

Biogeochemical cycling of PCBs in lakes of variable trophic status: A paired-lake experiment

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Abstract

A paired whole-lake experiment was conducted on two remote, atmospherically driven lakes in the Experimental Lakes Area (ELA) to examine the stresses of trophic condition on air–water exchange and settling fluxes of polychlorinated biphenyls (PCBs). Lake 227 (L227) and Lake 110 (L110) are similar in volume, surface area, and watershed area but differ significantly in trophic status. The two lakes have similar access to atmospheric PCBs but eutrophic L227 may exhibit enhanced air to water exchange due to greater biotic uptake of dissolved PCBs. Settling fluxes of PCB were significantly greater in eutrophic L227 ($40 \text{ ng m}^{-2} \text{ d}^{-1}$ in 1993; $29 \text{ ng m}^{-2} \text{ d}^{-1}$ in 1994) than in oligotrophic L110 ($22 \text{ ng m}^{-2} \text{ d}^{-1}$ in 1993 and $17 \text{ ng m}^{-2} \text{ d}^{-1}$ in 1994). Dissolved ΣPCB concentrations were not significantly different in the two lakes ($\sim 0.3 \text{ ng liter}^{-1}$). Greater ΣPCB settling fluxes in L227 vs. L110 coupled with similar dissolved concentrations after June supports the hypothesis that air–water exchange supports the water column PCB concentrations. Surprisingly, ΣPCB fugacity gradients in both lakes indicated that *net* volatilization dominated during the entire ice-free period, requiring another source. A ΣPCB mass budget in the epilimnion of each lake over the stratified period showed that the major PCB losses were due to settling and volatilization. ΣPCB settling losses were 2.4 times greater in L227 than in L110 due to higher settling particle fluxes. The mass budgets suggest that the major PCB input to these remote lakes is from the watershed. Our results indicate the intimate environmental linkage between atmospheric, land, and aquatic PCB reservoirs.

Two of the greatest problems affecting many freshwater lakes are eutrophication and contamination of fish with organochlorines, such as polychlorinated biphenyls (PCBs). For example, there are active programs to reduce both nutrient levels and PCB concentrations in several of the Great Lakes. Previous studies suggest there may be important interactions between PCB concentrations and trophic condition (Larsson et al. 1992; Taylor et al. 1991). An understanding of the interactions between trophic condition and PCB concentrations is essential for effective management. This study

used a unique paired-lake approach to examine the stresses of trophic condition on air–water exchange, particle-mediated settling fluxes, and the interaction between air–water exchange and settling fluxes of PCBs. In addition, our results led us to examine further the potential importance of PCB inputs to aquatic systems from watersheds.

A paired whole-lake study was conducted on two remote, atmospherically driven lakes in the Experimental Lakes Area (ELA). We hypothesize that eutrophic lakes having access to the same atmospheric PCB concentration as oligotrophic lakes can capture a greater chemical mass through enhanced air to water exchange analogous to enhanced atmospheric capture of CO_2 by eutrophic lakes (Schindler 1977). Lake 227 (L227), an artificially fertilized, eutrophic lake, and Lake 110 (L110), a naturally oligotrophic lake, are about 11 km apart. There are no point sources of PCBs to this remote region and the two lakes are similar in surface area, volume, and watershed area. The two lakes should receive similar atmospheric PCB loads unless aquatic biota lower dissolved phase concentrations sufficiently to increase inputs through enhanced air to water exchange.

PCB and organic carbon (OC) settling fluxes in both lakes were determined using sediment traps. Sediment traps have been used in aquatic systems to quantify particle and chem-

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ical fluxes such as PCBs and polycyclic aromatic hydrocarbons (PAHs) (Elder and Fowler 1977; Eadie et al. 1984; Knap et al. 1986; Lefkovitz 1987; Broman et al. 1988; Oliver et al. 1989; Baker et al. 1991; Lipiatou et al. 1993, 1997; Dachs et al. 1996; Sanders et al. 1996). These studies have documented efficient transport of PCBs and PAHs from the pelagic to benthic regions but inefficient burial in the sediments (Baker et al. 1991; Lipiatou et al. 1993, 1997). In some cases, positive relationships between PCB settling flux and OC settling fluxes were observed (Knap et al. 1986; Lefkovitz 1987), suggesting that more organic-rich particles in a eutrophic lake lead to higher PCB settling fluxes, thus decreasing dissolved PCB concentrations. The link between PCB settling fluxes and dissolved PCB concentrations and the entry of PCBs into the base of the aquatic food chain through enhanced air–water exchange have not been investigated.

Air–water exchange is an important process controlling semi-volatile organic chemical (SOC) concentrations in the Great Lakes and other aquatic systems (Baker and Eisenreich 1990; Achman et al. 1993; Iwata et al. 1993; McConnell et al. 1993, 1996; Hornbuckle et al. 1994, 1995; Jeremiason et al. 1994; Ridal et al. 1996; Eisenreich et al. 1997). The previous studies have documented the importance of *net* volatilization as an important output of PCBs from the Great Lakes and other systems. However, no studies have examined short-term changes in dissolved phase PCB concentrations due to settling fluxes. Settling particle fluxes of Σ PCBs should decrease dissolved PCB concentrations under stratified conditions assuming no other sources of input (Lefkovitz 1987; Oliver et al. 1989; Baker et al. 1991; Sanders et al. 1996). If dissolved PCB concentrations are maintained, air–water exchange may be the input pathway.

Air–water exchange and settling fluxes of PCBs both depend on the dissolved phase concentration (Fig. 1). The direction of the air–water exchange gradient is dependent on the dissolved PCB concentration, which depends on processes such as uptake into phytoplankton (Swackhamer and Skoglund 1993; Stange and Swackhamer 1994). In a system at equilibrium, aquatic particle PCB concentrations depend directly on the gas phase concentration through the equilibrium water–particle partition coefficient, (K_p), and Henry's law constant (Fig. 1). However, lakes are dynamic systems and chemical equilibrium is rarely achieved. In this study, we investigated the rate at which PCBs are supplied by the atmosphere via air–water exchange relative to the rate at which they are lost due to settling. Trophic status affects the amount of settling organic matter and thus affects PCB settling fluxes; by the same scenario, trophic status would affect air–water exchange fluxes by decreasing the dissolved phase concentration. This study will determine whether air–water exchange coupled with particle settling can “pump” gaseous PCBs from the atmosphere to eutrophic L227 to a greater degree than oligotrophic L110.

Study sites

Lake 227 (Fig. 2) and L110 (Fig. 3) are located in the Experimental Lakes Area (ELA) of northwestern Ontario,

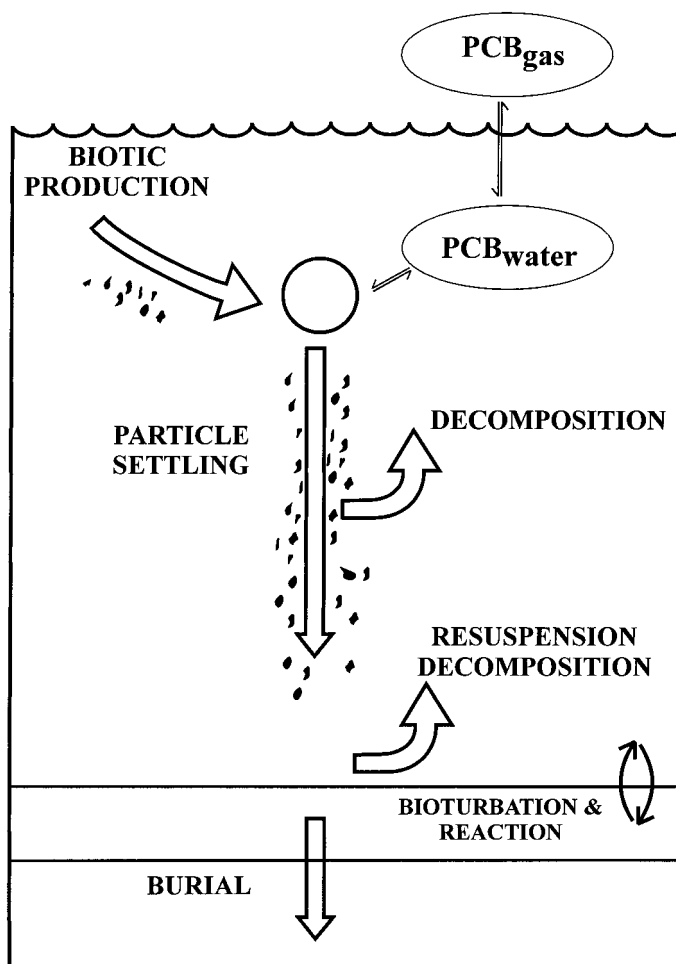


Fig. 1. PCB cycling within lakes and relationship between PCB settling fluxes and air–water exchange. “Pumping” of PCBs from air to water to settling particles.

Canada (93°41'W, 49°41'N). The watershed surrounding the lakes is typical of the southwestern Canadian Shield and consists of mature boreal forest growth. L110 is 11 km northwest of L227. These two remote, headwater lakes are similar in volume, surface area, and watershed area and receive no groundwater inputs (Table 1; Brunskill and Schindler 1971). Each lake typically stratifies in early to mid-May and turns over in mid–late September. L227 rarely experiences complete water column mixing in spring or fall (Findlay et al. 1994).

Lake 227 has been eutrophicated by epilimnetic additions of phosphorus and nitrogen since June 1969 (Schindler 1974, 1977; Findlay et al. 1994; Hecky et al. 1994; Hendzel et al. 1994). Nitrogen additions ceased in 1991 and currently 24 kg yr⁻¹ of phosphorus is added continuously during the ice-free season to the epilimnion in the form of phosphoric acid (Findlay et al. 1994). L110 has been left in its naturally oligotrophic state. Primary productivity on an areal basis was 2–5 times higher in 1993 and 1994 in L227 relative to L110 (Table 1). Total suspended matter (TSM) in the epilimnion can exceed 30 mg liter⁻¹ in L227, while TSM values in L110 ranged from 1 to 3 mg liter⁻¹. Particulate organic

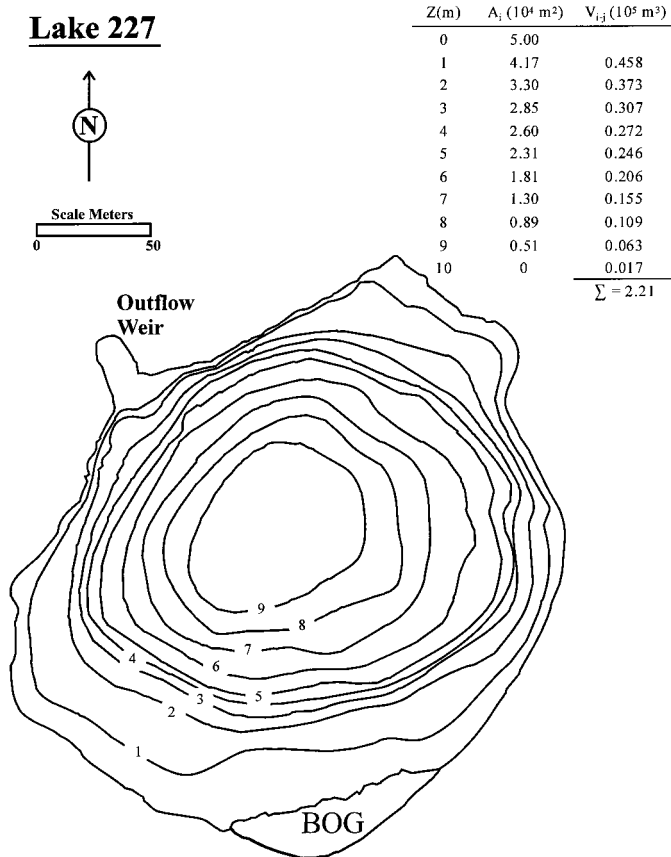


Fig. 2. Bathymetric chart of L227. Z is depth, A_i is water surface area at depth i, and V_{i,j} is volume between depths i and j.

carbon (POC) in the epilimnion ranged from 1 to 8 mg liter⁻¹ in L227 and 0.6 to 0.9 mg liter⁻¹ in L110 in 1994. Dissolved organic carbon (DOC) ranged from 7 to 13 mg liter⁻¹ in L227 and from 7 to 8 mg liter⁻¹ in L110 in 1994. DOC in L227 increased in the years following eutrophication from <10 mg liter⁻¹ to >20 mg liter⁻¹ at times (Schindler et al. 1992), suggesting that much of the DOC results from in-lake production.

During the stratified period of 1993 (1 June–9 September) the integrated OC settling flux (Fig. 4) was 1.8× greater in eutrophic L227 than in L110 (32 vs. 18 g m⁻²; Elser et al. 1995). Since L227 had ~10× more POC and ~5× higher primary productivity, autochthonous OC was more efficiently recycled in the epilimnion of eutrophic L227 relative to oligotrophic L110, consistent with findings by Baines and Pace (1994). During the stratified period (17 May–7 September 1994), the integrated OC flux was 3× greater in L227 than in L110 (49.7 vs. 16.4 g m⁻²). The majority of the OC flux (57%) in L227 occurred in August following the crash of a large *Microcystis* bloom. From mid-May to mid-August the OC flux was only 1.3× greater in L227 than L110, indicative of more efficient epilimnetic OC recycling in L227.

Field sampling procedures

The detailed experimental procedures are presented by Jeremiason (1997) with key data provided in Table 2.

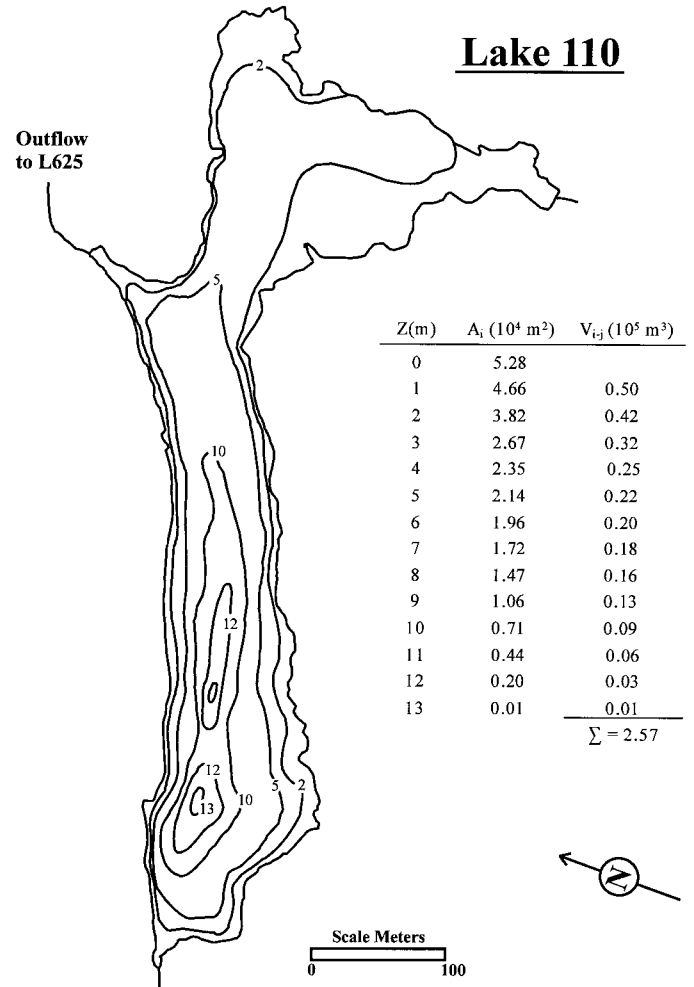


Fig. 3. Bathymetric chart of L110. Symbols same as Fig. 2.

Table 1. Bathymetric and limnological characteristics of L227 and L110.

	L227	L110
Volume (m ³)	2.21 × 10 ⁵	2.57 × 10 ⁵
Surface area (ha)	5.0	5.3
Total watershed area (ha)	34.4	34
Avg depth (m)	4.4	4.9
Max depth (m)	10	13
Epilimnion depth* (m)	1.2–2.1	2.4–4.0
Mean outflow 1994 (m ³ s ⁻¹)	0.04	0.04
Avg PP† (mg C m ⁻² d ⁻¹) 1993	553	122
Avg PP (mg C m ⁻² d ⁻¹) 1994	347	166
Avg POC‡ (mg liter ⁻¹) 1994	3.6	0.7
Avg DOC§ (mg liter ⁻¹) 1994	10.4	7.2
Avg TSM (mg liter ⁻¹) 1994	8.8	1.7

* The last meter depth interval prior to where temperature began to decrease at a rate > 1°C m⁻¹.

† Average primary productivity during ice-free period.

‡ Particulate organic carbon.

§ Dissolved organic carbon.

|| Total suspend matter.

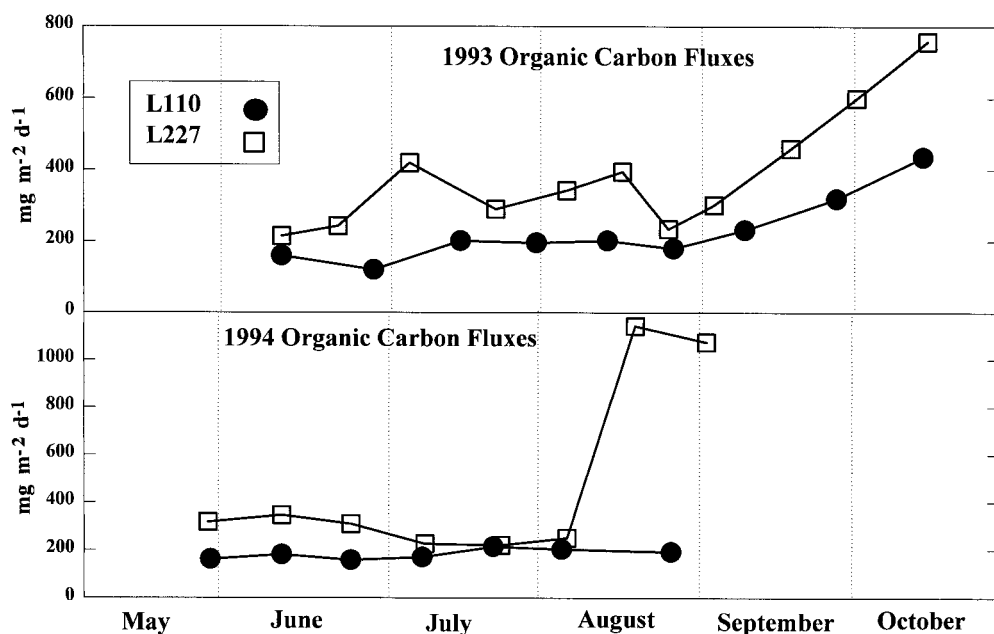


Fig. 4. Organic carbon settling fluxes in L227 and L110, 1993–1994 (Elser et al. 1995).

Sediment traps—Two types of sediment traps were deployed in L227 and L110 at a depth of 6 m in the deepest area of each lake during the ice-free seasons of 1993 and 1994. One set of traps was 1 m in diameter and funnel-shaped, designed to collect a large mass of solids to enhance PCB detection. A second set of smaller traps with a 10:1 aspect ratio was deployed in triplicate and collected concurrently to quantitatively measure organic carbon fluxes (Blomqvist and Hakanson 1981; Elser et al. 1995). Sediment trap samples were passed through a clean brass 500- μm sieve to remove large zooplankton and freeze-dried before laboratory analysis.

Water sampling—Epilimnetic water was pumped directly through precombusted (550°C, 24 h), 293-mm-diameter glass-fiber filters (GFFs, Schleicher and Schuell, 0.7 μm) from a depth of 1 m at center buoy to collect an operationally defined particulate phase. Filter samples typically consisted of three to four filters and total volume ranged from 45 to 150 liters. Filtered water (45–117 liters) was collected in 70-liter stainless steel containers and passed through an XAD-2 (Sigma Chem. Co., No. A-7643) resin column (2.5 \times 20 cm) to collect dissolved-phase PCBs. PCB surrogate standards were added to the XAD cartridge before sample collection to quantify analyte recovery. Five XAD columns were prepared and transported to the field and returned to

the laboratory as field blanks. Water samples were also collected for analysis of TSM, dissolved organic carbon (DOC), and particulate organic carbon (POC) (Jeremiason 1997).

Air sampling—Air samples were collected with a General Metal Works high-volume organics air sampler mounted on a 0.7-m platform at the ELA Meteorological Site. The flow rate through the sampler was calibrated before use at $\sim 0.5 \text{ m}^3 \text{ min}^{-1}$. Sampling time was generally 24 h. The air was passed through a 20 \times 25-cm quartz-fiber filter (0.7 μm , precombusted, 550°C for 24 h) to collect the particulate fraction, followed by a polyurethane foam (PUF) plug to collect the gas-phase PCBs.

Laboratory procedures

A brief summary of laboratory procedures is supplied here; details are given by Jeremiason (1997). All concentrations in all sample media were corrected for surrogate recovery. The PCB surrogates consisted of 3,5 dichlorobiphenyl, IUPAC congener No. 14; 2,3,5,6 tetrachlorobiphenyl, IUPAC No. 65; and 2,3,4,4',5,6 hexachlorobiphenyl, IUPAC No. 166.

Sediment traps—All samples, except for sediment trap particles from 1993, were extracted using a Soxhlet apparatus. The sediment trap samples in 1993 were extracted three times with dichloromethane (DCM) using a Polytron homogenizer (Brinkman Instruments, type PT10/35). The 1994 sediment trap samples were extracted using a Soxhlet apparatus with about 150 ml of DCM. Following extraction, the solvent was switched to hexane and reduced to $<1 \text{ ml}$ using a Buchi Rotavapor (No. RE111). Interfering compounds were removed by liquid-solid chromatography using 7 g of 1.25% by weight water-deactivated 60/100 mesh Flor-

Table 2. Samples collected from each lake.

	Year	Sampling period	Sampling frequency
Sediment trap	1993	1 Jun–19 Oct	\sim every 2 weeks
Sediment trap	1994	17 May–5 Oct	\sim every 2 weeks
Water samples	1994	17 May–19 Sep	1 d, \sim every 2 weeks
Air samples*	1994	17 May–19 Sep	24 h, once each week

* Collected at a central location.

isil (Fisher Sci.), previously activated at 550°C overnight. PCBs were eluted from the Florisil columns with 75 ml of hexane. The solvent was reduced in volume again using the rotavapor and further reduced to <100 μ l under a gentle stream of prepurified nitrogen before gas chromatographic (GC) analysis. Internal standards were added before the nitrogen blowdown and consisted of 2,4,6 trichlorobiphenyl, IUPAC No. 30, and 2,2',3,4,4',5,6,6' octachlorobiphenyl, IUPAC No. 204. PCB congeners were separated on a 60-m \times 0.25-mm-i.d. dimethyl diphenyl polysiloxane capillary column with a 0.25- μ m film thickness (DB-5, J&W Sci.). The GC was a Hewlett-Packard 5890 equipped with a 63 Ni electron capture detector and a Hewlett-Packard 7673 Autosampler. The ECD signal was acquired using Hewlett-Packard GC ChemStation.

Water and air samples—The GFFs and XAD-2 resin were placed in Soxhlet extractors and rinsed with 200–500 ml of methanol, then extracted for 24 h with methanol followed by 24 h with dichloromethane (DCM). All three extracts were combined in a 2-liter separatory funnel and methanol was removed by back extraction with water and DCM. PUFs were spiked directly with surrogates and extracted in Soxhlet extractors for 12–24 h with DCM. The remaining procedures for water and air samples were identical to those used for sediment trap samples.

Quantification of PCBs and quality control

The mass of individual PCB congeners in each sample was determined by the internal standard method. Each congener mass was determined relative to a standard calibration mix containing 610 ng ml $^{-1}$ of PCBs consisting of Aroclors 1232, 1248, and 1262 mixed in the ratios of 25:18:18, respectively (Mullin et al. 1984; Swackhamer 1988). In each sample, 76 congener peaks consisting of one or more PCB congeners were quantified. Total PCB (Σ PCB) refers to the sum of these 76 congener peaks. The quantification of PCB masses was determined by use of the software program Hewlett-Packard ChemStation for HPLC. The mass of each congener was corrected for recovery of surrogate PCB No. 166. PCB No. 166 was selected based on seven samples solvent-spiked with calibration mix containing no internal standards. Recoveries of PCB surrogates No. 14, No. 65, and No. 166 were statistically the same among the spike recovery samples. PCB congener No. 166 was chosen because it was least prone to co-eluting contaminants and had the most consistent recovery in actual samples. Surrogate recoveries for No. 166 were typically above 90% for sediment trap, particulate, and air samples, while dissolved-phase recoveries ranged from 60 to 80%.

Surrogate-corrected field blanks of each congener were subtracted from congener masses for all XAD samples. XAD-2 field blanks averaged 4.6 ± 4.8 ng, representing ~16% of the mass measured in XAD-2 samples. No blank correction was necessary for other sample matrices or for laboratory blanks.

The relative standard deviation for replicate samples ranged from 20 to 31%, 5 to 24%, and 7 to 15%, for dissolved, particulate, and sediment trap Σ PCB concentrations,

respectively. Dissolved and particulate replicates were collected on the same day. The sediment trap replicates consisted of subsamples from a single trap in each lake. Side-by-side air sampling performed with identical samplers as used in this study exhibited a relative standard deviation of ~20% for Σ PCB (Hornbuckle et al. 1993, 1995).

Results

Σ PCB settling fluxes— Σ PCB concentrations were measured on settling particles at about 2-week intervals during the ice-free seasons of 1993 and 1994 in L227 and L110. The average Σ PCB concentration (± 1 SD) in L227 was 115 ± 49 and 78 ± 34 ng g $^{-1}$ OC in 1993 and 1994, respectively. In L110, Σ PCB concentrations averaged 100 ± 37 and 113 ± 63 ng g $^{-1}$ OC, respectively, in 1993 and 1994. Σ PCB concentrations were not different between the two lakes at the 95% CI in 1993 ($P \leq 0.23$) or 1994 ($P \leq 0.06$).

The average fraction organic carbon (f_{oc}) of settling particles in L227 was 0.37 ± 0.03 and 0.39 ± 0.03 in 1993 and 1994; in L110 average f_{oc} values were 0.36 ± 0.03 and 0.34 ± 0.02 in 1993 and 1994. The dominance of algae over allochthonous material in the traps was confirmed by microscopic analysis and supported by carbon-to-nitrogen (C:N) molar ratios. Average C:N ratios in L227 were 6.8 ± 0.9 and 7.0 ± 0.8 in 1993 and 1994. In L110, C:N ratios were significantly greater ($P \leq 0.05$) than in L227 at 8.3 ± 1.3 and 8.2 ± 0.9 in 1993 and 1994. C:N ratios of suspended particles were 7.4 ± 1.2 in L227 and 9.6 ± 0.8 in L110.

Σ PCB settling fluxes (Fig. 5) were determined by multiplying Σ PCB concentrations (ng g $^{-1}$ OC) by OC fluxes measured in the smaller traps. Average Σ PCB settling fluxes were greater in L227 than L110 in 1993 (40 ± 10 vs. 22 ± 10 ; $P \leq 0.0007$) and 1994 (29 ± 7 vs. 17 ± 9 ; $P \leq 0.014$). The integrated settling flux of Σ PCBs measured at 6 m in L227 from 1 June to early September was 4.3 and 2.9 μ g m $^{-2}$ in 1993 and 1994. In L110 the Σ PCB fluxes over the same time periods were 1.9 and 1.3 μ g m $^{-2}$. Corresponding OC settling fluxes were 32 and 50 g m $^{-2}$ in L227 in 1993 and 1994, and 18 and 16 g m $^{-2}$ in L110 in 1993 and 1994.

PCB water concentrations— Σ PCB concentrations were measured at a depth of 1 m in both lakes at about 2-week intervals from 17 May to 19 September 1994 (Fig. 6). Total Σ PCB concentration in water (dissolved + particulate) was highest in L227 on 17 May (1.35 ng liter $^{-1}$). The highest Σ PCB water concentrations in L110 ranged from 0.65 to 0.80 ng liter $^{-1}$ and occurred between 18 May and 30 June. The fraction of Σ PCB found in the operationally defined particulate phase (f_p) was 0.22 ± 0.09 in L227 and 0.16 ± 0.09 in L110. POC was $\sim 10\times$ higher in L227 than L110, but f_p values were similar, so solid-water partition coefficients were lower in L227.

The high dissolved concentration measured on 17 May in L227 was an outlier at the 99% CI and was not included in further calculations. After June, dissolved-phase Σ PCB concentrations did not change within or between lakes. However, the high spring water concentrations of PCBs probably reflect efficient under-ice winter mineralization of OC and PCB release. Average dissolved-phase Σ PCB concentrations

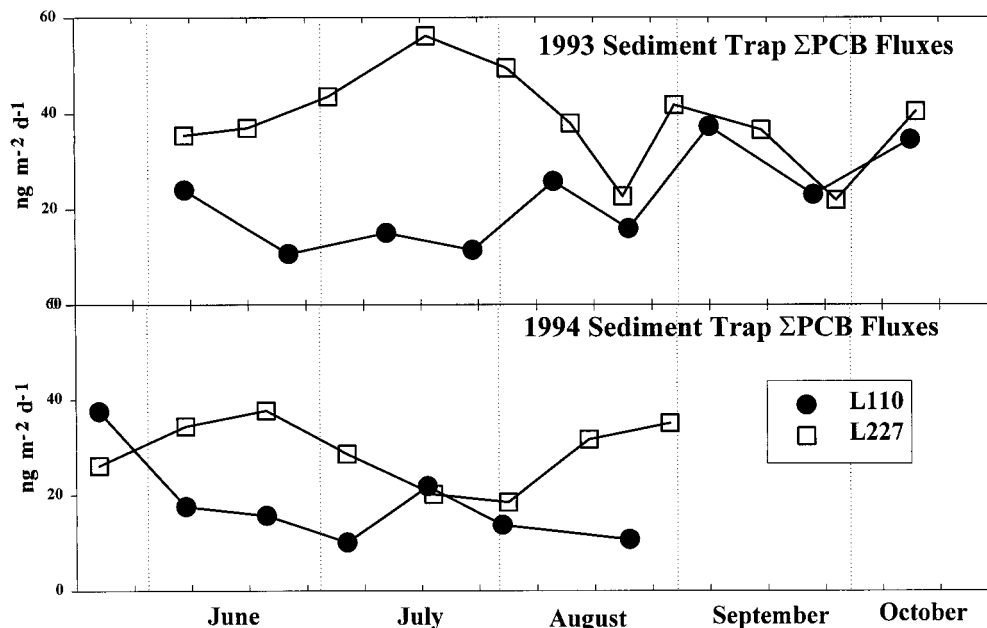


Fig. 5. Σ PCB settling fluxes in L227 and L110, 1993–1994.

were 0.29 ± 0.06 ng liter⁻¹ in L227 and 0.33 ± 0.06 ng liter⁻¹ in L110. These concentrations are statistically equal at the 95% CI based on a paired *t*-test. In comparison, dissolved Σ PCB concentrations in May and June 1993 (D. Muir pers. comm.) were similar at 0.62 and 0.44 ng liter⁻¹ in L227 and 0.45 and 0.93 in L110.

Suspended particle Σ PCB concentrations were higher in L110 than in L227 throughout the entire sampling period. The average particulate-phase concentration in L110 was 92 ± 24 ng g⁻¹ OC, similar to settling solids Σ PCB concentrations of 100 ± 37 and 113 ± 63 ng g⁻¹ OC in 1993 and

1994. In L227 the average Σ PCB concentration on suspended particles was 33 ± 17 ng g⁻¹ OC, significantly lower than concentrations on settling particles of 115 ± 49 and 78 ± 34 ng g⁻¹ OC in 1993 and 1994. Suspended particle Σ PCB concentrations in L227 were similar to the settling particle concentrations of 28 ng g⁻¹ OC (9–24 August) and 33 ng g⁻¹ OC (24 August–6 September) observed immediately after the *Microcystis* crash in August 1994. The maximum Σ PCB concentration on suspended particles in L227 occurred in May and early June prior to cyanobacteria blooms. Coupled with constant dissolved concentrations, lower par-

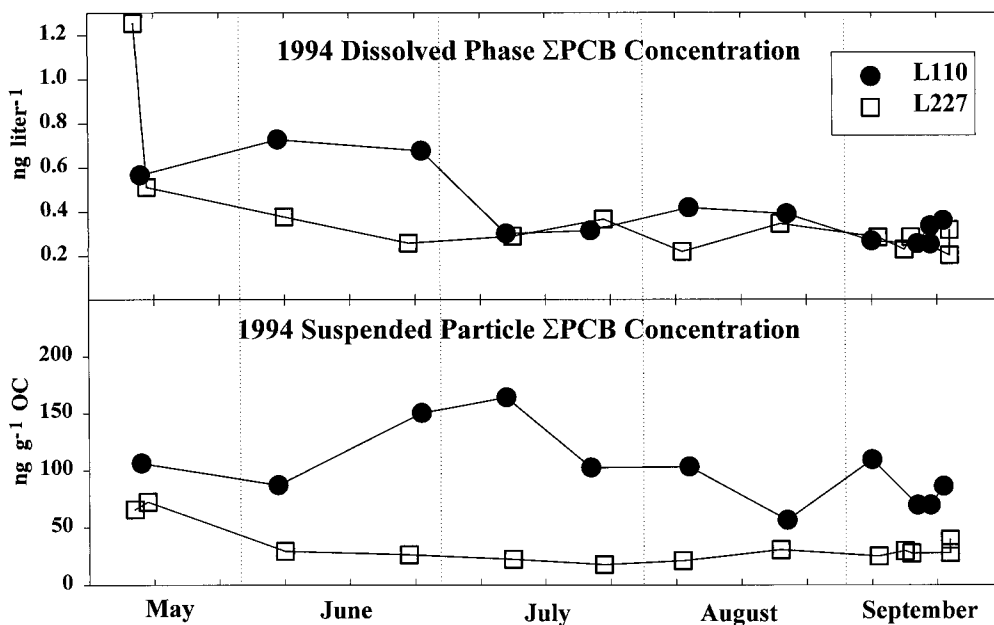


Fig. 6. Σ PCB dissolved and particulate water concentrations in L227 and L110, 1994.

ticulate PCB concentrations in L227 resulted from differences in phytoplankton species (Stange and Swackhamer 1994) rather than dilution by more particles (Taylor et al. 1991).

Air concentrations— Σ PCB concentrations in air were measured every week from 17 May to 19 September 1994 at the ELA Meteorological Site (Jeremiason 1997). The maximum Σ PCB gas-phase concentration was observed on 6 July (330 pg m⁻³), and the average was 170 ± 80 pg m⁻³. A correlation of log Σ PCB with inverse average daily temperature (°K) resulted in $r^2 = 0.52$ ($P = 0.00034$). The slope of the log C vs. 1/T line was -5,140, similar to slopes found by Hoff et al. (1992) and Hillery et al. (1997).

Homologs—Average homolog distributions in air, water, and sediment trap material were similar in both lakes. Tri- and tetra-chlorinated congeners dominated in all media. No significant change in homolog distribution within individual media was observed over time. To reach this conclusion, each homolog was first normalized to the total PCB concentration in each sample and then each sample was correlated with every other sample in the media. Correlation coefficients, r , typically ranged from 0.80 to 0.99 (Jeremiason 1997).

Air-water exchange fluxes—The method for determining the air-water exchange flux is discussed briefly here, but details can be found elsewhere (Baker and Eisenreich 1990; Achman et al. 1993; Hornbuckle et al. 1994; Jeremiason 1997). Chemical exchange flux across the air-water interface was based on a modified two-layer resistance model (Liss and Slater 1974; Schwarzenbach et al. 1993; Hornbuckle et al. 1994, 1995); windspeed correlations were used to determine mass transfer coefficients (e.g., Wanninkhof et al. 1991). The air-water exchange flux equation is

$$\text{Flux} = K_{ol} \left(C_{diss} - \frac{C_{gas}RT}{H} \right). \quad (1)$$

Flux (ng m⁻² d⁻¹) is the *net* chemical flux, K_{ol} is the overall liquid mass transfer coefficient, C_{diss} (ng m⁻³) is the dissolved chemical concentration, C_{gas} (ng m⁻³) is the gas-phase concentration, R is the universal gas constant, T is temperature (K) at the interface, and H is Henry's law constant. The derivation of the overall mass transfer coefficient is based on steady-state mass transport occurring across resistance layers on either side of the interface where chemical equilibrium is assumed. The overall mass transfer coefficient is (Hornbuckle et al. 1994, 1995):

$$\frac{1}{K_{ol}} = \frac{1}{k_w} + \frac{RT}{k_a H}. \quad (2)$$

k_w (m d⁻¹) is the mass transfer coefficient across the water layer, and k_a (m d⁻¹) is the mass transfer coefficient across the air layer. Correlations with empirical relationships based on windspeed were used to determine k_w and k_a for PCB congeners (Holmen and Liss 1984; Wanninkhof et al. 1991; Schwarzenbach et al. 1993). Windspeed was measured continuously at the ELA Meteorological Site and was corrected

to reflect windspeed above the wind-sheltered lakes at ELA using the relation (Solinske 1982)

$$X_o = -3.033 + 0.813X_1 + 0.059X_2. \quad (3)$$

X_o is the overlake windspeed (km h⁻¹) at a height of 1.3 m above the lake surface, X_1 is the windspeed measured at the meteorological site, and X_2 is the surface area of the lake (ha). The average corrected daily windspeed (X_o) in this study was 1.4 m s⁻¹ above L227. Windspeeds corresponding to days of air and water measurements were used to obtain mass transfer coefficients. Henry's law constants (Brunner et al. 1990) were corrected for temperature based on results from ten Hulscher et al. (1992) according to Hornbuckle et al. (1994):

$$\log H_T = \log H_{298} + 8.76 - \frac{2,611}{T}. \quad (4)$$

Dissolved congener concentrations were adjusted to reflect PCB binding to DOC (colloids) that passed through the GFFs. Based on previous work on DOC binding of SOCs in freshwater lakes and rivers (Landrum et al. 1984; Chin et al. 1997), the following relation was chosen between the colloid-water partition coefficient, K_c (liters kg⁻¹) and the organic carbon-water partition coefficient, K_{OC} :

$$K_c = 0.2 \times K_{OC}. \quad (5)$$

K_{OC} was determined from the octanol-water partition coefficient, K_{ow} (Karickhoff et al. 1979):

$$\log K_{OC} = 1.00K_{ow} - 0.21. \quad (6)$$

The truly dissolved phase concentration is then

$$C_{diss} = \frac{C_{d,meas}}{1 + K_c \times \text{DOC}}. \quad (7)$$

$C_{d,meas}$ (ng liter⁻¹) is the measured dissolved phase and DOC has units of kg liter⁻¹. Colloid-corrected dissolved Σ PCB concentrations after June were 0.16 ± 0.04 ng liter⁻¹ in L227 and 0.18 ± 0.03 ng liter⁻¹ in L110, about 40% lower than operationally measured values.

Net Σ PCB volatilization fluxes were calculated for the ice-free period in both lakes, except for the last sampling date in L227 (Fig. 7). Each point in Fig. 7 represents an air-water pair consisting of a water sample coupled with the nearest time-proximity air sample. Air-water exchange fluxes were determined for each PCB congener and summed to determine *net Σ PCB flux*. *Net* air-water exchange Σ PCB fluxes ranged from -0.8 (*net* absorption) to +31.7 ng m⁻² d⁻¹. The *net* volatilization Σ PCB flux integrated over the stratified period was 0.9 μ g m⁻² in L227 and 1.7 μ g m⁻² in L110 after adjusting all water concentrations for the presence of colloids.

Discussion

A eutrophic lake has the potential to retain enhanced quantities of atmospheric gaseous PCBs relative to an oligotrophic lake due to greater production of biotic particles. Biotic, OC-rich particles remove PCBs from the dissolved phase by passive partitioning and incorporate them into the

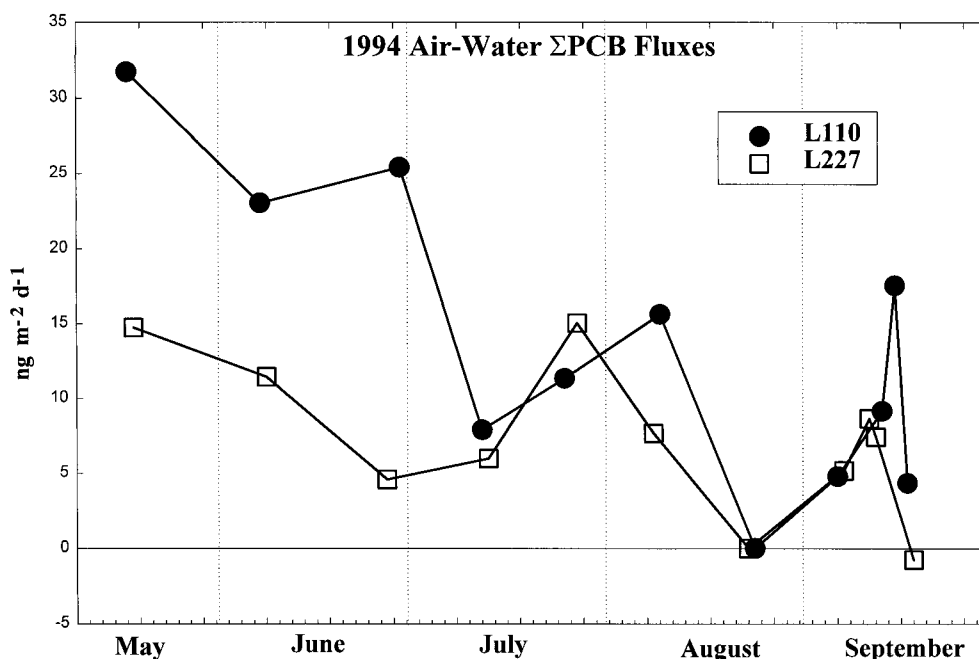


Fig. 7. Air-water exchange fluxes adjusted for the presence of colloids in L227 and L110, 1994. A positive flux indicates *net* volatilization.

particulate phase (phytoplankton). The phytoplankton can then be lost due to settling, mineralization, consumption, or outflow. In a eutrophic lake, greater masses of phytoplankton (or organic carbon) are likely to settle from the epilimnion relative to an oligotrophic lake (Fig. 4). We hypothesize that the same would hold true for PCBs and settling fluxes in Fig. 5 demonstrate this to be the case.

Under stratified conditions, settling represents a loss of PCBs from the epilimnion. Enhanced PCB settling fluxes may lower PCB water concentrations in L227 relative to L110, thereby decreasing volatilization losses. During the stratified period of 1994, Σ PCB settling fluxes removed $\sim 5\%$ d^{-1} and $\sim 2\%$ d^{-1} of the epilimnetic burden in L227 and L110, respectively. These calculations were based on epilimnetic depths of 1.5 m in L227 and 3.0 m in L110. In the absence of other sources these fluxes would significantly lower PCB water concentrations in both lakes, but especially in L227. PCB dissolved concentrations were, in fact, lower in L227 in May and June (Fig. 6), but effectively constant in both lakes throughout the rest of the stratified period.

Higher PCB settling fluxes in L227 coupled with constant dissolved concentrations support the hypothesis that *net* gas absorption is enhanced in eutrophic L227 relative to L110. However, fugacity gradients indicate *net* volatilization occurring throughout the stratified period in both lakes (Fig. 7). Thus, PCBs are lost due to settling *and net* volatilization, but eutrophication lowered *net* volatilization fluxes. *Net* volatilization over the entire stratified period ($0.9 \mu\text{g m}^{-2}$ in L227 vs. $1.7 \mu\text{g m}^{-2}$ in L110) is reduced in L227 relative to L110 due to enhanced retention of PCBs by greater biotic production. *Net* volatilization fluxes are of the same magnitude as settling fluxes ($2.4 \mu\text{g m}^{-2}$ in L227 and $0.9 \mu\text{g m}^{-2}$ in L110) and also represent a significant loss of PCBs

from the epilimnion. What is the additional source of PCBs supporting *net* volatilization losses and settling fluxes?

Possible sources of PCBs to the epilimnia of L227 and L110—Sources of PCBs potentially contributing to volatilization and settling fluxes are mixing of hypolimnetic and epilimnetic waters, release from epilimnetic sediments, wet and dry atmospheric deposition, and watershed releases.

Mixing with the hypolimnion: Hypolimnetic water, potentially higher in PCB concentration, may turbulently mix with epilimnetic water. However, hypolimnetic water samples taken from each lake in September 1994 showed that hypolimnetic and epilimnetic concentrations were similar in both lakes (Jeremiason 1997). Vertical mixing is unlikely because both lakes strongly stratify and there is little wind energy on these rock and forest-sheltered lakes to induce mixing. Tracer studies in L227 demonstrate that mixing rates between the hypolimnion and epilimnion are only slightly greater than diffusion rates (Hesslein 1980; Quay et al. 1980).

Epilimnetic sediments: In L227, 26% of the total sediment area is in the epilimnion (upper 1.5 m), and in L110 49% is in the epilimnion. Previously deposited PCBs may diffuse out of the epilimnetic sediments in response to decreasing water column concentrations. Alternatively, recently deposited sediment rich in labile organic carbon may mineralize and release associated PCBs. Sediment grab samples, integrating the top 5 cm of epilimnetic sediment, contained no measurable PCBs ($\leq 10 \text{ ng g}^{-1} \text{ OC}$) in 0–2-m and 2–4-m depth strata in L227. A grab sample from L227 in the 4–6-m depth stratum exhibited Σ PCB concentrations of $17.7 \text{ ng g}^{-1} \text{ OC}$. In L110 no measurable PCBs were found in sedi-

ment collected at water depths of 0–8 m. The two grab samples from below 8-m water depth averaged 24.4 ng g⁻¹ OC. The integration time corresponding to 5 cm of sediment is unknown, but low PCB concentrations in the epilimnetic sediments suggest storage is minimal. On a short-term basis, epilimnetic sediments may supply PCBs to the epilimnion. However, our calculations assume that PCBs settling onto epilimnetic sediments are recycled back to the epilimnion or focused to deeper waters.

Dry and wet deposition: Another possible pathway supporting the PCB settling fluxes is atmospheric inputs in the form of wet and dry deposition and(or) gas absorption. The magnitude of PCB flux by dry deposition in remote areas is small relative to other PCB sources and certainly small relative to settling fluxes in L227 and L110. Hoff et al. (1996) estimated a dry deposition flux of Σ PCB to Lake Superior of 0.33 $\mu\text{g m}^{-2} \text{yr}^{-1}$ (0.9 ng m⁻² d⁻¹). Applying these data, dry deposition of Σ PCB is maximally ~ 5 mg over the stratified period to each lake, indicating that dry deposition is negligible compared to Σ PCB settling fluxes. Local dry deposition sources (i.e., pollen) may be more significant at ELA.

Total precipitation from ice-cover 1993 to ice-cover 1994 was 77.17 cm (66.55 cm of rain and 10.62 cm of snow). The volume-weighted mean Σ PCB concentration in rain at ELA in 1992 was 1.4 ng liter⁻¹ (D. Muir pers. comm.). Over the stratified period in 1994, the area received 40.71 cm of rain resulting in wet deposition of ~ 29 mg of Σ PCBs to L227 and ~ 32 mg to L110 (~ 5.3 ng m⁻² d⁻¹). Hoff et al. (1996) reported volume-weighted mean Σ PCB concentrations in the western Great Lakes region of 1–2 ng liter⁻¹.

Watershed inputs: L227 and L110 have ratios of watershed to lake surface area exceeding 5 (29.4:5.0 ha for L227 and 28.7:5.3 ha for L110); thus the possibility that PCBs leak from the watershed must be considered. Soil horizons at ELA are thin and the soil consists of sandy brunisols (Brunskill and Schindler 1971). To evaluate the potential importance of PCB inputs via runoff, we determined the amount of water entering the lake from the watershed. Both are headwater lakes and outflow from L227 is monitored continuously. Because L110 outflow was not measured, we assumed that outflow from L110 was similar to L227. The average water renewal time in L227 is 2.8 yr (Newbury and Beaty 1980). A water budget for L227 and L110 constructed over the stratified period in 1994 (Table 3) shows that inflow from the watersheds accounted for $\sim 60\%$ of the water inputs to the lakes. PCB inputs and estimated concentrations in runoff from the watershed were determined by completing a PCB mass budget for each lake (*see below*).

Gas absorption: The final atmospheric source to be considered is gas absorption. Σ PCB *net* air–water exchange fluxes (Fig. 7) were from the water to the air and represent a net loss from the epilimnion. Thus, gas absorption cannot be the PCB input supporting constant epilimnetic PCB concentrations because volatilization losses more than offset inputs by gas absorption. To further demonstrate this, we determined average instantaneous Σ PCB gas absorption fluxes

Table 3. Water budget during stratified and ice-free period, 1994 for L227 and L110.

	L227	L110
Stratified		
Precip. (m ³)	20,400	24,000
Runoff* (m ³)	33,700	33,400
Outflow (m ³)	33,200	32,800
Evap. (m ³)	18,600	21,900
Δ storage (m ³)	2,300	2,700
Ice-free season		
Precip. (m ³)	33,400	39,500
Runoff* (m ³)	69,100	66,900
Outflow (m ³)	75,200	76,100
Evap. (m ³)	25,000	29,500
Δ storage (m ³)	1,400	1,700

* Outflow + evaporation \pm Δ storage – precipitation.

during the air–water sampling period. Instantaneous gas absorption fluxes were determined by multiplying PCB air concentrations by appropriate mass transfer coefficients, K_{og} ($K_{\text{og}} = K_{\text{o}}RT/H$). This calculation is of gross gas absorption as opposed to *net* transfer determined in Eq. 1. Average mass transfer coefficients were determined during intervals corresponding to the water sampling frequency. Σ PCB gas absorption fluxes averaged 5.8 ± 3.1 ng m⁻² d⁻¹ in L227 and 6.1 ± 3.2 in L110 and led to integrated loadings of 34 and 36 mg, respectively, during the stratified period. Gas absorption is a fraction of the PCB settling fluxes which averaged 26 and 12 ng m⁻² d⁻¹ in L227 and L110 during the stratified period of 1994. Thus, gas absorption could not be the dominant input to these lakes because its magnitude was small relative to settling fluxes and the net direction of air–water exchange flux was from the water to the air.

Epilimnion mass budget—The epilimnetic Σ PCB mass budget for each lake was constructed over the stratified period for mid-May to early September 1994 (Figs. 8 and 9). The depth of the epilimnion in L227 was 1.5 m and in L110 was 3.0 m. The epilimnetic mass balance equation in mg of Σ PCB is

$$\Delta\text{burden} = \text{inputs} - \text{outputs.} \quad (8)$$

Δ burden (mg) is the change in epilimnetic Σ PCB burden over the stratified period:

$$\Delta\text{burden} = \Delta C_{\text{w}} \times V_{\text{epi}} \times 10^{-3}. \quad (9)$$

ΔC_{w} (ng liter⁻¹) is the change in epilimnetic Σ PCB concentration over the stratified period, V_{epi} is the volume of the epilimnion, and 10^{-3} is a conversion factor.

Outputs of Σ PCB considered in the mass balance were outflow by water, particle settling, and volatilization. Outflow (mg) over the stratified period was determined as

$$\text{outflow (mg)} = \sum (C_{\text{w},i} \times Q_i \times t_i \times 10^3). \quad (10)$$

$C_{\text{w},i}$ (ng liter⁻¹) was the Σ PCB water concentration over time period i , Q_i (m³ d⁻¹) was the average outflow during time period i , t_i (d) was the length of time period i . The time

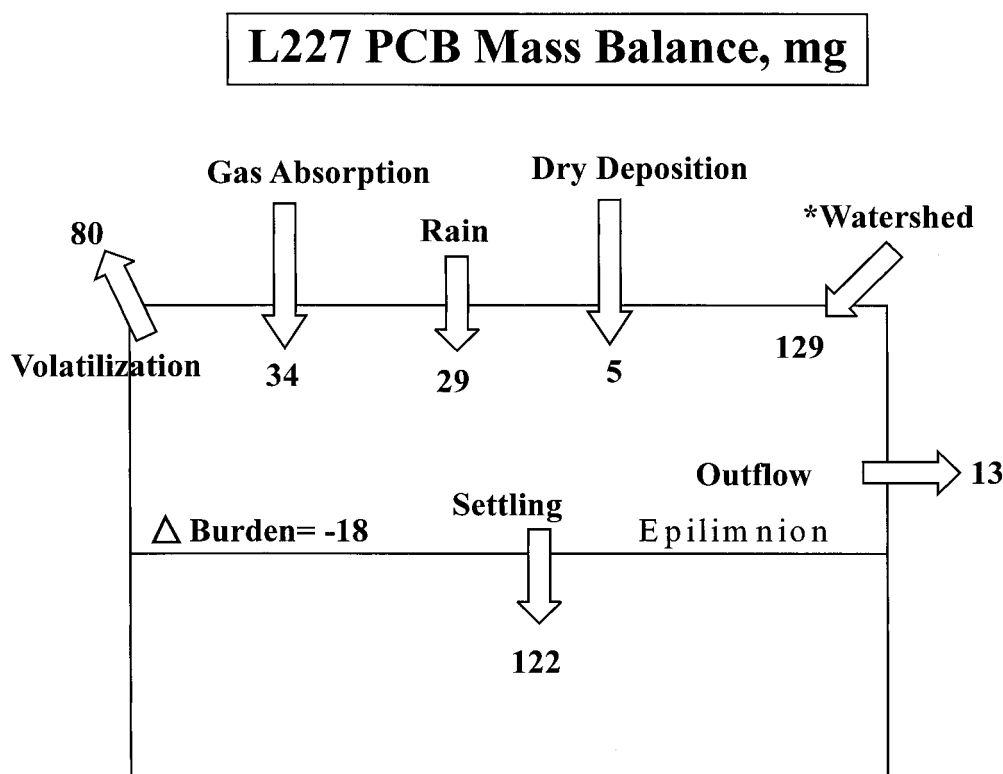


Fig. 8. L227 Σ PCB epilimnion mass balance (mg), 1994. *Watershed = Δ burden - inputs + outputs.

periods, i , were determined by the time between water samples in each lake. Settling was determined as

$$\text{settling (mg)} = \sum (\text{flux}_j \times t_j \times SA_z \times 10^{-6}). \quad (11)$$

Flux_j ($\text{ng m}^{-2} \text{d}^{-1}$) was the Σ PCB settling flux during trap deployment j , t_j (d) was the time of trap deployment j , SA_z (m^2) was the surface area at epilimnion depth z , and 10^{-6} converts from ng to mg. Volatilization over the stratified period was determined as

$$\text{volatilization (mg)} = \sum (\text{Vflux}_i \times t_i \times SA \times 10^{-6}). \quad (12)$$

Vflux_i ($\text{ng m}^{-2} \text{d}^{-1}$) was the instantaneous volatilization flux applied to time period i , SA (m^2) is the surface area of the lake, and 10^{-6} converts ng to mg.

Inputs of PCBs occur by wet and dry deposition, gas absorption, and watershed inputs. Wet and dry deposition was determined previously. Gas absorption was determined as

$$\text{gas absorption (mg)} = \sum (\text{Gflux}_k \times t_k \times SA \times 10^{-6}). \quad (13)$$

Gflux_k ($\text{ng m}^{-2} \text{d}^{-1}$) is the instantaneous gas absorption flux applied to time period k , t_k (d) was the time period between air samples, and 10^{-6} a unit conversion factor.

Solving the mass balance for watershed inputs to each lake yields

$$\text{watershed} = \Delta\text{burden} - \text{inputs} + \text{settling} + \text{volatilization} + \text{outflow}. \quad (14)$$

Watershed inputs were 129 and 72 mg for L227 and L110 during the stratified period.

Assuming watershed inputs were from overland runoff,

we estimated the average Σ PCB concentration in runoff based on the volume of runoff during the stratified period (Table 3):

$$C_{\text{runoff}} = \frac{\text{runoff (mg)} \times 1,000}{\text{runoff volume (m}^3)}. \quad (15)$$

C_{runoff} (ng liter^{-1}) was the Σ PCB concentration in potential runoff from the watershed. The estimated Σ PCB concentration in runoff was $3.8 \text{ ng liter}^{-1}$ into L227 and $2.2 \text{ ng liter}^{-1}$ into L110.

Statistical evaluation of watershed inputs—Because watershed Σ PCB inputs are determined by difference, their accuracy depends on the accuracy of the other inputs and outputs in the mass budget. Settling and volatilization have the greatest impact on watershed inputs and thus the accuracy in quantifying these two processes is especially important. The error associated with watershed PCB inputs during the stratified period was determined by propagating the error (Table 4) associated with volatilization, settling, outflow, rain inputs, gas absorption, dry deposition, and Δ burden (Shoemaker et al. 1989; Hoff 1994). All inputs and outputs were assumed to be independent. This is not the case for volatilization, outflow, and Δ burden, because all depend on C_{diss} . Since outflow and Δ burden are small relative to volatilization, this assumption has little impact on the final result. The propagated error for each input or output was: volatilization, 47%; particle settling, 14%; outflow, 25%; rain, outflow, and Δ burden, 50%; and gas absorption, 54%. Overall propagated

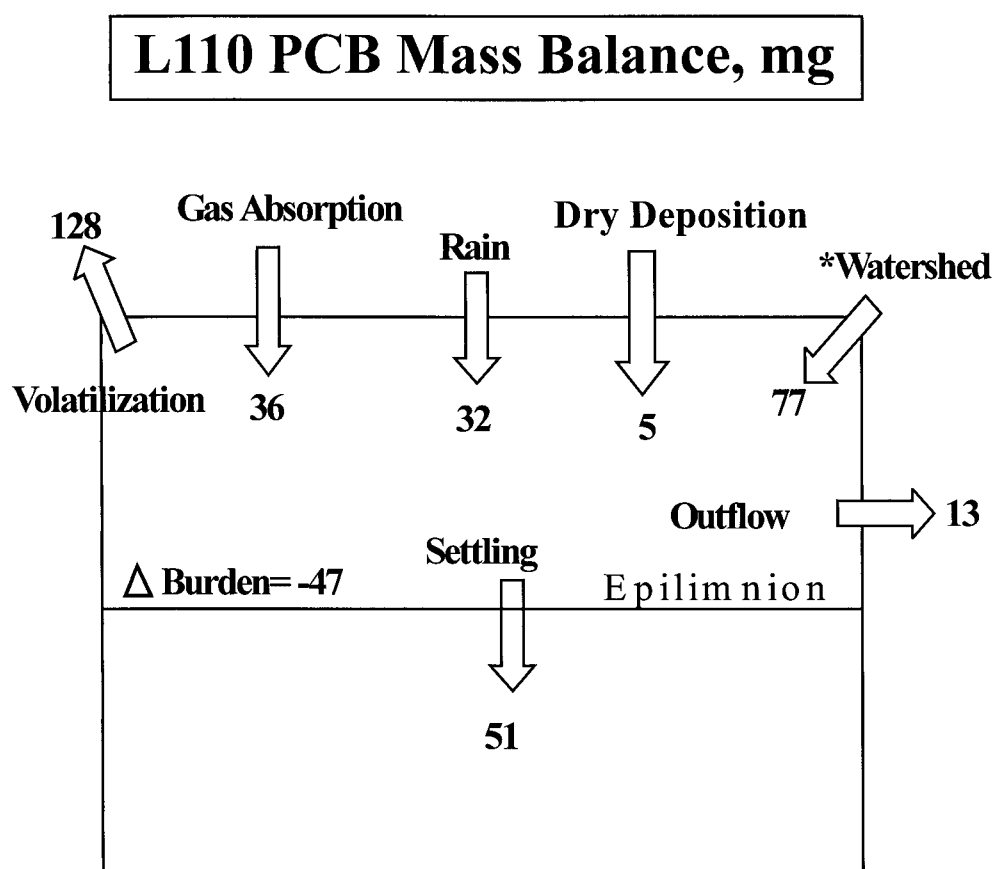


Fig. 9. L110 Σ PCB epilimnion mass balance (mg), 1994. *Watershed = Δ burden - inputs + outputs.

Table 4. Propagation of error analysis summary.

Mass balance component*	Parameter	ϵ	Propagated ϵ
Settling (S)	C_{sett}	0.10	0.14
	OC flux	0.10	
Volatilization (V)	C_{diss}	0.25	0.47
	K_{ol}	0.40	
Δ burden (B)	C_w	0.25	0.25
Outflow (O)	C_w	0.25	0.25
Gas absorption (G)	C_{gas}	0.20	0.45
	K_{og}^\dagger	0.40	
Rain (R)	C_{rain}	0.30	0.30
Dry deposition (D)	?	0.50	0.50
Watershed ‡ (W)	All components	—	0.35 § , 0.90 $^\parallel$

* All components (c) are of the form $c = axy$ and thus for independent variables x and y , and a being constant, the propagated error (ϵ_c) is: $\epsilon_c^2 = \epsilon_x^2 + \epsilon_y^2$.

$^\dagger K_{\text{og}} = K_{\text{ol}}/H'$ and is assumed to have the same ϵ as K_{ol} .

‡ Watershed propagated error (ϵ_w) was determined from $W^2\epsilon_w^2 = S^2\epsilon_s^2 + V^2\epsilon_v^2 + B^2\epsilon_b^2 + O^2\epsilon_o^2 + G^2\epsilon_g^2 + R^2\epsilon_r^2 + D^2\epsilon_d^2$.

§ ϵ_w in watershed inputs for L227 during the stratified period.

$^\parallel$ ϵ_w in watershed inputs for L110 during the stratified period.

error in the estimate of the watershed contribution of Σ PCB in L227 was 35%. In L110, the propagated error in watershed inputs over the stratified period was 90%. The propagation of error analysis indicates that watershed Σ PCB inputs were >0 at the 95% CI during stratification in L227 and at the 67% CI in L110. Based on the error analysis, the watershed PCB inputs may also be much greater than those determined from the mass budgets.

Evaluation of watershed inputs—The Σ PCB concentrations estimated in potential runoff (2.2–3.8 ng liter $^{-1}$) are greater than volume-weighted rain concentrations observed at ELA (1.4 ng liter $^{-1}$) and Lake Superior (0.7 ng liter $^{-1}$) for the same period (Hoff et al. 1996). Evaporation and evapotranspiration may lead to an increased chemical concentration in runoff relative to rainfall. For the years 1969–1996, the average annual precipitation at ELA was 690.6 mm (182.9 mm as snow and 507.6 mm as rain). The average annual runoff over this same period was 204 mm. The average runoff yield was thus 29%, meaning that on average 71% of precipitation falling on the watersheds is lost by evapotranspiration and evaporation. If PCBs in rainfall are concentrated by evapotranspiration and evaporation, then rainfall with a Σ PCB concentration of 1.4 ng liter $^{-1}$ corresponds to potential runoff concentrations of 4.8 ng liter $^{-1}$. This calculation assumes the watershed does not retain any

PCBs from rain which is unlikely due to their hydrophobic nature (Rapaport and Eisenreich 1988).

Watershed inputs of PCBs by a given storm event are influenced by the relative water saturation of the watershed and the intensity and duration of the storm. The relative moisture saturation of the soil will influence the amount of runoff from a rain (Linsley et al. 1949). At ELA, 1–39% of total rainfall volume entered Rawson Lake following a storm (Newbury and Beaty 1980). High storm yields (runoff-rainfall) occurred when the basin was saturated by snowmelt water or a previous storm. Moisture content thus impacts the residence time of water from a rainfall in the watershed, which may also influence PCB concentrations in the runoff. Longer and more intense storms typically result in more runoff and higher runoff:rainfall ratios (Linsley et al. 1949; Newbury and Beaty 1980). Further research is needed to determine the relationship between watershed yield and PCB inputs by runoff.

Snowmelt in spring is often a major proportion of the total runoff volume that enters ELA lakes. Snowmelt represented 26% of precipitation volume from 1969 to 1996. The proportion of snowmelt entering the lakes by runoff is a function of the saturation of the soil and whether the soil is frozen (Linsley et al. 1949). In winter 1993–1994 there was an extreme moisture deficiency and below average snowfall (10.62 cm) at ELA, resulting in very low spring runoff. Thus, snow probably did not contribute significantly to runoff inputs in 1994. Σ PCB concentrations in snowfall in Minnesota are typically 1–2 ng liter⁻¹, similar to rain concentrations (Franz 1994). Thus a large spring snowmelt could result in significant PCB loading by runoff. A large PCB input by snowmelt did not occur in 1994 but may have occurred in 1993 when there was more runoff in spring, which may explain the higher PCB settling fluxes in 1993 when compared to 1994.

Forested watersheds are especially efficient at collecting gaseous atmospheric chemicals such as PCBs (Paterson et al. 1990; Shreiber and Schonherr 1992; Simonich and Hites 1994; Hornbuckle and Eisenreich 1996). Although PCBs are known to actively cycle between forest vegetation (needles, leaves, tree bark) and the atmosphere, a fraction is retained (Hornbuckle and Eisenreich 1996). As vegetation accumulates in the forest floor, a combination of organic matter mineralization and water flow will leach an unknown but likely small fraction. This will result in “leakage” of the watershed burden of atmospheric PCBs focused into potential runoff and, when added to contributions from rainfall, constitute the watershed contribution.

The significant watershed Σ PCB inputs to the lake mass budgets stress the importance of considering watershed inputs in all types of aquatic systems. Bremle and Larsson (1997) found PCB concentrations similar to rain in a Swedish River during high flow events, suggesting PCB washout from the watershed. Rivers and lakes with large ratios of watershed to lake surface area may be particularly susceptible to watershed PCB inputs. In rivers that supply significant PCB loads to water bodies despite discontinued or unknown point sources, the possibility of watershed inputs must be considered. Examples include tributaries to northern Lake Michigan (Marti and Armstrong 1990) and the Sus-

quehana River which drains into Chesapeake Bay (Godfrey et al. 1995). Other lakes, such as the Great Lakes, with relatively small watershed areas compared to lake surface area and volume are likely less susceptible to watershed PCB inputs. However, further research is needed to determine relationships among PCB inputs by runoff and ratio of watershed to lake surface area, watershed characteristics, soil type, and climate.

Conclusions

Eutrophication of L227 impacted settling fluxes and air-water exchange of PCBs. Eutrophication resulted in lower PCB concentrations on suspended particles, higher PCB settling fluxes, and lower volatilization fluxes during stratification relative to oligotrophic L110. Lower PCB concentrations on suspended particles were a result of differences in phytoplankton species as dissolved PCB concentrations were similar between L227 and L110. Lower PCB concentrations in fish and other higher trophic levels (Taylor et al. 1991; Larsson et al. 1992) may result from lower phytoplankton PCB concentrations in eutrophic systems as observed here. However, other eutrophic systems, with different phytoplankton species composition, may not be impacted in the same manner as L227. Higher PCB fluxes were synonymous with greater organic carbon fluxes. Our original hypothesis, that net gas absorption would be enhanced in L227 relative to L110, was not valid. However, increased retention of watershed-derived PCBs was reflected by lower volatilization fluxes and higher PCB settling fluxes. Thus, eutrophic lakes may temporarily or permanently amass greater PCB burdens than oligotrophic lakes. In other systems where air-water exchange is the dominant PCB input, *net* gas absorption may be enhanced by eutrophication.

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