

## Towards a complete mass balance and model for PCBs and PAHs in a small rural lake, Cumbria U.K.

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### Abstract

This paper summarizes the processes of exchange/fluxes for polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) in a small well-studied rural lake, Esthwaite Water in northwest England. Measurements of PCB and PAH concentrations have been made in rain, air, water, dated sediment cores, and sediment trap samples over a 2-yr study period and used to determine fluxes to and from the lake. A steady state mass balance model was used to construct an input–output budget for the chemicals and to investigate the relative importance of transport into and out of the lake. The hydraulic transport from the lake was the most important loss mechanism for both PCBs and PAHs. Volatilization, not sedimentation, is currently the dominant loss process for PCBs in the water column, whereas, sedimentation exceeds volatilization for PAHs. The data further suggest that the current sediment–water flux is upward for PCBs and downwards for PAHs, indicating that the sediments might be acting as a secondary source for PCBs but continue to act as a sink for PAHs. Riverine, catchment runoff, or both are believed to be the most important input for PCBs and PAHs to the lake although direct aerial deposition to the lake is also important for PCBs. Differences in the mixtures of compounds in the various compartments suggests significant fractionation of PCBs and PAHs in the air–water–sediment system in the lake.

Semivolatile organic compounds (SOCs) like polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in the atmosphere and enter the aquatic environment by a variety of routes. The major inputs to the water column of lakes are riverine inputs, direct atmospheric deposition (both wet and dry), and sediment re-suspension (Neff 1979; Swackhamer and Eisenreich 1991). The fate of PCBs and PAHs in the aquatic system has been a subject of extensive study for a number of years (McVeety and Hites 1988; Swackhamer et al. 1988; Baker and Eisenreich 1990; Achman et al. 1993; Helmstetter and Alden 1994). Upon entry into the aquatic environment they rapidly associate with suspended particulate material and sediments. Their ultimate fate is dictated by a variety of physical, chemical, and biological interactions, including partitioning between water and particles in the water column, hydraulic transport out of the lake, volatilization, uptake by biota, photolytic and biological degradation, sedimentation and recycling within the water column and between bottom sediments and water column (Baker et al. 1985; Mackay et al. 1986; Swackhamer et al. 1988; Jeremiason et al. 1994; Pearson et al. 1996).

Studies of the behavior of these compounds, particularly PCBs, in large lakes have shown that, historically, the atmosphere has been a net source and the sediments a net sink (Eisenreich et al. 1979; Gschwend and Hites 1981; Swackhamer and Armstrong 1986; Fuoco et al. 1995; Gevao et al. 1997). There is overwhelming evidence from sediment core studies that in the past the net fluxes of PCBs and PAHs

have been from the atmosphere through the water column to the sediments. However, more recent evidence suggests that as the atmospheric concentrations of PCBs and PAHs decrease following restrictions on their releases to the environment, the sediments are beginning to act as a secondary source of these compounds to the water column and then the atmosphere (Jeremiason et al. 1994; Gevao et al. 1997).

This study forms part of a long-term project aimed at understanding the biogeochemical cycling of organic pollutants in Esthwaite Water (EW), a biologically productive, semi-rural lake. It has a surface area of 1 km<sup>2</sup>, maximum and mean depths of 15.5 m and 6.4 m respectively, and a hydraulic residence time of 13 weeks (Ramsbottom 1976). The choice of EW for this study stems from the fact that it has been extensively studied (Lund 1950; Bark 1981; Tipping et al. 1981; Ochsenein et al. 1983; Davison and Tipping 1984; Hilton and Lishman 1985); in fact it is probably the most widely studied lake in the world. It has a catchment area to lake surface ratio of 17:1. The catchment area for the lake is mostly grazing land typical of the lower valleys of the English Lake District. The lake is situated at latitude 54°N and an altitude of 65 m in a region of cool oceanic climate and high annual rainfall (~2 m yr<sup>-1</sup>), and has been extensively used for scientific purposes. However, the majority of the chemical studies that have been carried out so far have been on trace metals and nutrients (Davison 1980; Tipping et al. 1981; Davison et al. 1982; Tipping and Woof 1983; Hilton and Lishman 1985; Heaney et al. 1986) and studies of the trace organics in the lake have just recently begun (Sanders et al. 1992; 1993; Gardner et al. 1995; Gevao et al. 1997; 1998*a,b*). There is no known point source of PCBs in the catchment area. The nearest localized sources of PAHs are a minor road that circumscribes the lake and some houses at 50–100 m distance. Two small villages are located less than 1 km, and there are a number of small towns within a 20-km radius. The nearest large town is Barrow, 40 km

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Table 1. Information on sampling times and numbers for air, bulk deposition and sediment traps.

Air		Bulk deposition		Sediment trap Dry weight of sediment (g)		
Date	Volume (m <sup>3</sup> )	Date	Volume (L)	Date	Depth (m)	
					6 m	14 m
11 Sep 95	516	3 Jan 96	3.7	4 Aug 95	0.46	7.09
26 Sep 95	577	27 Feb 96	5.5	3 Sep 95	1.88	1.89
10 Oct 95	538	26 Mar 96	2.5	2 Oct 95	1.11	2.72
24 Oct 95	559	23 Apr 96	3.2	3 Nov 95	0.94	2.87
7 Nov 95	556	23 May 96	2.0	5 Jan 96	0.89	2.38
21 Nov 95	520	20 Jun 96	4.6	4 Feb 96	0.93	2.89
5 Dec 95	555	18 Jul 96	3.3	3 Mar 96	0.71	1.74
19 Dec 95	519	20 Aug 96	4.0	4 Apr 96	0.63	2.75
3 Jan 96	598	15 Sep 96	1.9	5 May 96	0.22	0.79
16 Jan 96	503	19 Oct 96	3.8	5 Jun 96	0.91	1.94
30 Jan 96	562	28 Nov 96	5.5	2 Jul 96	0.35	0.43
13 Feb 96	542	20 Dec 96	5.0			
27 Feb 96	555					
12 Mar 96	548					
26 Mar 96	540					
23 Apr 96	1112					
10 May 96	630					
23 May 96	551					
6 Jun 96	512					
20 Jun 96	551					
4 May 96	551					
18 May 96	551					
29 May 96	472					

south-west. EW is used exclusively for scientific and recreational purposes and motorized boats have never been used on the lake.

Measurements of PCB and PAH concentrations have been made in air, atmospheric deposition, sediment traps, the main stream discharging to EW and have been reported in previous papers (Gevao et al. 1997, 1998a,b). The main aim of this paper is to develop a mass balance model, based on these published data, and hence obtain a better understanding of the overall biogeochemical cycling behavior of PCBs and PAHs in EW. A secondary aim is to address the fractionation of compounds from the air through to the buried sediments of EW based on comparisons of the concentrations/fluxes of these compounds in and between the different compartments of the lake. The physical-chemical properties, such as volatility and aqueous solubility, vary across the range of PAHs and PCBs found in the environment so that fractionation of the compounds in lake systems may be expected.

### Experimental methods

The sampling and analytical methods have been described in detail elsewhere (Halsall et al. 1993; Gevao et al. 1997, 1998a,b) and as such, only summaries are given here. Details of sampling times and numbers are given in Table 1. Air sampling was carried out using a high volume air sampler (Hi-Vol.) stationed ~15 m off the east shoreline of the lake. Air is initially filtered through a Whatman GF/A glass fiber filter to remove particles from the air stream while the vapor phase compounds were trapped on a polyurethane foam

(PUF) trap contained in an aluminium cylinder. The samples were extracted and analyzed as reported previously (Halsall et al. 1993; Gevao et al. 1997, 1998a,b).

Bulk deposition was collected monthly between January and December 1996, using an inverted Teflon-coated metal Frisbee (surface area 0.0434 m<sup>2</sup>) (Halsall et al. 1997; Jones and Duarte-Davidson 1997). The concentrations of PCBs and PAHs were measured in river and lake water samples collected at times of year representative of the different seasons in the U.K. The analytical methods were similar to that used previously for deposition samples and given elsewhere (Gevao et al. 1998a). The simultaneous air-water sampling campaign used in the estimation of fluxes across the air-water interface was undertaken a year after the deposition and sediment trap measurements due to practical constraints (Table 2). However, the air concentrations were within a factor of two over the two years. Consequently, estimates of air-water fluxes are considered to be representative of fluxes at the time of deposition measurements.

A sediment core of approximately 1 m in length was obtained from the deepest part of EW with a Mackereth minicorer in July 1995 (Gevao et al. 1997). The mean sedimentation rate for the dated portion of the core was determined to be  $0.995 \pm 0.153 \text{ kg m}^{-2} \text{ yr}^{-1}$  using <sup>210</sup>Pb chronology, details of which are given in Gevao et al. (1997).

The PCB samples were analyzed on a Hewlett-Packard HP-5890 gas chromatograph equipped with a <sup>63</sup>Ni electron capture detector using splitless injection on a cross-linked 5% phenyl methyl silicone chromatographic column for separation (50 m × 0.2 mm id, and 0.11 mm film thickness).

Table 2. Details of simultaneous air–water sampling campaign.

Sample number	Sampling date	Air volume (m <sup>3</sup> )	Water volume (L)	Air temp. (°C)	Water temp. (°C)
1	20 Jul 96	108	20	24.0	22.0
2	15 Sep 96	81	20	18.0	16.0
3	27 Nov 96	51	20	2.5	5.2
4	25 Feb 97	57	20	6.3	10.0
5	17 Mar 97	84	20	11.6	11.2
6	6 Jun 97	81	20	21.0	20.0

Operating conditions were identical to those of Lead et al. (1996). Analysis of the sample extracts for PAHs was carried out by high performance liquid chromatography (HPLC) with fluorescence detection.

*Quality assurance*—A strict regime of quality control was followed in the laboratory. Quality assurance efforts for this study have been published in previous papers (Halsall et al. 1993, 1997; Gevao et al. 1997, 1998a,b). Briefly, an analytical blank was processed for every 5 samples. Field and laboratory blanks were also routinely included in the analyses. The analytes present in the appropriate blanks were subtracted from those in the sample extracts. Sample peaks are reported only if the signal exceeded 3 times the baseline noise. Additional quality assurance procedures included spiking of samples prior to extraction to monitor recoveries.

Accuracies of the analytical techniques were determined by the analysis of three reference materials that have been certified for certain PCB congeners and PAH compounds. The results obtained were within 6–15% of the quoted value for >95% of the certified congeners in the three reference materials for PCBs, and within 10–20% of the quoted value for >80% of the certified PAHs. Confirmation of the identity of the PCB congeners and PAH compounds in 10% of the samples was carried out by GC/MS. The limit of detection (LOD) for the PAHs quantified in this study ranged from 0.05–1.5 ng g<sup>-1</sup> dry weight. The mean, standard deviation, and range of PCB congeners in 12 blanks were 5.2 ± 1.8 and 0.4–8.5 ng sample<sup>-1</sup>.

### Model development and calculations

Simple mass balance calculations were undertaken to estimate the various inputs and outputs to and from the lake. The mass balance assumes that the system is at steady state over the study period. The model requires that masses ( $M$ ) of pollutants into the lake are balanced by outputs from the lake. Thus:

$$M_{\text{in}} = M_{\text{out}} \quad (1)$$

where

$$M_{\text{in}} = M_{\text{bulkdeposition}} + M_{\text{inflow}} \quad (2)$$

$$M_{\text{out}} = M_{\text{burial}} + M_{\text{outflow}} \pm M_{\text{gasexchange}} \quad (3)$$

Other potential losses such as photolytic and microbial deg-

radation, or biotic uptake were not measured and not included in the model, but their importance in the overall budget will be considered in the discussion. The mass balances are based on a consistent range of PCB congeners and PAH compounds to ensure comparability between the various flux estimates between compartments. The congeners and compounds selected span the entire range of physico-chemical properties. The PCB congeners selected for the analyses are: 18, 28, 33, 37, 44, 49, 52, 66, 82, 81/87, 110/77, 119, 138, 141, 156, 157, 202/156, 193, 170, 189, 198, 194, 205, 206; whereas for PAHs, the following compounds were chosen for the mass balance assessment: acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[k]fluoranthene, benzo[b]fluoranthene, dibenz[ah]anthracene, benzo[a]pyrene, benzo[ghi]perylene and coronene. Sample concentration data have been reported in previous papers and have not been reported here because of the volume of data involved (Gevao et al. 1997; 1998a,b). However, the data can be obtained by request from the authors.

*Atmospheric deposition*—Direct atmospheric deposition to the lake was estimated as the product of the mean monthly deposition flux to the bulk deposition collector (wet + dry) and the surface area of the lake, summed over a twelve month period.

$$D = 12F_{\text{B}}A_{\text{LS}} \quad (4)$$

where  $D$  is the total amount deposited (mass yr<sup>-1</sup>),  $F_{\text{B}}$  is the mean monthly bulk deposition flux (mass m<sup>-2</sup> month<sup>-1</sup>),  $A_{\text{LS}}$  is the surface area of the lake (10<sup>6</sup> m<sup>2</sup>). Bulk deposition samplers are poor at assessing gaseous exchange at the air–water interface and the deposition of small particles. The collection efficiency of the deposition sampler used in this study has been assessed previously (Jones and Duarte-Davidson 1997). Gas exchange across the air–water interface was, as a result, independently assessed by carrying out simultaneous air–water measurements at various representative times of the year.

*Gas exchange at the air–water interface*—The two film resistance model of Liss and Slater (1974) was used to assess gas exchange of contaminants across the air–water interface. The mean annual net flux ( $F_{\text{net}}$ ) was estimated using the following equation:

$$F_{\text{net}} = (365\text{d yr}^{-1})K_{\text{ol}}(10^3 C_{\text{w}} - C_{\text{a}}RT/H) \quad (5)$$

$$\sum F = F_{\text{net}}A_{\text{LS}} \quad (6)$$

where  $\Sigma F$  is the net mass exchanged with units of mass  $\text{yr}^{-1}$ ,  $K_{ol}$  is the overall mass transfer coefficient ( $\text{m day}^{-1}$ ),  $C_w$  is the concentration of the contaminant in the dissolved phase ( $\text{mass l}^{-1}$ ) in the surface water of the lake,  $C_a$  is the vapor phase concentration of the contaminant in the atmosphere ( $\text{mass m}^{-3}$ ),  $R$  is the universal gas constant ( $8.21 \times 10^{-5} \text{ m}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$ ),  $T$  is the surface water temperature (K) and  $H$  is the Henry's Law constant ( $\text{atm m}^3 \text{ mol}^{-1}$ ). This equation predicts that the gas flux across the lake surface is a balance between volatilization from and absorption to the water surface, and is controlled by Henry's Law, the concentration gradient, and the overall mass transfer velocity (Liss and Slater 1974; Mackay and Yeun 1983). A correct assessment of  $H$  as a function of temperature is needed to determine the direction and magnitude of compound flux across the air-water interface. The Henry's Law correction applied for PCBs were estimated using the equation proposed by Tataya et al. (1988). In the case of PAHs,  $H_{298}$  values used were those measured by Bamford et al. (1999). For those PAHs not measured, their correction was carried out by the equation below:

$$\ln H_T = \ln H_{298} + 26.39 - (7,868/T) \quad (7)$$

where  $H_T$  and  $H_{298}$  are the Henry's Law constants at temperature  $T$  and 298 K, respectively. The gas exchange mass transfer coefficient was estimated from correlations with wind speed (as a surrogate measure of surface turbulence) and molecular diffusivity in air and water, as described in Hornbuckle et al. (1993). It has been reported that  $H$  for PCBs can increase by a factor of 10 with a 25°C increase in temperature and decrease by a factor of 2 between 25 and 15°C (Baker et al. 1985; Schwarzenbach et al. 1993). Details of calculations of instantaneous air-water fluxes together with uncertainties in these calculations have been previously reported (Gevao et al. 1998a).

**Lake burden**—The burden is defined as the amount of pollutant in the lake and calculated as the mean total (dissolved + particulate) concentration in the water (samples collected at a water depth of 5 m) and the lake volume.

$$B = VC_{w,t} \quad (8)$$

where  $B$  is the burden (units of mass),  $V$  is the volume of the lake ( $6.4 \times 10^6 \text{ m}^3$ ) and  $C_{w,t}$  is the mean water concentration at 5 m ( $\text{mass m}^{-3}$ ).

**Inflow**—This term was estimated as the product of the concentration in water collected from Black Beck (the major inflow immediately upstream of the lake), and the hydraulic input ( $F_w$ ) into the lake around the time of sampling, summed over the sampling year. The U.K. North-West Water Authority (NWWA) keeps a record of flow information for EW.

$$I = \sum_1^{i=6} C_b F_w \quad (9)$$

where  $I$  ( $\text{mass yr}^{-1}$ ) is the total riverine input to the lake from the catchment,  $C_b$  is the concentration ( $\text{mass m}^{-3}$ ) in water from Black Beck.

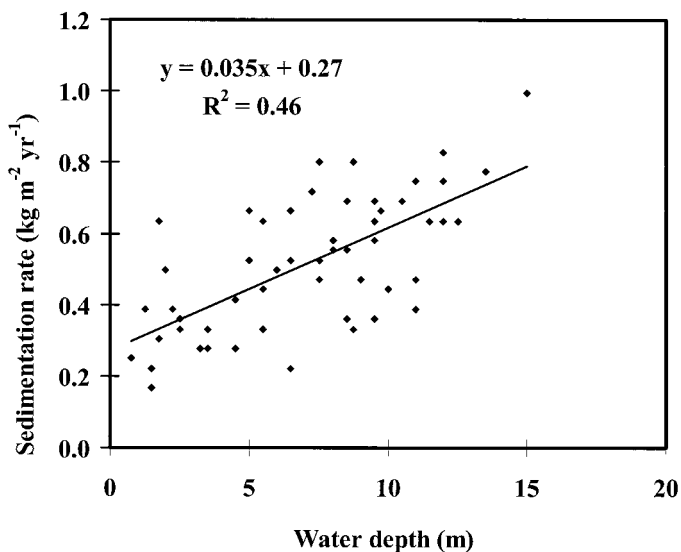


Fig. 1. Plot of sedimentation rate as a function of water depths in Esthwaite Water (adapted from Hilton et al. 1986).

**Outflow**—The loss of compounds through hydraulic discharge out of the lake was estimated as the surface water concentration and the mean hydraulic outflow from the lake around the sampling period as reported by the U.K. NWWA.

$$\sum_1^{i=6} O = C_{s,w} Q_i \quad (10)$$

where  $O$  is the total outflow ( $\text{mass yr}^{-1}$ ),  $C_{s,w}$  is the concentration ( $\text{mass m}^{-3}$ ) in the surface waters and  $Q_i$  is the outflow of water from the lake ( $\text{m}^3$ ) around the sampling period.

**Surficial sediment accumulation rate**—The net sedimentation rates of PCBs and PAHs to the surficial sediments have been estimated from the contaminant concentrations in the uppermost 2 cm of a dated sediment core from the deepest point in EW (Gevao et al. 1997, 1998b). In order to extend these data to whole-lake budgets, information is needed concerning the lake-wide variation in sedimentation rates. Hilton et al. (1986) has provided a detailed review of the sedimentary processes in EW based on 64 sediment cores collected throughout the lake. The results demonstrated that the sedimentation rate in EW increases with water depth, a characteristic commonly referred to as sediment focusing. The mass sedimentation rates ( $R$  in  $\text{kg m}^{-2} \text{ yr}^{-1}$ ), shown in Fig. 1, are derived from the data given in Hilton et al. (1986). The original data corresponded to the thickness of sediment ( $Z$ ) above a distinct marker horizon with respect to water depth. The sedimentation rates in Fig. 1 were calculated as follows:

$$R = (Z/Z_{15m})R_{15m} \quad (11)$$

where  $Z$  is the sediment thickness measured by Hilton et al. (1986) at any water depth,  $Z_{15m}$  is the mean sediment thickness at the deepest point in the lake (Hilton et al. 1986), and  $R_{15m}$  is the total mass sedimentation rate at the same deep-water site based on  $^{210}\text{Pb}$  dating (Gevao et al. 1997). The sedimentation rates, thus corrected for sediment focusing,

Table 3. Estimated sedimentation rates for different contoured areas of Esthwaite Water (adapted from Ramsbottom 1976).

Water depth (m)	Area between contour intervals, $A_i$ in $\text{km}^2$ —(from Ramsbottom 1976)	Estimated sedimentation rate ( $R_i$ in $\text{kg m}^{-2}\text{yr}^{-1}$ )
0–2	0.25	0.306
2–5	0.2	0.392
5–8	0.145	0.496
8–10	0.12	0.582
10–12	0.167	0.651
12–14	0.084	0.719
14–15.5	0.028	0.780

were then combined with the hypsographic data for EW (Ramsbottom 1976) to give the net sedimentation rates ( $S$  in  $\text{mass yr}^{-1}$ ) of PAHs and PCBs for the whole lake:

$$S = \sum [C_{15m}R_iA_i] \quad (12)$$

where  $C_{15m}$  is the contaminant concentration ( $\text{mass kg}^{-1}$ ) in the surface sediment at the deepest point in the lake,  $A$  is the lake area between various water-depth contours (Ramsbottom 1976),  $R$  is the sedimentation rate at the mid-depth of each contour interval derived from Fig. 1. Table 3 summarizes the  $A$  and  $R$  data.

**Error Estimates**—This section addresses the errors and uncertainties in the mass balance calculations, some of which involved parameters with unmeasured errors, estimates of which were therefore made wherever possible. For simplicity, errors have been calculated from the data in its original linear form. The results of the estimates, represented as error bars in the figures, indicate the likely order of magnitude of errors, rather than any precise estimate. The results of this project have propagated statistical errors and model design errors. The propagated statistical errors have been considered at each step of the model analysis. The uncertainties associated with some of the derived terms (e.g., net input/sediment accumulation) are also a function of year-to-year variability. These have been taken into account, wherever possible. Error of products ( $\chi_1, \chi_2, \dots$ ) were estimated by means of the relationship:

$$\text{var}(\chi_p) = \chi_p^2 \left[ \text{var} \frac{\chi_1}{\chi_1^2} \oplus \text{var} \frac{\chi_2}{\chi_2^2} \oplus \dots \right] \quad (13)$$

and those of quotients ( $\chi_1/\chi_2$ ) by

$$\text{var}(\chi_q) = \chi_q^2 \left[ \text{var} \frac{\chi_1}{\chi_1^2} \oplus \text{var} \frac{\chi_2}{\chi_2^2} \right] \quad (14)$$

The relative standard deviation for inflow to the lake is 24–190% and the relative standard deviation for the annual hydraulic discharge out of the lake is 19–84%. The year-to-year variability in flow for the catchment area is ~25% over a 5-yr period (data supplied by the U.K. NWWA). Since there was no discernible correlation between discharge and atmospheric concentrations of pollutants, the effect the variability will have on the mass balance calculations is unclear.

The contaminant content of the lake was determined as the product of the lake volume and mean contaminant concentration in the water from three different depths. Errors in the lake volume due to fluctuating water levels are small for EW (typically ~5%) and have therefore been ignored. Water was collected at three depths on two sampling occasions to determine vertical variability during thermal stratification and again for periods when the lake is uniformly mixed. The relative standard deviations were calculated to be  $\pm 38\%$  and  $\pm 26\%$  for PAHs when the lake is stratified and mixed respectively. In the case of PCBs, they were  $\pm 49\%$  and  $\pm 29\%$  for periods when the lake was stratified and mixed respectively. These values give an indication of variation of contaminant with depth. The relative standard deviations for dissolved water concentrations, used in the estimates of volatilization fluxes, were estimated to be about 15–25% for PCBs and 20–35% for PAHs. Relative standard deviations for atmospheric concentrations of contaminants is considered to be in the region of 60–90% due to fluctuations in the annual air concentrations, rather than the precision in the measurements which is estimated to be approximately  $\pm 10\%$ . The combination of these errors leads to errors in a typical instantaneous net volatilization flux of ~45%. The overall error in the mass balance is estimated at ~15% and ~25% for PCBs and PAHs, respectively.

**Review of mass balance models**—Models have been used in the past to help identify the major lake processes that affect the distribution, behavior, transport, and ultimate fate of contaminants in aquatic systems. Although different mathematical models are currently available, mass balance models are popular, with several good examples already published in the literature. Currently, most of the mass balances are based on work carried out on the Great Lakes and other remote lakes in North America with little or no information from Europe. These lakes are mostly either far removed from any pollution sources or have an insignificant catchment influence. The major inputs to the lakes already studied are mostly atmospheric deposition (Swackhamer et al. 1986; 1988; McVeety and Hites 1988) and the major loss pathways are volatilization and sedimentation.

Strachan and Eisenreich (1988) gathered concentration data for environmental compartments in all the Great Lakes for the mid 1980s, and based on mass balance calculations, suggested that volatilization dominated all inputs and outputs for many SOCs although the uncertainties in the concentrations and parameterizations were uncertain and high. They calculated that  $\Sigma$ PCB losses from the Great Lakes for example ranged from 46% of the total losses for Lake Erie to 87% for Lake Superior (Eisenreich et al. 1998). Net volatilization exceeded losses by sedimentation (11–45%) in all systems. Pearson et al. (1996) reassessed their 1980 mass budget for Lake Michigan using data collected in 1991 of PCB inputs and outputs. A huge imbalance of ~1,600 kg was attributed to errors associated with their estimates of dry deposition flux and the omission of a sediment–water flux.

Mass balances for smaller lakes comes from the work of McVeety and Hites (1988) and Swackhamer et al. (1988) for PAHs and PCBs respectively, carried out on Siskiwit Lake on Isle Royale located in the central basin of remote Lake

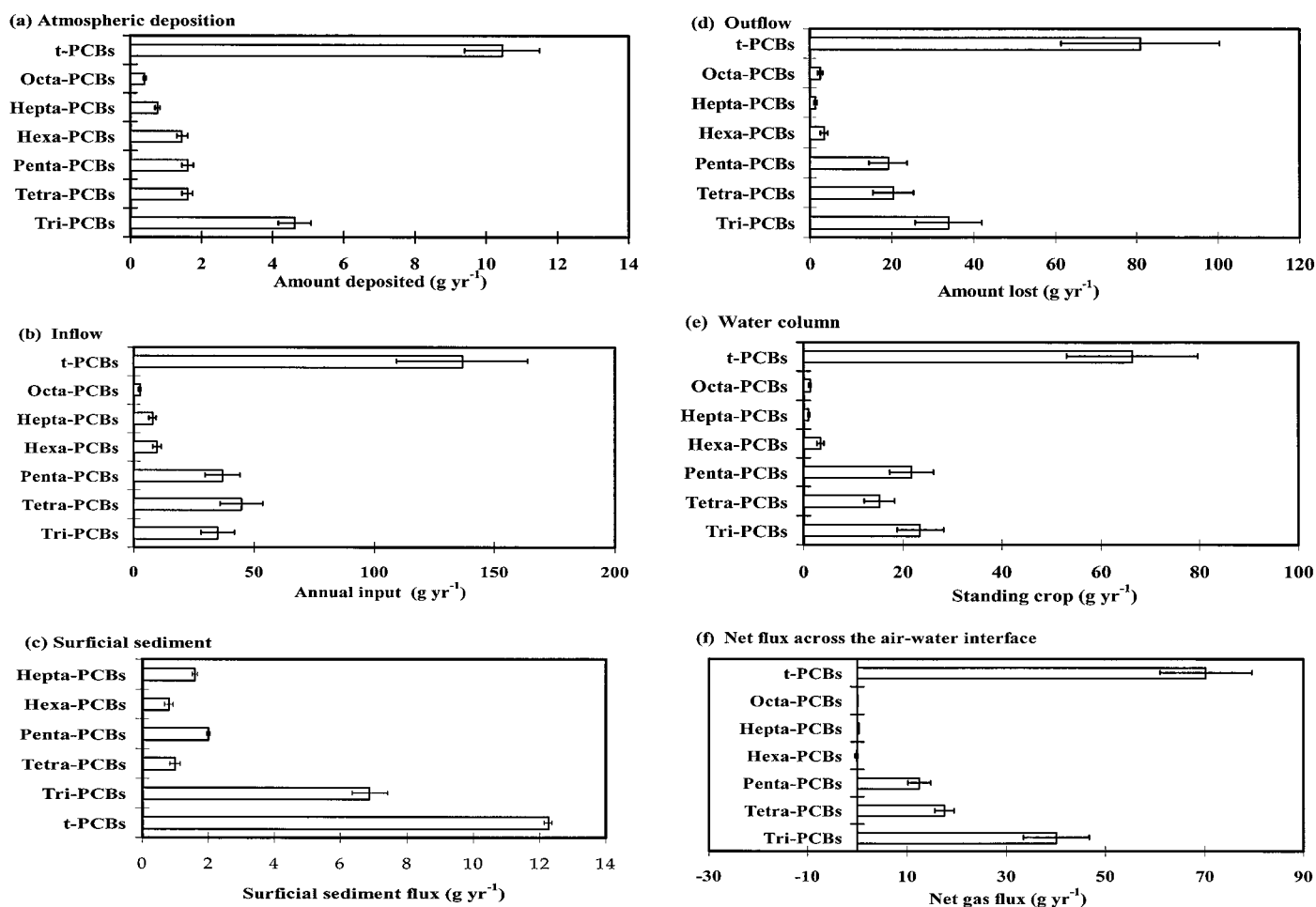


Fig. 2. Loading estimates for PCBs into and out of Esthwaite Water. (a) Atmospheric deposition. (b) Inflow. (c) Surficial sediment. (d) Outflow. (e) Water column burden. (f) Net flux across the air-water interface.

Superior. Isle Royale is dominated by atmospheric deposition as it is removed from all local sources and is a national park. Inputs were determined to be dominated by atmospheric deposition with an insignificant contribution from its watershed of  $\sim 35$  km<sup>2</sup>. Outputs included sedimentation and net volatilization, with outflow by lake water making an insignificant contribution.

In summary, most mass balance studies have been carried out on relatively larger lakes with long hydraulic and pollutant residence times, relatively low sedimentation rates (especially the Great Lakes) and low catchment:lake surface area ratios. The processes that govern the dynamics of pollutant delivery, retention, cycling and removal are expected to be different from those of smaller lakes especially EW, with a large catchment influence and low particle residence times. The present study emphasizes the importance of catchment derived inputs for such lakes, which is frequently downplayed in the literature.

## Results and discussions

*Compartmental fluxes and loadings*—The concentrations of PCBs and PAHs in the various compartments have been

discussed in previous papers, including detailed consideration of the controlling processes (Gevao et al. 1997, 1998a,b). In these previous papers, clear and systematic differences in the compound and congener fingerprints between the various compartments and transport pathways were put forward. These trends were related in various ways to the physico-chemical properties of the compounds.

*Inputs—Atmospheric loadings:* Direct atmospheric PCB loadings range from  $0.4 \pm 0.03$  g yr<sup>-1</sup> for octa-PCBs to  $4.6 \pm 0.36$  g yr<sup>-1</sup> for tri-PCBs with a  $\Sigma$ PCB loading estimated at  $10 \pm 0.72$  g yr<sup>-1</sup> (Fig. 2A). PAH atmospheric loadings to the surface of EW range from  $2.3 \pm 0.2$  g y<sup>-1</sup> for anthracene to  $93 \pm 8.6$  g yr<sup>-1</sup> for phenanthrene with a  $\Sigma$ PAH loading of  $402 \pm 22$  g yr<sup>-1</sup> (Fig. 3A).

The percentage contribution to the sedimentation from direct aerial deposition onto the lake surface is estimated to be equivalent to 6% for  $\Sigma$ PAHs, with the contributions varying from 0.9% for coronene to 51% for phenanthrene. In general, the direct atmospheric inputs are relatively more important for the low molecular weight PAH compounds. Direct aerial deposition of compounds which are principally associated with the particles ( $\geq 4$  rings in their structure)

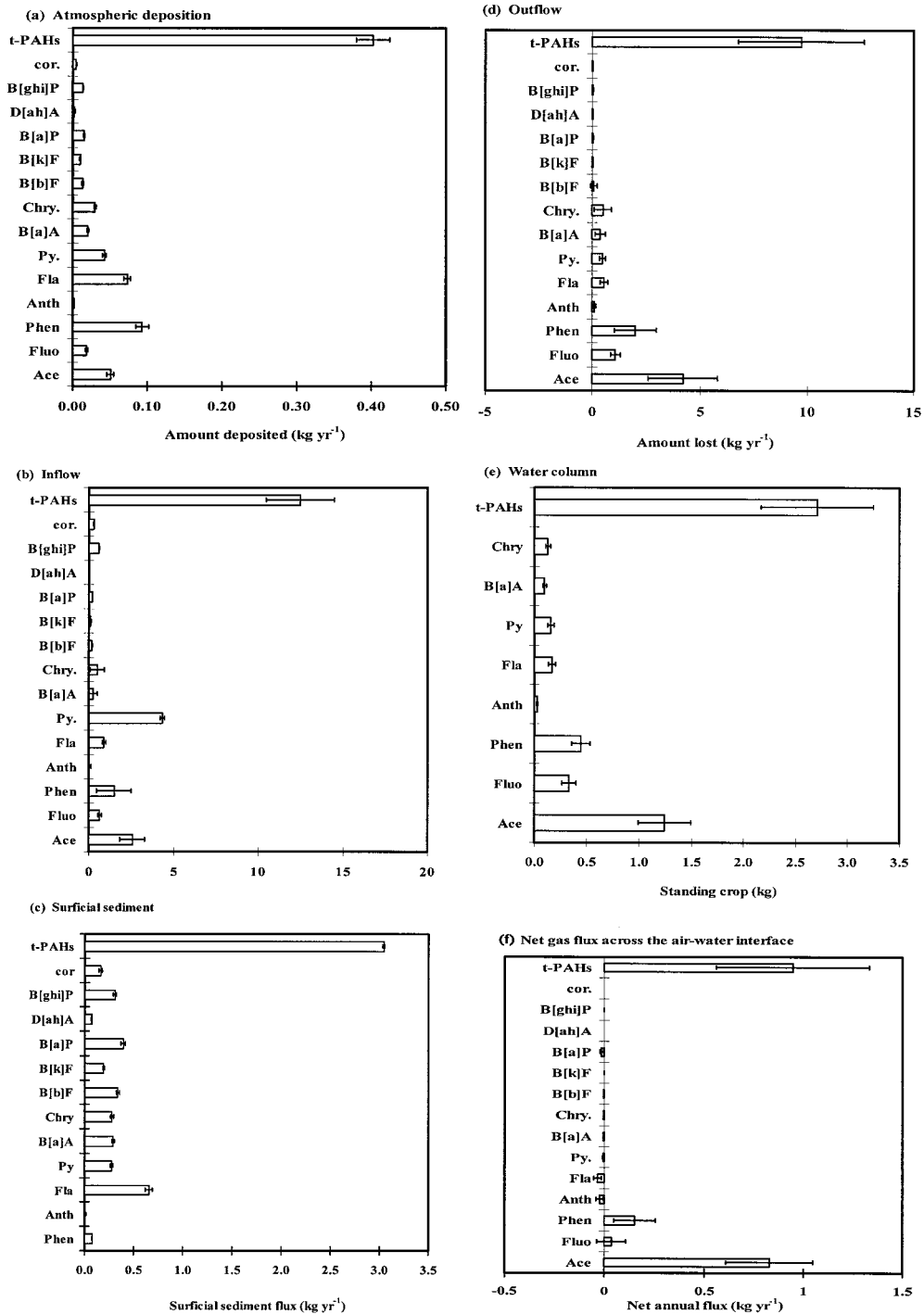


Fig. 3. Loading estimates for PAHs into and out of Esthwaite Water. (a) Atmospheric deposition. (b) Inflow. (c) Surficial sediment. (d) Outflow. (e) Water column burden. (f) Net flux across the air-water interface. Ace., acenaphthene; Anth., anthracene; Fla., fluoranthene; py., pyrene; B[a]A, benzo[a]anthracene; Chry., chrysene; B[b]F, benzo[b]flouranthene; B[k]F, benzo[k]flouranthene; B[a]P, benzo[a]pyrene; D[ah]A, dibenzo[ah]anthracene; B[ghi]P, benzo[ghi]perylene; Cor., coronene.

contribute  $\leq 2\%$  of their total sediment flux, with the rest coming from catchment inputs. On the contrary, direct atmospheric fluxes for PCB are equivalent to a much greater fraction of the sediment fluxes. It is estimated that atmospheric deposition to the lake may contribute as much as  $\sim 40\%$  of the  $\Sigma$ PCB total sediment loading.

*Comments on the deposition collector:* The design of the Frisbee collector used in this study has been used extensively to study the deposition of metals and has had some limited use in the U.K. for the collection of trace organics (Halsall et al. 1997; Jones and Duarte-Davidson 1997). Their collection efficiencies for dry particle deposition have been tested in wind tunnel studies and found to vary with wind speed, direction, and particle size, and to drop to  $< 50\%$  for particles  $> 50 \mu\text{m}$  above the wind speed of  $\sim 4 \text{ m s}^{-1}$  (Hall 1988). The Frisbee used for this work is coated with Teflon to improve its capacity to retain particulates. Clearly, a potential problem of using any artificial surface with such a design to collect bulk deposition for compounds with a significant vapour-phase component is that they behave differently to real environmental surfaces (e.g., water and land) because (i) they are smooth and as a result, less efficient at entraining fine particles, (ii) PCBs and PAHs (especially the lower molecular weight compounds) have a significant vapour phase component, and (iii) target compounds in wet deposition may be sorbed to the Teflon surface. Although measures were taken to minimize (iii) and the sampling methodology was kept consistent throughout the study period, it is uncertain how fluxes measured by such samplers are underestimated as a consequence of these factors. Horstmann and McLachlan (1997) conducted a comparison of a similar design of collector to that used in this work and a more robust system involving in situ extraction from wet deposition. It was observed that the two techniques were comparable even over a month long collection period.

*Inflow:* The amount of  $\Sigma$ PCBs estimated to enter the lake via river inflow is estimated at  $\sim 140 \pm 15 \text{ g yr}^{-1}$  and that for  $\Sigma$ PAHs at  $\sim 12 \pm 3 \text{ kg yr}^{-1}$ . The distribution of compounds again favors the lower chlorinated PCBs homologues and low molecular weight PAHs, especially acenaphthene, phenanthrene, and pyrene (Figs. 2B, 3B respectively). Clearly, river inflow is the dominant input function of both classes of pollutants to the lake. These large inputs into the lake from riverine flow can be due to one or more of the following reasons: (i) the inflow into EW is via a stream which receives discharges from a sewage treatment works before entering the lake; (ii) there is a road circumscribing the lake which is heavily used by vehicles. Traffic emissions and carbon debris from the road are expected to enter the lake by surface runoffs after precipitation events; (iii) catchment runoff. The catchment to lake surface area ratio is 17:1. Assuming that atmospheric deposition per  $\text{m}^2$  is similar for the catchment as it is for the lake, then the contribution from catchment inputs are likely to make a significant contribution to the total lake inputs. In a recent study, Jeremiason et al. (1999) estimated that catchment inputs accounted for  $\sim 60\%$  of water inputs to two lakes with catchment to lake surface area of 5. They estimated that the  $\Sigma$ PCB contribution from

potential runoff was greater than volume-weighted rain concentrations at the same site. They also highlighted the need for further research in determining the relationships among contaminant inputs by runoff and ratio of catchment to lake surface area, catchment characteristics, soil type, and climate.

*Outputs—Sedimentation/burial:* The recent net sediment loading for the lake was estimated to be  $13 \pm 2 \text{ g yr}^{-1}$  for  $\Sigma$ PCBs. The tri-PCB congeners dominated the  $\Sigma$ PCB homologue distribution, contributing  $\sim 7 \pm 1.5 \text{ g yr}^{-1}$  to the  $\Sigma$ PCB loading (Fig. 2C). The sediment loading is estimated to be in the region of  $3 \pm 0.5 \text{ kg yr}^{-1}$  for  $\Sigma$ PAHs and was dominated by the higher molecular weight, low aqueous soluble compounds (Fig. 3C). The recent sediment flux is effectively the average flux of the uppermost 2 cm of the sediment core. The similarity of the trap and sediment fluxes for total mass and PAHs indicates no resuspension at the deep site. Bioturbation is relatively unimportant, as indicated by  $^{137}\text{Cs}$  profile (Gevao et al. 1997) probably due to the anoxic character of the sediments.

Unlike PCBs, the distribution of PAHs in the sediment was skewed in favor of the high molecular weight, low aqueous soluble compounds, and was relatively depleted in the three-ringed PAHs relative to that observed in other compartments. This observation may be related to the mode of delivery of these compounds to water systems. Whereas the low molecular weight PAHs are predominantly in the vapor-phase in the atmosphere, the high molecular weight PAHs are predominantly associated with aerosol particles (Eisenreich et al. 1979; Andren and Strand 1981; Bidleman et al. 1986; Ligocki and Pankow 1989; Simcik et al. 1998). On their delivery to a water body, they rapidly become incorporated into organic rich particles and delivered to the bottom sediments. PCBs and the low molecular weight PAHs are weakly associated with the organic fraction and are more easily removed from the particles at or near the sediment water interface by either mineralisation of the organic particles or physical perturbation and are released back in to the water column (Eadie et al. 1984; Baker et al. 1991; Lipiatou et al. 1993; Sanders et al. 1996). The high molecular weight PAHs, on the other hand, being more tightly bound are less affected by this process and get incorporated into the sediments (Chambers and Eadie 1981; Eadie et al. 1984).

*Outflow:* The amounts of  $\Sigma$ PCBs and  $\Sigma$ PAHs removed from the lake through hydraulic outflow are estimated to be  $\sim 80 \pm 20 \text{ g yr}^{-1}$  and  $\sim 10 \pm 4 \text{ kg yr}^{-1}$  respectively. The mass of compounds lost by river outflow shows a positive relationship to their aqueous solubility (Fig. 2D, 3D). As water flows out of the lake, it carries with it dissolved pollutants and those associated with suspended particles. The particle residence time in the water column of EW has been estimated previously to be between 8 and 21 days (Sanders et al. 1996). This means that the particle residence time is relatively short and therefore, the more hydrophobic compounds also have a short residence time in the water column due to particle settling. The more aqueous soluble compounds have a higher residence time in the water column (Baker et al. 1991; Lipiatou et al. 1993), long enough to

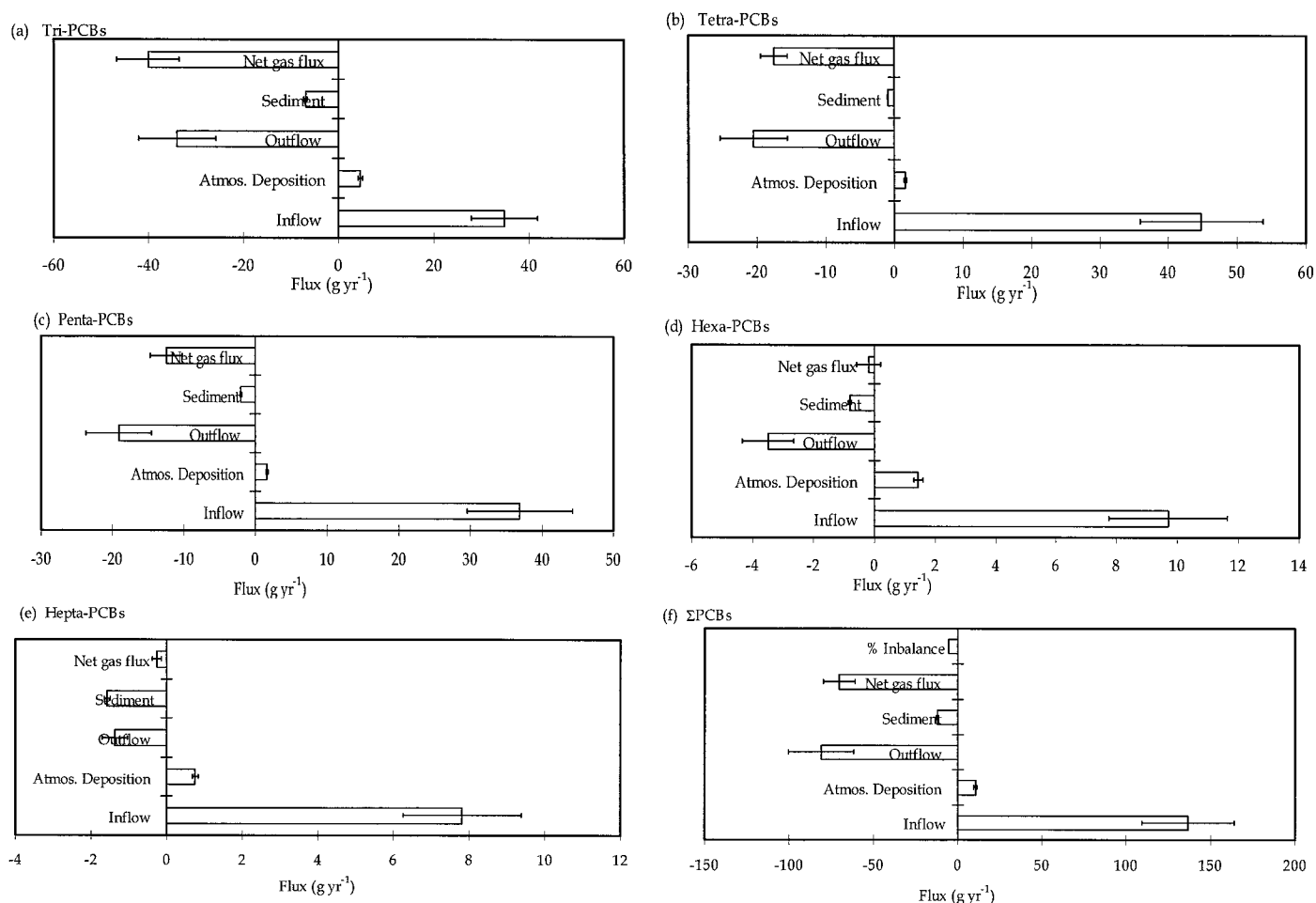


Fig. 4. Contribution from various measured parameters to the mass balance estimates for PCBs. (a) Tri-PCBs. (b) Tetra-PCBs. (c) Penta-PCBs. (d) Hexa-PCBs. (e) Hepta-PCBs. (f)  $\Sigma$ PCBs.

remain in the water column and get flushed out of the lake, compared with their higher molecular weight, or higher chlorinated counterparts.

**Water column burden:** At any one time, the water column burden is estimated to be in the region of  $\sim 65 \pm 15$  g  $\Sigma$ PCBs and  $\sim 2.8 \pm 0.8$  kg  $\Sigma$ PAHs. For both classes of compounds, the lower molecular weight congeners/compounds dominate total burden in the water (Figs. 2E, 3E). The PAH compounds present at a relatively high proportion in the water column are the more water soluble tricyclic PAHs (acenaphthene, fluorene, and phenanthrene), all of which are relatively depleted in the surficial sediments as discussed earlier.

**Air-water gas exchange:** The net flux of  $\Sigma$ PCBs across the air-water interface of EW was estimated from six water samples as previously reported (Gevao et al. 1998a) and is thought to be in the region of  $\sim 70 \pm 20$  g yr<sup>-1</sup>, with that for  $\Sigma$ PAHs in the region of  $\sim 1 \pm 0.3$  kg yr<sup>-1</sup> (Figs. 2F, 3F respectively). The net flux is volatilization (i.e., out of the lake) throughout the year for both  $\Sigma$ PAHs and  $\Sigma$ PCBs. Indeed, net volatilization is calculated for all the PCB homo-

logue groups. For PAHs the situation is more complex; whilst the net annual  $\Sigma$ PAH is estimated to be out of the lake (i.e., volatilization), deposition > volatilization flux during some months in winter when the atmospheric concentrations of the compounds were high. In addition, it is clear from Fig. 3F that the net annual flux of  $\Sigma$ PAHs is dominated by the more volatile tricyclic PAHs (acenaphthene, fluorene, and phenanthrene), whilst the net fluxes of all the other PAH compounds is depositional.

**PCB mass balance**—The resulting mass balance for selected homologues and  $\Sigma$ PCBs are presented in Fig. 4. Clearly, the inflow to the lake is the dominant input function for PCBs, while outflow and net gas exchange are almost equal in importance in accounting for the loss of PCBs from the lake. Sedimentation/burial is considered relatively unimportant as a removal mechanism, implying that apart from hydraulic transport of the chemical, the major process controlling the removal of PCBs at the present day is volatilization. This is in line with the sediment core study (Gevao et al. 1997) which pointed to the remobilization of these compounds from buried sediments as the environmental levels fall. Observation of the homologue mass balances shows

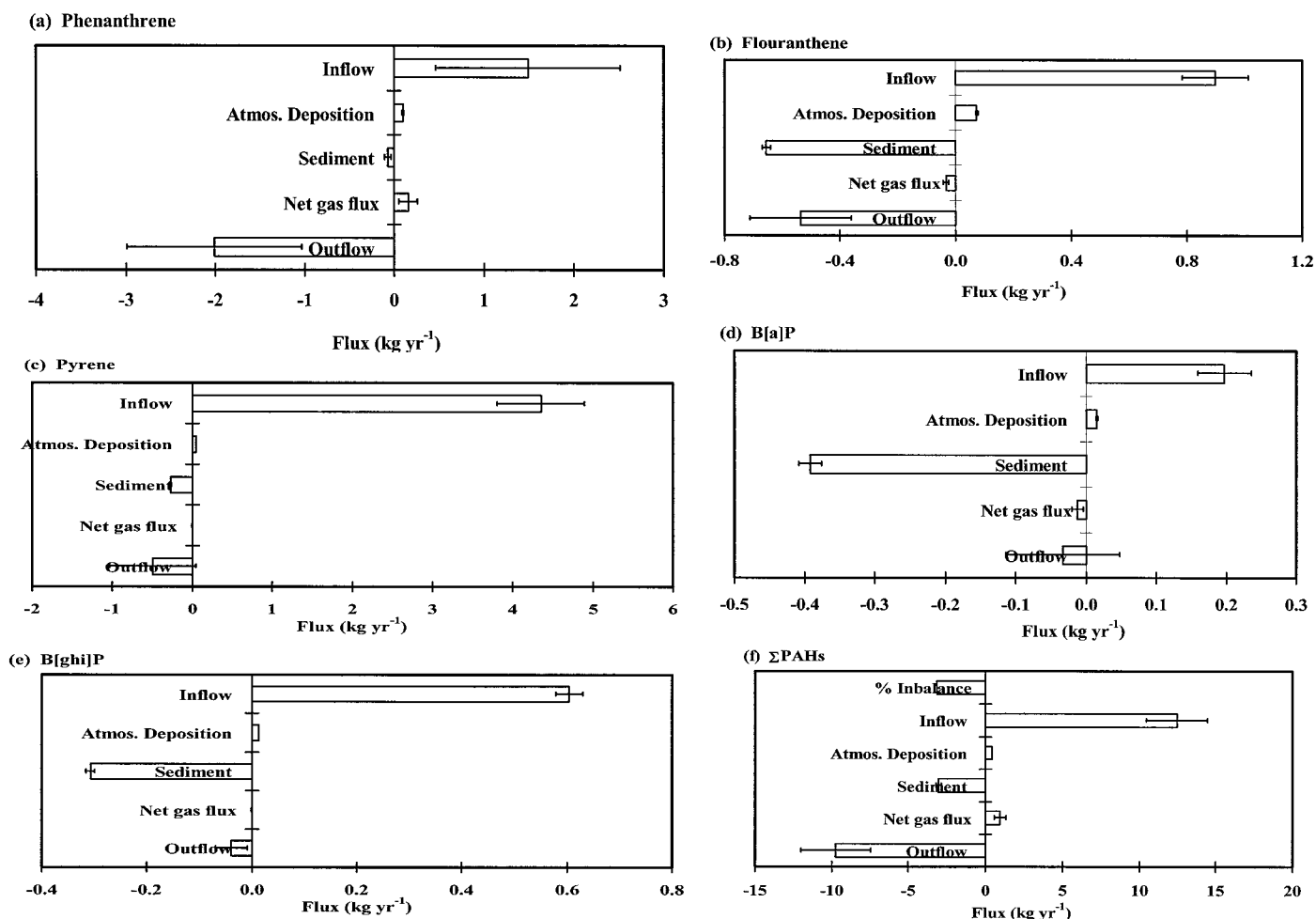


Fig. 5. Contribution from various measured parameters to the mass balance estimates for PAHs. (a) Phenanthrene. (b) Fluoranthene. (c) Pyrene. (d) Benzo[*a*]pyrene. (e) Benzo[*ghi*]perylene. (f)  $\Sigma$ PAHs.

that the importance of gas exchange as a loss mechanism diminishes with increase in chlorination. Studies carried out on the Great Lakes supports this observation. Recent studies suggest that air–water exchange of SOCs play an important role in the mass balancing of inputs in large aquatic systems such as the Great Lakes, and the world oceans (Hornbuckle et al. 1993, 1995; Tolosa et al. 1997). For example, the calculated volatilization flux of PCBs out of the North American Great Lakes (Jeremiason et al. 1994; Eisenreich et al. 1998) has been estimated to be comparable to sedimentation losses and may, in fact, be substantially greater in low sedimentation ecosystems such as Lake Superior (Jeremiason et al. 1994; Eisenreich et al. 1998). In large lakes, there is convincing evidence that SOC concentrations and their residence times are influenced, if not controlled by air–water exchange (Hornbuckle et al. 1993; Jeremiason et al. 1994; Pearson et al. 1996)

The removal by outflow from the lake is also important for the lower chlorinated compounds. These observations are linked to the physico-chemical properties of the compounds. The lower chlorinated, more aqueous soluble compounds have a relatively high residence time in the water column

and are hence more available for gas exchange and more susceptible to hydraulic transport out of the lake.

*PAH mass balance*—The mass balances for selected PAHs is depicted in Fig. 5. As with  $\Sigma$ PCBs, the inputs of  $\Sigma$ PAHs to EW is dominated by inflow and the outputs by outflow. Inspection of the mass balance for the selected PAH compounds reveals that as the molecular weight of the compounds increase: (i) the importance of gas exchange as a loss mechanism diminishes; (ii) the relative efficiency of preservation in bottom sediments increases (burial increases in importance); (iii) the importance of inflow as an input term to the lake increases. All of these observations are linked to the form of these compounds in the atmosphere and the water column.

Figs. 4, 5 highlight an interesting difference in the fates of  $\Sigma$ PCBs and  $\Sigma$ PAHs. If outflow is ignored, it is clear that net gas exchange (i.e., volatilization) then dominates the loss of  $\Sigma$ PCBs from the water column of EW; for  $\Sigma$ PAHs burial/incorporation into sediments exceeds volatilization. This difference can again be attributed to the differences in the physico-chemical properties of the two classes of compounds,

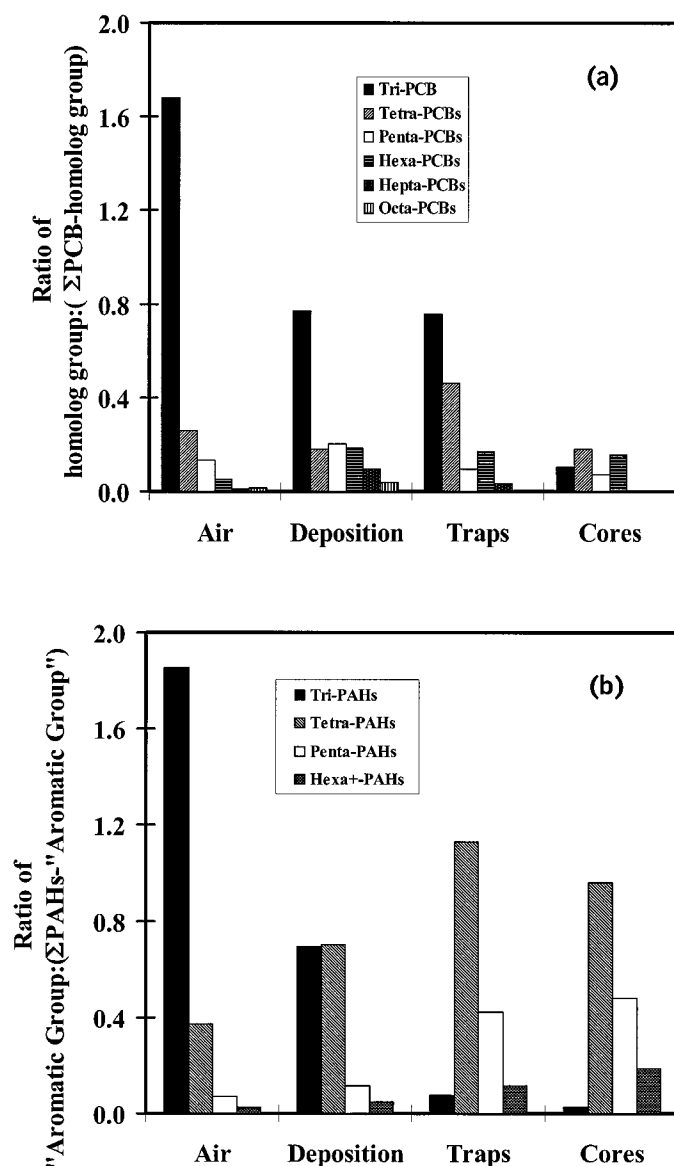


Fig. 6. Relative abundance of homologue groups in different lake compartments for (a) PCBs and (b) PAHs.

their mode and form of introduction to the lake, and their present-day atmospheric levels. In general, the imbalance in the mass balances for both  $\Sigma$ PCBs and  $\Sigma$ PAHs are good considering the composite error in the whole analysis. This supports the view that the major inputs and outputs have been accounted for in the analysis.

**Fractionation of compounds**—The relative contribution of PCB and PAH homologues in air, atmospheric deposition, sediment traps and sediment cores in EW are shown in Figs. 6A,B, respectively. The physico-chemical characteristics generally vary as a function of chlorination (PCBs) and aromaticity (PAHs), so that comparisons between the various groupings provide a basis for determining the extent of compound fractionation in the EW system. In general, there are clear trends in the sequence, air–deposition–sediment traps–

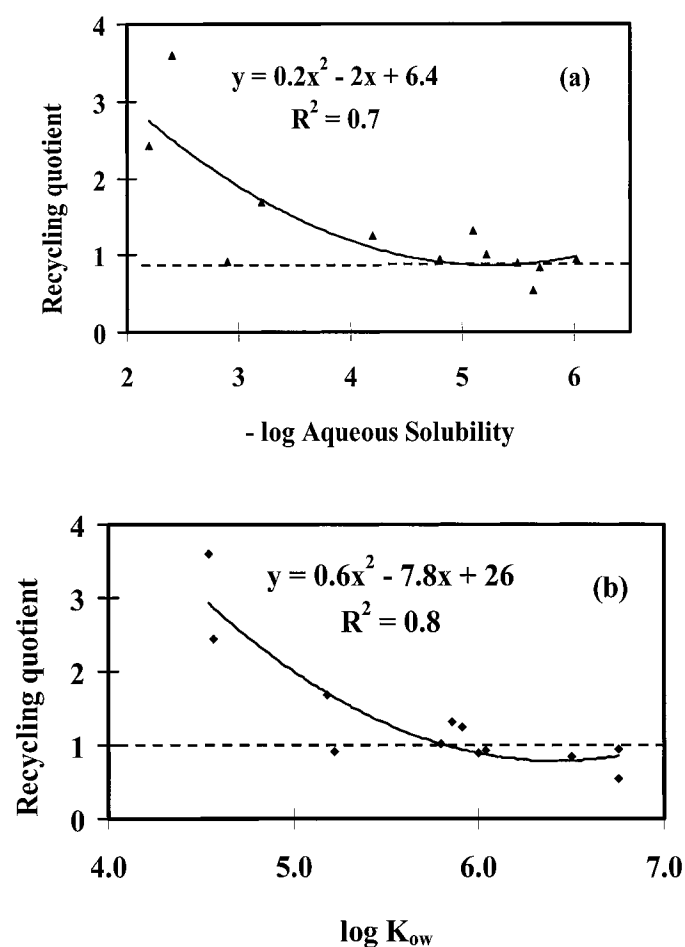


Fig. 7. Relationship between the recycling quotient and (a) aqueous solubility and (b)  $\log K_{ow}$ .

bottom sediments. Reasons for relative differences in composition may include some combination of changes in: (i) relative transfer efficiency to the lake, and (ii) relative scavenging and recycling efficiency within the lake and between surficial sediments and the overlying water. The comparisons of absolute flux can help distinguish between these.

It can be seen that for PCBs (Fig. 6A), the homologue distributions in air, deposition, and sediment trap materials are dominated by tri-PCBs. However, in the surficial sediment the mixture is more even. For PAHs (Fig. 6B), the tri-PAHs are only dominant in the air samples with the tri- and tetra-homologues being equally important in deposition samples. In the sediment trap and surficial sediments, the importance of tri-PAHs diminishes and the heavier compounds become dominant.

**Recycling of PCBs and PAHs in EW**—This fractionation of compounds in the vertical column of the air–water–sediment system can be related to the recycling of compounds in the water column which is more efficient the more soluble (less hydrophobic) the compound. Internal recycling of PCBs and PAHs has been previously reported in EW (Sanders et al. 1996; Gevao et al. 1997, 1998b), other lakes (Chambers and Eadie 1981; Eadie et al. 1984; Baker et al.

Table 4. Recycling quotients for selected PCB congeners.

PCB congener	Recycling quotient
18	20 ± 10
28	24 ± 8
33	18 ± 7
44	14 ± 3
66	17 ± 4
138	15 ± 2
101	12 ± 2
155	13 ± 3
202/156	10 ± 3
180	6 ± 2
193	5 ± 2
206	3 ± 1

1991) and other water bodies (Lipiatou et al. 1993; Tolosa et al. 1997). Recycling is determined by comparing the settling fluxes with the net burial rate in the bottom sediments. A recycling quotient (sediment flux/trap flux) >1 indicates that there is a significant recycling near the sediment-water interface. On the other hand, ratios <1 infer an additional source(s), one of which may be focusing of sediments from near-shore, nonsedimenting areas of the lake basin to the deepest, quiescent depositional basin as is the case with EW (Gevao et al. 1998b). Another source may be pore water transport of contaminants away from regions of higher concentrations.

The recycling quotients of PAHs and PCBs were evaluated in relation to solubility and octanol-water partition coefficients to determine if empirical relationships exist between the flux rates and these physico-chemical parameters which could be used to predict behavior of similar chemicals in different aquatic systems. The ratios were found to be correlated with solubility and inversely with  $K_{ow}$  for PCBs and low molecular weight PAHs (Sanders et al. 1996; Gevao et al. 1998b), indicating that the low molecular weight compounds are more efficiently recycled (see Table 4). These compounds therefore have a higher residence time in the water column and the wider environment.

In the sediment core study reported previously (Gevao et al. 1997), evidence of compositional variations in the vertical distribution of PCBs emerged when various homologue groups were ratioed. Sediments deposited in the last ~10 years and sediments deposited prior to their manufacture were relatively enriched in the less chlorinated homologue groups (Gevao et al. 1997). A similar analysis revealed surface enrichment for phenanthrene (Gevao et al. 1998b). These enrichments provide evidence for a possible postdepositional mobility of more aqueous soluble and volatile compounds. These results provide further evidence for fractionation of PCBs and PAHs in sediments.

## Conclusions

The mass balance presented here serves as a useful guide to the magnitude of fluxes into and out of EW and of their relative importance. Catchment inputs are clearly the major input term for both PCBs and PAHs for this small lake. This

implies that, for this system, temporal changes in the catchment balance will have a significant influence on the levels of pollutants in the lake. This situation is different from that indicated in studies on the Great Lakes (Eisenreich et al. 1979; Baker et al. 1985; Swackhamer and Armstrong 1986; Hornbuckle et al. 1995; Pearson et al. 1996). The catchment: lake surface area ratio (C/L) for Lake Superior, for example, is 0.6:1 compared to that for EW of ~17:1 (Sanders et al. 1996). For such a system or for remote lakes, atmospheric deposition has a significant influence on their pollutant levels. For EW and other small water bodies, catchment runoff (perhaps ultimately "fed" by atmospheric deposition and nonatmospheric sources) are likely to play an important role to the contaminant inputs. Omitting hydraulic transport of the compounds from the lake, volatilization losses > burial losses for  $\Sigma$ PCBs and the reverse hold for  $\Sigma$ PAHs.

Because these compounds are recycled through the atmosphere, and because evidence is emerging for their remobilization from soils and sediments (especially of the more aqueous soluble compounds), their residence times in the wider environment may be much longer than previously expected.

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