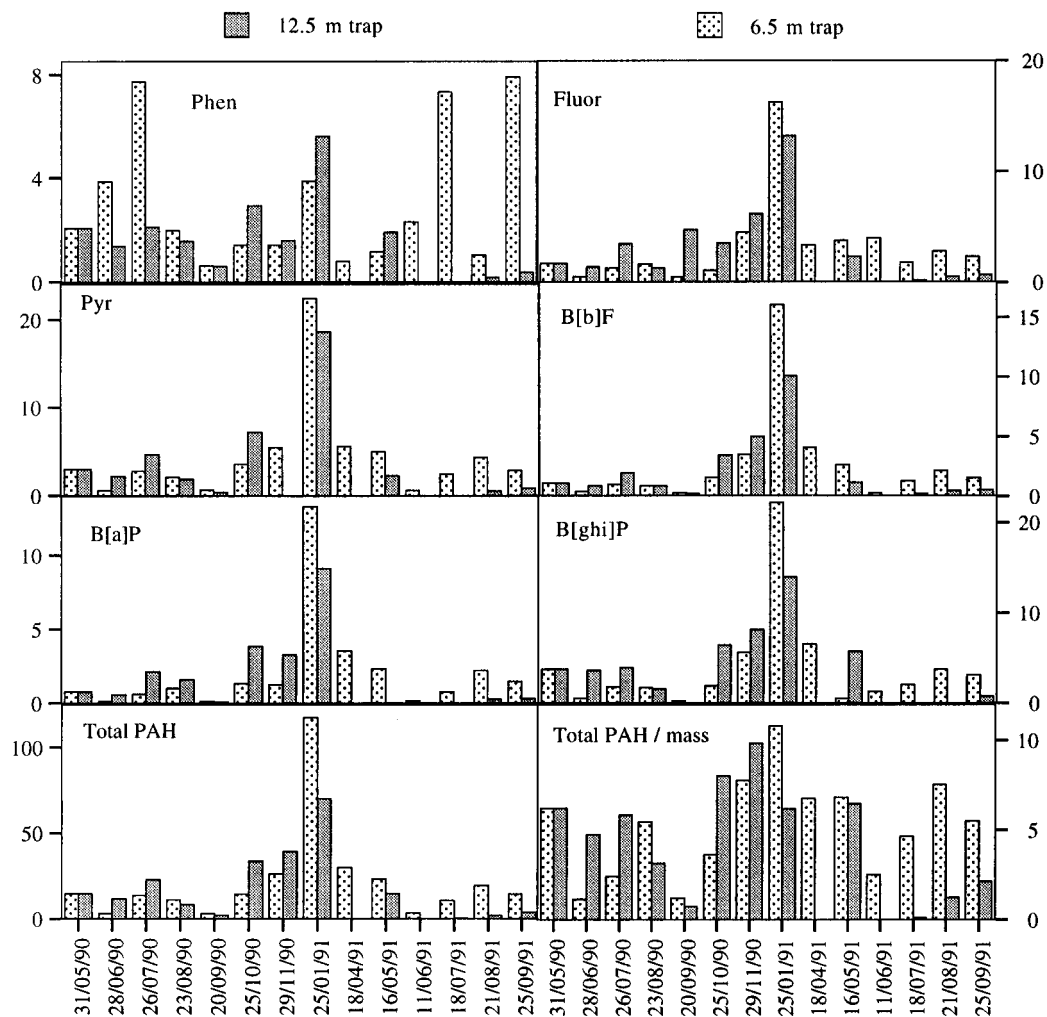where *Z* is the water depth (15.5 m) and *J* is the settling flux.

FIGURE 2. Sediment trap fluxes of selected PAH compounds and total PAHs ($\mu g\ m^{-2}\ d^{-1}$), together with the total PAH flux normalized to the particle mass flux ($\mu g\ g^{-1}$), in Esthwaite Water between May 1990 and September 1991. The selected compounds are phenanthrene (phen), fluoranthene (fluor), pyrene (pyr), benzo[*b*]fluoranthene (B[b]F), benzo[*a*]pyrene (B[a]P), and benzo[*ghi*]perylene (B[ghi]P).

The typical wintertime settling flux at 12.5 m of 4 g m^{-2} d^{-1} was used in the calculation. The resulting estimates of *t* based on settling flux and settling velocity are 8 and 21 d, respectively, lending support to the potential role of river inputs as a controlling factor. The much longer particle residence time in Lake Superior compared to Esthwaite Water results primarily from the far greater depth (maximum 405 m) of Lake Superior.

The C contents of the trap material were relatively low in the winter months (generally 10–15% by wt) compared to summer (~20%), whereas C:N ratios were relatively high in winter (~10) compared to summer (6–8) (Figure 1). As with similar previous observations in both Esthwaite Water (*25*) and nearby Windermere (*19*), these variations are attributed principally to the greater contribution from autochthonous algae during the more productive summer period. The winter values are compatible with both catchment runoff and sediment resuspension sources (e.g., ref 29). The lowest depositional fluxes of C occurred in August and September during the latter stages of summer stratification. This corresponds to the period after deposition of the spring algal bloom (*9*) but prior to overturn on October 9.

Figure 1 highlights a generally close correspondence between the 6.5-m and 12.5-m data sets. This probably reflects a combination of factors including the shallow nature of the lake, the relative efficiency of mixing, the small vertical separation between the two sampling depths, and the fact that both depths lie below the well-mixed surface layer during summer stratification (*9*). The correspondence between traps precludes neither organic matter decomposition in the water column nor sediment resuspension. It is concluded that temporal variations in algal productivity, sediment resuspension, and river discharge probably all make a significant contribution to the observed variations in mass flux, C contents and flux, and the C:N ratio.

Depositional Fluxes of PAHs. Figure 2 shows the temporal variations in the trap-derived depositional fluxes of selected PAH compounds and ∑PAH, where ∑PAH is the sum of the 14 quantified PAH compounds. Pyrene, benzo-[*ghi*]perylene, fluoranthene, and benzo[*a*]pyrene were the four most abundant compounds. The relative concentrations of individual PAH compounds generally showed very little variation throughout the year and corresponded well with their concentrations in the bottom sediment (*14*). The most striking feature of the PAH flux data, for all compounds except phenanthrene, is a seasonality similar to that shown by the total particle mass flux (cf. Figures 1 and 2). The PAH fluxes were greatest during the period of complete water column mixing between October 9, 1990, and May 14, 1991, accounting in total for more than 70% of the total

TABLE 1

Comparison of Depositional Fluxes of Total PAHs Measured in Various Sediment Trap Studies

| location and source	ΣPAH flux (μg m^{-2} d^{-1})	comments
Esthwaite Water (this study)	32	averaged over 1 yr
Stockholm arphipelago, Baltic Sea (34)	2−35	six sites with various degrees of urban influence; various seasons
Puget Sound (35)	6.7	influenced by proximity to Seattle; seasonally averaged
Siskiwit Lake (36)	0.27	remote island lake, N Lake Superior; averaged over 1 yr
NW Mediterranean Sea (7)	0.30−0.91	four sites between Nice and Corsica ranging from near-shore to ~50 km off-shore; March−June period only
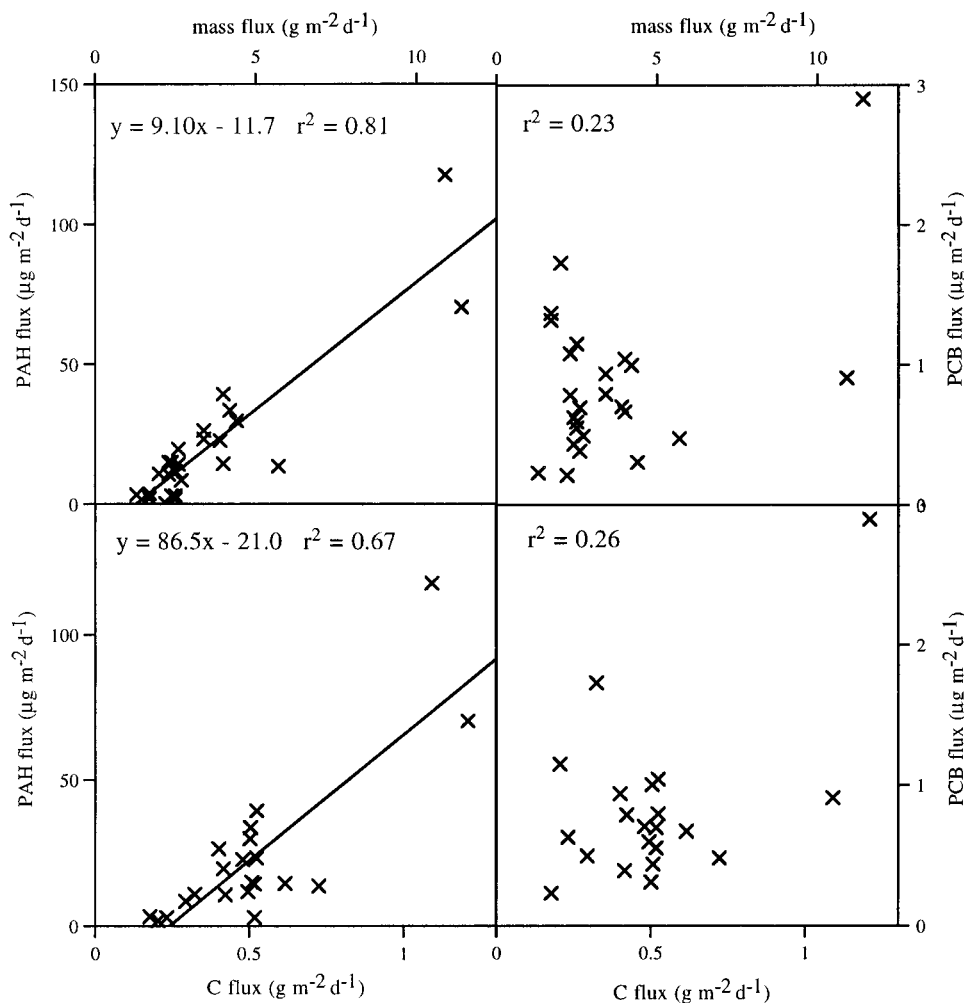
FIGURE 3. Plots of total PAH flux and total PCB flux against particle mass and C fluxes measured in the 6.5- and 12.5-m sediment traps deployed in Esthwaite Water between May 1990 and September 1991.

annual PAH inventory to both traps. As with particle mass, no consistent differences were apparent in the PAH fluxes between the 6.5- and 12.5-m traps. The ΣPAH flux at 12.5 m averaged over 1 yr in Esthwaite Water is compared in Table 1 with ΣPAH fluxes reported in other sediment trap studies, in which the number and range of PAH compounds measured were similar. The Esthwaite Water value lies at the upper end of the range and is similar to fluxes measured at sites with a significant degree of local urbanization and with both riverine and direct atmospheric PAH sources. Although in a rural setting, Esthwaite Water is ~100 km north of the Manchester and Liverpool conurbations and ~30 km inland of a coastline having several centers of population and industry. In addition, Esthwaite Water is surrounded by minor roads, a small sewage treatment works discharges into the main river inflow within 1 km of the

lake, and there is a substantial local community in which wood-based and fossil fuel-based heating is common.

The relationship between the ΣPAH and particle mass fluxes is shown more clearly in Figure 3. The relationship between ΣPAH and C fluxes is also shown as organic matter is generally considered to be the main carrier phase for HOCs, and it is common to normalize HOC concentrations to organic C (6, 37). Broman et al. (38) have presented evidence that spheroidal carbonaceous particles derived from fossil fuel combustion are important as specific carriers of PAHs in the settling particulate matter found close to urban sources in the Baltic Sea. It is therefore significant that in the case of the trap material from Esthwaite Water the ΣPAH flux correlates more closely with total particle mass than with C (Figure 3). Close examination of the data shows that this is essentially because the seasonal increase
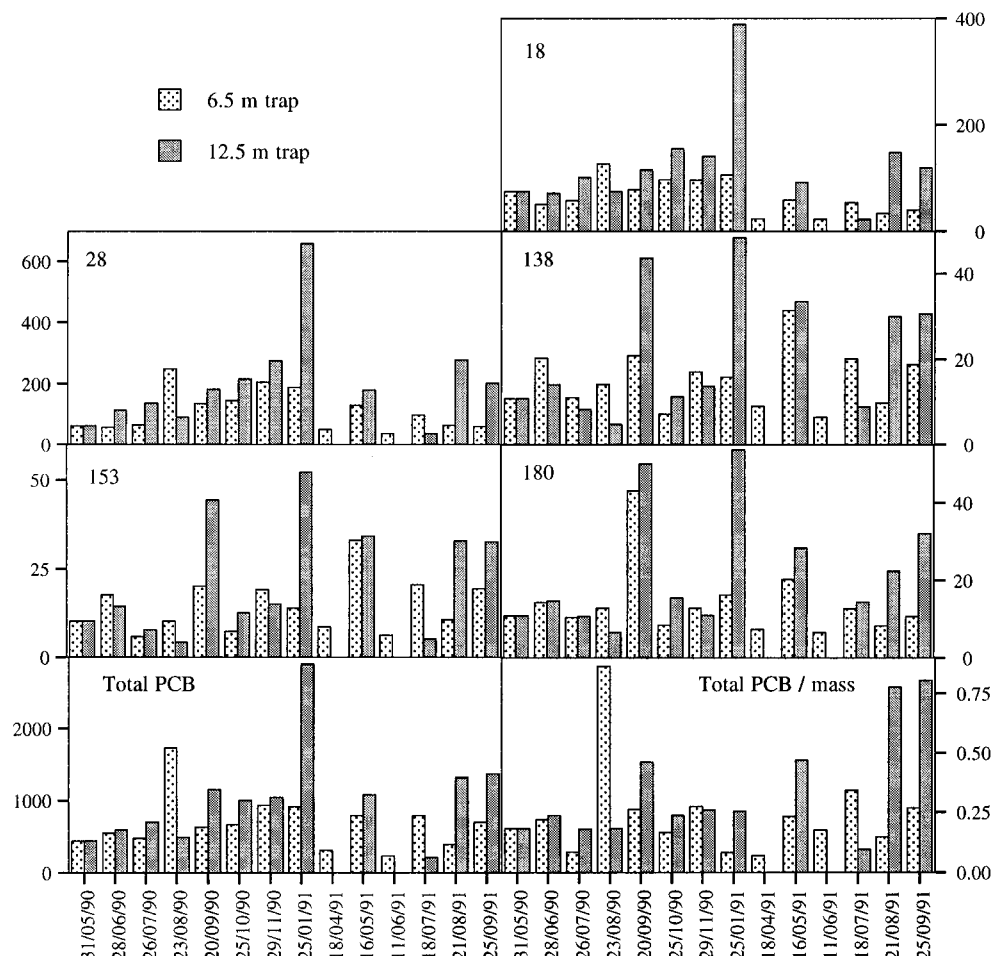
FIGURE 4. Sediment trap fluxes of selected PCB congeners and total PCBs (ng m^{-2} d^{-1}), together with the total PCB flux normalized to the particle mass flux (μg g^{-1}), in Esthwaite Water between May 1990 and September 1991.

in C flux during spring and summer (Figure 1), associated with increased algal productivity, is not matched by an increase in ΣPAH flux (Figure 2).

The observed flux relationships involving ΣPAH may be related to a number of factors. Particle deposition rates may act directly to control ΣPAH flux through in situ scavenging. Alternatively and perhaps more likely given the fact that ΣPAH correlates less strongly with the C than with total particle mass, the relationships may be related to a factor with the same seasonality resulting in the high deposition rates between October and May. The most likely candidates are sediment resuspension and either causally linked or coincidental increased inputs to the lake from external sources. Runoff is the main external source of particles, whereas direct atmospheric deposition and catchment-derived inputs may both be important for ΣPAHs. Scavenging is a more likely control in large aquatic systems with long residence times, such as the oceans and large lakes. In smaller and especially shallower water bodies with relatively short particle and pollutant residence times, temporal variations in external inputs are more likely to be important. Such influences are apparent when comparing variations in trace metal concentrations between water bodies of contrasting sizes (*39*). Although not observed in all sediment trap studies, winter maxima in depositional fluxes of PAHs have been reported in other aquatic systems and similarly have been linked to a combination of increased emissions, higher catchment washout, and resuspension (*34, 40*).

Depositional Fluxes of PCBs. Figure 4 shows the temporal variations in the trap-derived depositional fluxes of selected PCB congeners and ΣPCB, where ΣPCB is the sum of the 43 quantified congeners. The highest fluxes again generally occurred during autumn and winter months, but the seasonal dependence was less well-defined than with PAHs, and the correlations with total mass and C fluxes were relatively poor (Figure 3). The PCB fluxes to the 12.5-m trap tended to be greater than to the 6.5-m trap, especially in January 1991 when the flux to the lower trap was 3-fold higher. However, a considerable degree of scatter is evident in the data. When averaged over 1 yr, the flux of ΣPCBs at 12.5 m (1270 ng m^{-2} d^{-1}) was 1.6 times that at 6.5 m (793 ng m^{-2} d^{-1}). As with ΣPAHs, the ΣPCB flux in Esthwaite Water is at the top end of the range reported in other comparable studies (Table 2).

Congeners with structures containing $\leq$4-Cl dominated the mixture of PCBs extracted from the trapped material. Most significant contributors were congeners 18 and 28, constituting over 10% each of the ΣPCB entering both traps. Congeners 14, 44, 66, 101, 77/110, 138, 149, 153, and 180 were the other most abundant PCBs quantified.

As with PAHs, seasonal trends in depositional fluxes of PCBs are reported in only a limited number of studies, but in comparison the trends are considerably more diverse. In Lake Ontario, greater PCB fluxes in winter were attributed to sediment resuspension (*40*). In the Western Baltic, the PCB concentration in settling material was inversely related to the depositional flux of particle mass, which peaked in

TABLE 2

Comparison of Depositional Fluxes of Total PCBs Measured in Various Sediment Trap Studies

location and source	$\sum$PCB flux (ng m^{-2} d^{-1})	comments
Esthwaite Water (this study)		
6.5 m	793	averaged over 1 yr
12.5 m	1270	
two Swedish lakes and coastal bay, S Baltic Sea (8)	40−360	summer period only
Lake Ontario (40)	80−1900	winter fluxes at various sites
Lake Superior (6)	370	average during stratification
	160	average during nonstratification
W Baltic Sea (41)	66−307	range over 2 yr
Sargasso Sea (42)	1−11	range over 2 yr

winter (41). A similar situation was reported in Lake Superior, where PCB (and phenanthrene) fluxes were higher during summer stratification despite lower mass fluxes, implying either higher surface water concentrations or more efficient scavenging (6). Depositional fluxes also decreased with depth in Lake Superior during stratification, suggesting significant water column recycling (6). The behavior of PCBs in aquatic systems appears relatively complex, reflecting the combined effects of varying inputs and mixing conditions, and various scavenging and recycling processes.

Comparison of Depositional Fluxes with Redox Cycling of Fe and Mn. Iron and manganese oxides are well-known as important carrier phases for trace substances in natural waters. The iron oxides formed in Esthwaite Water contain relatively high organic impurities (8−36% by mass) (43), increasing the likelihood of significant HOC uptake. The seasonal dependences of the depositional fluxes of Fe and Mn in Esthwaite Water have previously been determined at the same site as that used in the present study (18). Significant and varying fluxes of iron and manganese oxides occurred through the spring and summer months, linked to the progressive growth and decay of the anoxic hypolimnion. The highest oxide fluxes of all occurred over a short time period immediately following overturn, associated with mixing and re-oxidation of the anoxic hypolimnion. In the present study in 1990, hypolimnetic anoxia commenced in mid-June and ended with overturn in early October (unpublished data, Institute of Freshwater Ecology). Based on the absence of any related temporal deposition patterns, it is concluded that iron and manganese oxides are not a dominating influence on the depositional fluxes of PAHs and PCBs. However, the slightly elevated 12.5-m fluxes of $\sum$PAHs and $\sum$PCBs in July 1990 may be related to deep-water iron oxide fluxes that peak at this time (18). The fact that no comparable effect was associated with the slightly higher iron oxide fluxes following overturn (18) may be due to masking by the generally high particle fluxes during complete water column mixing.

Comparison of Depositional Fluxes with Sedimentation Rates. PAH and PCB concentrations have recently been measured in dated sediment cores collected approximately 200 m from the trap site (13, 14). Figure 5 shows for selected compounds the ratios of the annual trap fluxes at 12.5 m to the previously reported accumulations rates in the surface sediment layer (0−2 cm). This layer is dated as representing the period 1985−1990 (14). Hilton et al. (28) suggest that bioturbation is relatively unimportant in Esthwaite Water sediments, and this is supported by profiles of ^{134}Cs, ^{137}Cs, and ^{210}Pb, which show no well-mixed surface layer at a scale of 2 cm sediment slicing (14). The ratios calculated for most individual PAHs and $\sum$PAHs lie
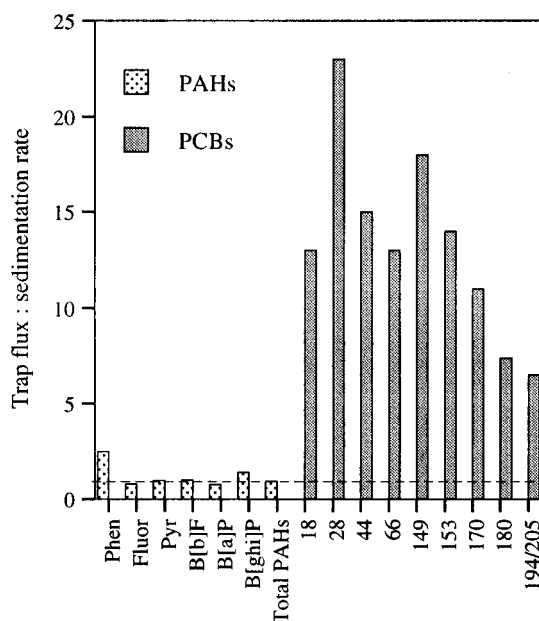

FIGURE 5. Ratios of selected depositional fluxes in the 12.5-m trap (lake depth = 15 m) to sedimentation rates previously measured at the same location in the surface sediment layer, dated as 1985−1990. Sediment data from Sanders et al. (13, 14). The dashed line indicates a ratio of 1:1.

close to 1, suggesting that the PAHs reaching the sediment surface are not generally subject to recycling effects and providing independent support for the integrity of the trap data.

In comparison to the other PAHs, the ratios of trap flux: sediment accumulation are substantially greater in the case of phenanthrene (2.5) and the PCBs (Figure 5). The highest ratios (13−23) were observed among the low molecular weight PCB congeners, whereas congener numbers 170 (i.e., heptachlorinated) and above appeared to show a decreasing ratio with increasing molecular weight. The high ratios may be due to recently increased inputs of phenanthrene and PCBs to Esthwaite Water, but this is unlikely given that U.K. emissions of PCBs to the atmosphere have declined in recent years, resulting in a decline in air concentrations and hence deposition (13, 44, 45). The most probable explanation is that phenanthrene and PCBs are undergoing some form of recycling (i.e., solubilization and diffusive release) from the sediments to the water column. It seems unlikely that this change could be strongly influenced by biological or chemical degradation, since a number of studies have shown the recalcitrance of PCBs to breakdown in soils and sediment systems (46−48).

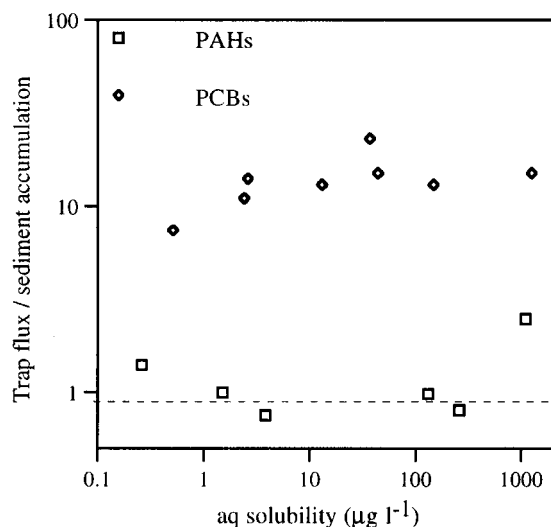Evidence of active recycling has been reported in several other studies. In the Mediterranean Sea, Lipiatou et al. (7)

FIGURE 6. Ratios of sediment trap fluxes:sediment accumulation rates of various PAHs and PCBs plotted against their aqueous solubilities.

observed trap flux:surface sediment flux ratios substantially greater than 1 for the low molecular weight PAHs, fluoranthene, pyrene, and especially phenanthrene and ratios ≤ 1 for the high molecular weight PAHs with >4 rings. McVeety and Hites (36) also observed relatively high trap flux:surface sediment flux ratios for low molecular weight PAHs, again especially with phenanthrene, in their study of a wilderness lake in the northern Lake Superior region. Larson (8) found that trap material was enriched in PCBs relative to the underlying sediments in two southern Swedish lakes and a coastal bay in the southern Baltic Sea and speculated that the enrichment was due to some recycling process. The most detailed study of this sort, however, is that of Baker et al. (6), who measured a similar range of PAHs and PCBs in traps and surface sediments in Lake Superior to that reported in the present work. The overall picture in Lake Superior was very similar to that observed in Esthwaite Water. The trap flux:surface sediment flux ratios were close to 1 for the high molecular weight PAHs but $\gg 1$ for phenanthrene, fluorene, and all PCB congeners. The main differences from Esthwaite Water were in the degree and location of recycling. Between 90% and 99.9% of the PCB and low molecular weight PAH annual fluxes were recycled in Lake Superior (i.e., equivalent flux ratios of $\sim 10-1000$), of which 67–83% of the PCB recycling occurred in the water column. Water depths at the four sites occupied by Baker et al. (6) ranged from 100 to 270 m, and the decrease in trap fluxes with depth occurred only during periods of water column stratification. The absence of water column recycling of PCBs and low molecular weight PAHs in Esthwaite Water, whether real or apparent, is probably linked to the much shallower depth and hence to the shorter particle settling times and the more effective mixing of the water column (see previous discussion). Thus, water column recycling may actually occur, but its effects may be masked by the physical characteristics of Esthwaite Water.

Baker et al. (6) noted that the degree of recycling in Lake Superior tended to increase with water solubility and that PCBs exhibited substantially greater recycling than PAHs with the same water solubility. Similar trends were observed in Esthwaite Water, but the water solubility dependence was less distinct (Figure 6). Baker et al. (6) linked these and

other observations to the combined effects of water solubility and HOC source. It is hypothesized that PCBs and low molecular weight PAHs exist in the air primarily in the vapor phase. Conversely, the high molecular weight PAHs are associated primarily or exclusively with combustion-derived aerosols. HOCs will enter the lake via dry gaseous deposition, dry particulate deposition, and wet deposition with the relative importance of each depending on the physicochemical properties of the compound. Once in the water column, it is envisaged that the PCBs and low molecular weight PAHs may partition, according to water solubility, between the aqueous phase and lacustrine particles and be prone to subsequent recycling (e.g., due to decomposition of algal remains). The high molecular weight PAHs do not participate in such lacustrine recycling as they remain tightly locked up in combustion-derived aerosols (see also ref 38).

It was suggested above that temporal variation in catchment-derived inputs was an important factor in addition to sediment resuspension in contributing to the higher wintertime trap fluxes of sediment mass and $\sum$PAHs. During the period of highest trap fluxes of particle mass and PAHs in December 1990–January 1991, the concentrations of individual PAH compounds in the trap material were typically half those measured in the surface sediments (14). Conversely, concentrations of PCB congeners in the same trap material were typically between 4 and 19 times greater than those in the surface sediments (13). These compositional differences indicate that the high deposition rates observed in December 1990–January 1991 were unlikely to have been due to sediment resuspension alone and, therefore, give further credence to the importance of varying catchment inputs.

Comparison of Depositional Fluxes with Atmospheric Inputs. The atmospheric depositional fluxes of a similar range of PAH compounds to that reported in this study were measured on the shore of Esthwaite Water in 1990/1991 using a wet and dry deposition collector (49). The atmospheric deposition of $\sum$PAHs for the period July 17, 1990–July 9, 1991, was 964 μg m^{-2} yr^{-1}, equivalent to $\sim$8% of both the measured sediment trap flux and the accumulation rate in the surface sediments. The relatively low atmospheric fluxes may possibly be due to undercollection, although a concurrent study of a second lake in an industrial area of Lancashire, using the same wet and dry collector, found that up to 90% of the $\sum$PAH input was attributable to direct atmospheric deposition (49). It may well be that lakes such as Esthwaite Water, with a high catchment area:lake surface area ratio, receive major catchment-derived inputs of PAHs in contrast to systems dominated by direct atmospheric inputs, like Lake Superior. In the case of Esthwaite Water, indirect atmospheric inputs via catchment erosion will be supplemented by the local effects of road run-off and sewage discharges. Although the atmospheric depositional fluxes measured to artificial deposition collectors were relatively low at Esthwaite Water, there was a distinct seasonality with winter atmospheric fluxes in 1990/1991 being a factor of $\sim$5 higher than the rest of the year (49) and coinciding with high atmospheric concentrations (11). These effects were attributed to the proximity of Esthwaite Water to local combustion sources (11) and further support the contention that the high wintertime sediment trap fluxes of PAHs in the lake are due at least in part to seasonally varying inputs.

Atmospheric depositional fluxes of PCBs have not been measured at Esthwaite Water but are available for a rural site ~50 km to the south in 1992/1993 (~140 μg of ΣPCB m^{-2} yr^{-1}, C. Halsall and K. C. Jones, unpublished data). This flux is more than adequate to account for the net deposition of PCBs in Esthwaite Water (22 μg of ΣPCB m^{-2} yr^{-1}), based on the surface sediment studies (13) but insufficient to account for the measured trap fluxes (290 μg m^{-2} yr^{-1} at 6.5 m, 460 μg m^{-2} yr^{-1} at 12.5 m). The data are therefore compatible with direct atmospheric deposition being the main external source of input for PCBs and with the occurrence of biogeochemical recycling between the sediments and water column of Esthwaite Water.

Concluding Remarks

The sediment trap study in Esthwaite Water adds to a growing body of evidence that PCBs and low molecular weight PAHs (especially phenanthrene) undergo rapid biogeochemical recycling in lakes and marine basins. Recycling is apparent in these various systems not withstanding substantial differences in their physical characteristics (e.g., water depth and mixing conditions), which affect particle and pollutant dynamics. Sedimentary incorporation and subsequent burial have traditionally been regarded as efficient removal and hence detoxification processes for PCBs. However, this and other studies (e.g., ref 6) clearly show that permanent sedimentary removal may account for only a small percentage of the PCB flux reaching the sediment surface. Clearly much still remains to be understood about the precise nature of the recycling processes in aquatic systems. However, it is apparent that such processes have important implications for the long-term fate of PCBs in the environment.

Acknowledgments

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