

## PCB Decline in Settling Particles and Benthic Recycling of PCBs and PAHs in Lake Superior

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Sediment traps were deployed at five sites in Lake Superior at multiple depths during lake stratification in 1987 and 1991. Mass, organic carbon, PCB, and PAH fluxes were determined. PCB concentrations on settling solids declined from 1984 to 1991 with a first-order rate constant of  $0.26 \text{ yr}^{-1}$  similar to reported water column concentration decreases ( $0.20 \text{ yr}^{-1}$ ). Total PCB settling fluxes from the upper 35 m of water averaged  $121 \pm 40 \text{ ng/m}^2\text{-d}$  in 1987 and  $48 \pm 23 \text{ ng/m}^2\text{-d}$  in 1991. Settling fluxes are greater than reported wet and dry deposition fluxes ( $2.8 \text{ ng/m}^2\text{-d}$ ) and demonstrate the intense recycling of PCBs within the lake. A large fraction (>50%) of the total Lake Superior water PCB burden is transported each year by settling particles to within 5 m of the lake bottom, but only 2-5% of settling PCBs accumulate in bottom sediments. Thus, most of the PCBs are recycled in the benthic region, possibly representing a major entry point for PCBs into higher trophic levels through the benthic food web. Benthic recycling of PAH compounds with three and four rings occurred, but a larger fraction of these settling PAHs accumulated in bottom sediments (8-33%). No consistent temporal trends were observed in PAH concentrations on settling particles from 1984 to 1991.

### Introduction

Relatively few studies have employed sediment traps to evaluate the biogeochemistry of settling solids and its role in organic contaminant cycling in aquatic systems (1-8). Settling particles play an integral role in aquatic food chains and contaminant cycling in aquatic systems (1, 3, 6, 7, 9, 10). The collection of settling solids is a powerful tool in determining how contaminants are processed within aquatic systems and can provide insight into how and where contaminants are introduced to the food web. The cycling of organic contaminants such as polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) is intimately linked to production and cycling of organic matter (3, 11, 12). Organic carbon produced by primary production can be cycled many times through the pelagic food chain or

transported quickly from surface to bottom waters and introduced to the benthic food web where it may undergo further recycling (13-15). Thus, a small percentage of primary production in Lake Superior accumulates in bottom sediments (16, 17). However, efficient carbon recycling, such as occurs in Lake Superior, results in efficient contaminant transfer through the benthic food web. Lake Superior has anomalously high PCB concentrations in lake trout relative to other small regional lakes that have even higher water PCB concentrations (18, 19). PAHs are not biomagnified in food webs, but many are suspected carcinogens.

PCB concentrations in Lake Superior surface waters decreased from 2.4 to 0.18 ng/L at a first-order rate of  $0.20 \text{ yr}^{-1}$  between 1980 and 1992 (20). Volatilization was the dominant removal mechanism over this time period, while permanent sediment burial was of minor importance. Despite burial being an insignificant removal mechanism, settling solids efficiently transport PCBs to bottom waters (3). However, most PCBs are recycled back into the water column and not incorporated into bottom sediments. Intense internal PCB recycling is also reflected by settling fluxes being 10-50 times greater than atmospheric deposition (21). The current study suggests that settling particles efficiently transport PCBs and PAHs from the surface waters, providing a direct and effective link to the benthic food web.

The present study builds on the 1984-1985 Lake Superior trap study (3). Results from 1984 to 1985 demonstrated that settling solids were enriched in PCBs, phenanthrene, and fluorene relative to suspended solids collected by filtration. PCBs were efficiently recycled in the water column with less than 1% of settling PCBs accumulating in the sediments. Lower molecular weight PCBs, fluorene, and phenanthrene were recycled to a greater extent and settled faster than the higher molecular weight PCBs and PAHs (3). The 1984-1985 study extended over both stratified and unstratified periods. In the current study, traps were deployed only during the stratified period. The objectives of the current study were (i) to quantify trends in PCB concentrations on settling solids since 1984; (ii) to reexamine PCB, PAH, and organic carbon recycling behavior in Lake Superior; and (iii) to examine the potential of recycling enhancing PCB concentrations in the food web of Lake Superior.

### Methods

**Field Sampling.** Sediment traps were deployed during the stratified period in 1984 (3), 1987, and 1991 in Lake Superior at five locations and multiple depths (Table 1). The 4 or 8 in. diameter Plexiglass traps had height-to-width ratios of 5:1 (3, 13). Samples were collected in a 500-mL polyethylene bottle below a funnel with a 1 in. diameter opening. Chloroform (20 mL) was placed in each bottle to prevent degradation of trapped material. Sodium azide (30 mM) was used as a preservative in each duplicate trap depth in 1987 (22). However, Lee et al. (23) later showed that sodium azide was not a recommended preservative for organic matter at five times this concentration. Overlying water was siphoned off upon trap recovery, and the remaining sample containing residual beads of chloroform was air-dried at 60 °C, weighed, and stored frozen. Total sample masses collected ranged from 15 mg to several grams.

**Laboratory.** Samples were placed in Pyrex extraction thimbles and extracted for 24 h in Soxhlet extractors with approximately 150 mL of dichloromethane (DCM). A Buchi Rotavap (model RE111) was used to switch the solvent to hexane and reduce the sample volume to ~1 mL. The extracts were transferred to 4-mL amber vials and quantitatively split

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TABLE 1. 1984, 1987, and 1991 Lake Superior Sediment Trap Deployment Data

year	site	dates	latitude	longitude	water depth	trap depths
1984	1	Jul 11–Sep 10	47.76	86.78	274 m	10, 10, 35, 140, 264, 269, 273
	2	Jul 12–Sep 11	47.80	88.34	222	10, 10, 35, 120, 197, 212, 217
	3	Jul 12–Sep 11	47.33	89.25	183	10, 10, 35, 100, 158, 173, 178
	4	Jul 12–Sep 14	47.18	87.76	100	10, 10, 35, 75, 90, 95
1987	1	Aug 1–Oct 11	47.76	86.78	274	10, 10, 140, 140, 248, 268, 288
	2	Aug 2–Oct 9	47.80	88.34	222	10, 10, 212, 217
	3	Aug 2–Oct 10	47.32	89.26	183	10, 10, 100, 158, 173
	4	Aug 3–Oct 8	47.18	87.77	100	10, 10, 75, 90, 95
	5	Jul 31–Sep 27	46.74	84.78	122	10, 10, 35, 97, 112, 117
1991	1	Jun 28–Sep 24	47.58	86.86	273	15, 15, 35, 140, 248, 263, 268
	2	Jun 29–Sep 13	47.80	88.34	222	15, 15, 35, 120, 197, 212, 217
	3	Jun 29–Sep 13	47.32	89.26	183	15, 15, 35, 100, 158, 173, 178
	4	Jun 26–Sep 12	47.18	87.76	100	15, 15, 35, 90, 95
	5	Jun 25–Sep 28	46.71	84.77	91	63, 63, 78, 78

in a ratio of ~3:1 for PCB and PAH analysis, respectively. PCB extracts were fractionated by liquid–solid chromatography using Florisil as the stationary phase (20). A Hewlett-Packard 5890 gas chromatograph equipped with a 60 m DB-5 (J&W Scientific) capillary column and an electron capture detector was used to analyze PCB extracts. PCBs were quantified using Hewlett-Packard HPLC ChemStation software. PAH extracts were eluted from a microcolumn of 0.7 g of silicic acid (5% water deactivated) with 10 mL of 10% DCM in hexane. PAHs were separated using a 30 m DB5-MS (J&W Scientific) gas capillary column and analyzed on a Hewlett-Packard 5970 mass selective detector operated in single ion monitoring (SIM) mode.

**Ancillary Measurements.** A Perkin-Elmer CHN analyzer using acetonitrile as a standard was used for carbon and nitrogen analyses. A semiquantitative compositional analysis of the near-surface traps and the deepest trap at each site was performed under microscope in an Utermohl chamber (24, 25). Particles were counted at two magnifications (150 $\times$  and 750 $\times$ ) on an inverted microscope. The particles counted at 150 $\times$  are generally particles greater than 20–50  $\mu$ m and are referred to as the "large fraction" in subsequent discussions. Particles counted at 750 $\times$  are generally less than 20–50  $\mu$ m and are referred to as the "small fraction".

**Quality Assurance.** A total of 74 PCB congeners or combination of coeluting congeners and 24 PAHs were quantified. A calibration standard consisting of Aroclors 1232, 1248, and 1262 mixed in the ratio of 25:18:18, respectively, was used to quantify individual congener relative response factors (26–28). PCBs were quantified by the internal standard method. PAHs were quantified as outlined by Simcik et al. (29). Surrogate standards consisting of deuterated PAHs naphthalene-*d*<sub>8</sub>, fluorene-*d*<sub>10</sub>, fluoranthene-*d*<sub>10</sub>, perylene-*d*<sub>12</sub>, and PCBs 14 (3,5-dichlorobiphenyl), 65 (2,3,5,6-tetrachlorobiphenyl), and 166 (2,3,4,4',5,6-hexachlorobiphenyl) were added to samples prior to extraction. If a correction was necessary due to a known laboratory incident (i.e., spillage), all PCB congeners were corrected to the recovery of congener 166. PAH concentrations were corrected for recovery relative to the nearest eluting deuterated surrogate. The recovery of PCB 166 averaged 105  $\pm$  11%. The average recovery of PAH surrogates was 70  $\pm$  16%, 97  $\pm$  14%, 96  $\pm$  12%, and 82  $\pm$  29%, respectively, for naphthalene-*d*<sub>8</sub>, fluorene-*d*<sub>10</sub>, fluoranthene-*d*<sub>10</sub>, and perylene-*d*<sub>12</sub>.

Several procedural blanks consisting of only solvent were run through the entire laboratory procedure for the purpose of quantifying a laboratory blank. The total mass of PCBs in the laboratory blanks averaged 1.2  $\pm$  0.6 ng ( $\pm$ 1 standard deviation; *n* = 5). No correction to the PCB concentrations in Lake Superior samples was made for laboratory blanks. PAH laboratory blanks averaged 3.1  $\pm$  2.2 ng of  $\Sigma$ PAH, and no correction was necessary. Benzo[*e*]pyrene and benzo-

[*a*]pyrene were not able to be quantified due to an unknown coeluting contaminant.

Surface traps spiked with sodium azide in 1987 exhibited lower  $\Sigma$ PCB concentrations than those spiked with chloroform (250  $\pm$  170 ng/g (*n* = 5) vs 1100  $\pm$  440 ng/g (*n* = 5)) due to poor organic carbon preservation. Sodium azide-spiked traps still had lower concentrations when normalized to organic carbon content (1440  $\pm$  1130 vs 2440  $\pm$  790 ng/g of OC). A greater loss of PCBs relative to organic carbon occurred in the sodium azide-spiked traps. A similar phenomenon is observed between settling particles and bottom sediments, with bottom sediments being much more depleted in PCBs relative to organic carbon. Tetrachlorinated PCBs were released to the greatest extent by the loss of organic carbon in the sodium azide-poisoned traps.

## Results and Discussion

**Concentrations on Settling Particles.** PCB concentrations on settling particles collected during stratified periods between 1984 and 1991 from the surface waters of Lake Superior have decreased at a rate similar to surface water PCBs (Figure 1). PCBs in the surface waters decreased with a first-order rate constant of 0.20 yr<sup>-1</sup> between 1980 and 1992 based on 25 PCB congeners (20). Based on the sum of 35 congeners ( $\Sigma$ PCB<sub>35</sub>) analyzed in 1984 (3), 1987, and 1991, PCBs on settling solids collected at depths of 10–35 m have decreased with a first-order rate constant of 0.26<sup>-1</sup> yr. Normalizing concentrations to organic carbon results in a rate constant for PCB change of 0.22 yr<sup>-1</sup>. Thus, settling solids have responded to a decrease in PCB water concentrations. PCB concentrations at the top of the Lake Superior food chain (lake trout) decreased at a first-order rate of 0.12 yr<sup>-1</sup> from 1977 to 1990 but was lower in recent years (30). Jeremiason et al. (20) reported a greater water column PCB loss rate for congeners with higher octanol–water partition coefficients, but no such correlation was found for settling particles. Lake Superior receives the majority of its PCB inputs from the atmosphere (20, 21, 31–33). Atmospheric PCB concentrations have remained constant near Lake Superior but have decreased with a first-order rate constant of approximately 0.12 yr<sup>-1</sup> from 1990 to 1996 near Lake Michigan and Lake Erie (34). Therefore, concurrent decreases in water, settling solids, and fish PCB concentrations are indicative of the lake responding to decreased atmospheric loading.

$\Sigma$ PCB concentration was 1100  $\pm$  440 ng/g (*n* = 5) in settling solids collected in surface traps ( $\leq$ 35 m) in 1987 and 420  $\pm$  380 ng/g (*n* = 12) in 1991. Tri- to pentachlorinated congeners were the dominant PCBs found in settling particles at all depths in both years (25). Separating the traps into surface

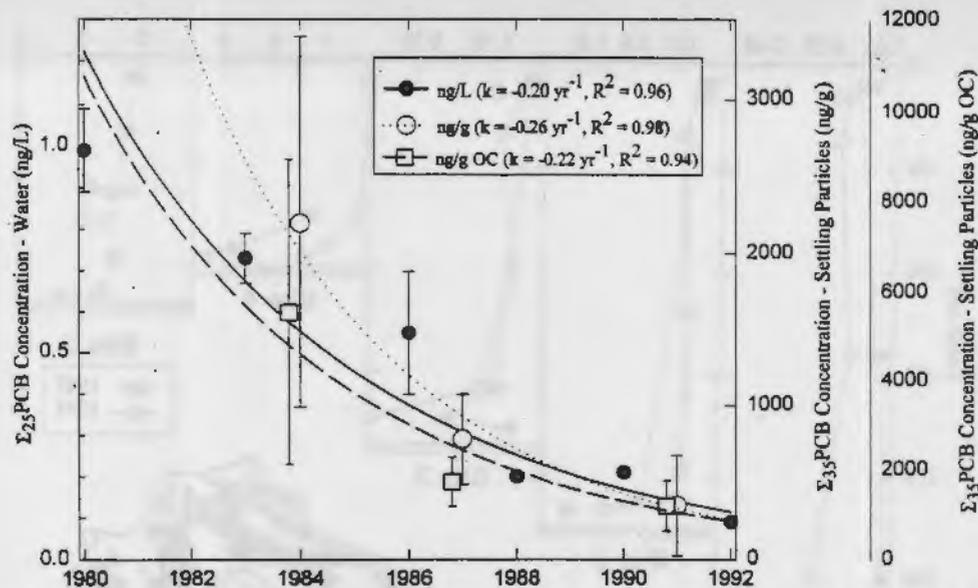


FIGURE 1. First-order PCB decrease in Lake Superior water (ref 20; 25 congeners) and settling solids (35 congeners) collected from surface traps.

TABLE 2.  $\Sigma$ PCB Concentrations on Suspended Solids and  $\leq 35$ -m Sediment Traps in Lake Superior

year	solids type	concentration (ng/g)	no. of congener peaks	ref
1984 <sup>a</sup>	trap	2017 $\pm$ 1116 (7)	35	3
1984-1985 <sup>b</sup>	trap	807 $\pm$ 601 (8)	35	3
1986	suspended	31.4 $\pm$ 14.9 (9)	35	3
1987	trap	1101 $\pm$ 436 (5)	74	this study
1988	suspended	270 $\pm$ 48 (9)	82	40
1990	suspended	104 $\pm$ 49 (8)	82	40
1991	trap	423 $\pm$ 384 (12)	74	this study
1992	suspended	182 $\pm$ 33 (5)	82	40

<sup>a</sup> Stratified period. <sup>b</sup> Unstratified period.

(10–35 m), bottom (<25 m from the bottom), and mid-depth (all other depths) traps indicated no change in homologue distribution with depth in 1987 or 1991 (*t*-test; *p* < 0.05).  $\Sigma$ PCB concentrations on suspended solids in Lake Superior were generally lower and in some cases (1986) much lower than settling particle  $\Sigma$ PCB concentrations (Table 2). Differences in organic carbon content does not account for the higher PCB concentrations on settling particles. Homologue distributions in suspended solids (1988–1992) were not statistically different from settling solids (*t*-test; *p* < 0.05) but were different than bottom sediments (Figure 2). Baker and Eisenreich (35) also found that Lake Superior bottom sediments were depleted in lower molecular congeners relative to suspended, settling, and benthic nephroid layer particles. Differences in  $\Sigma$ PCB concentration are likely due to the type of particles collected in settling versus suspended solids. Suspended solids samples are unlikely to contain fecal pellets or other large PCB-enriched settling particles (3, 9, 36). Suspended solids from surface waters are likely to consist of phytoplankton and a high percentage of slow-settling detritus depleted in PCBs relative to settling material.

Near-surface trap material in 1991 (*n* = 12 traps) consisted of mostly diatoms, detritus, and fecal material (25). Globules of lipids that apparently had detached from cells were identified in the small particle fraction of the two traps with

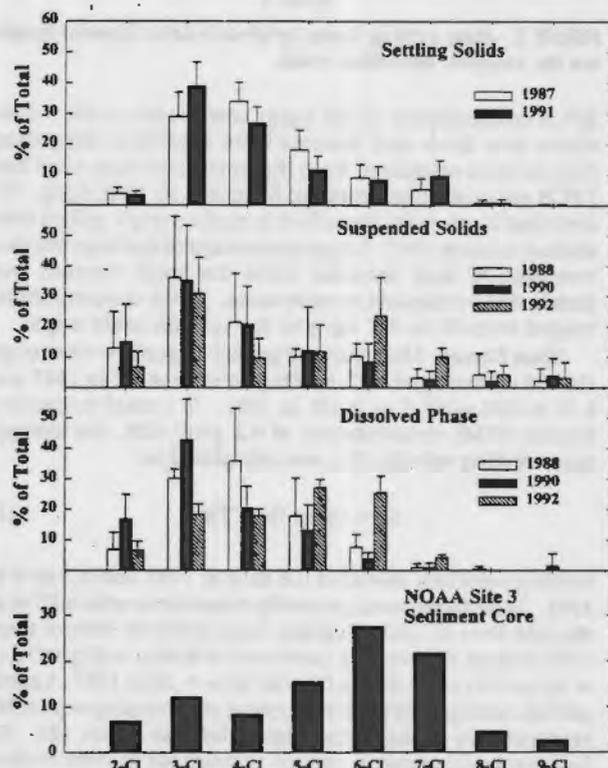


FIGURE 2. PCB homologue distributions in settling solids, suspended solids (40), the dissolved phase (20), and surficial sediment (40) in Lake Superior.

the highest PCB concentrations (site 2-15m, 779 ng/g, and site 4-15m, 1496 ng/g). No lipid globules were identified under the microscope in any of the other traps in 1991 but may have still been present, just not detached from the cells. Sediment traps at a few sites (site 1-15m, site 3-35m, and site 4-15m) contained some zooplankton remains but exhibited similar  $\Sigma$ PCB concentrations to the rest of the surface traps. The lowest  $\Sigma$ PCB concentrations were generally found in traps containing mostly diatoms and fecal material. All surface traps in 1987 spiked with chloroform as a preservative contained detached lipids in the small fraction. The highest

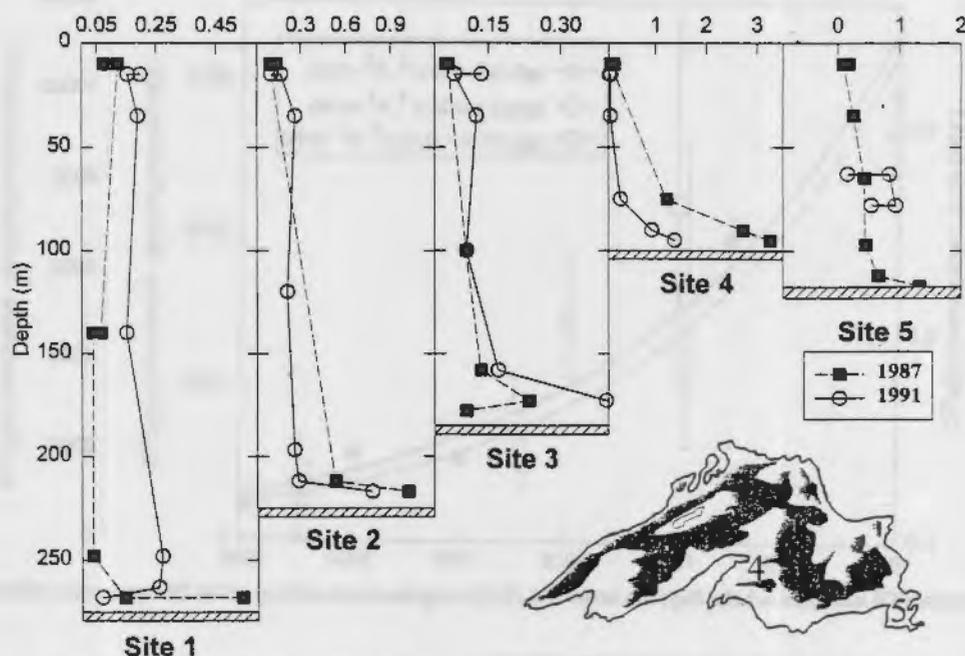


FIGURE 3. Mass settling fluxes ( $\text{g}/\text{m}^2\cdot\text{d}$ ) in Lake Superior measured in sediment traps in 1987 and 1991. The shaded areas on the map are the sediment deposition zones.

$\Sigma\text{PCB}$  concentration ( $1725 \text{ ng}/\text{g}$ ) was found at site 3-10m where only lipids and diatoms were identified, suggesting that the lipid originated from diatoms. The other sites had  $\Sigma\text{PCB}$  concentrations ranging from 814 to  $1389 \text{ ng}/\text{g}$ . No detached lipids were identified in surface traps spiked with sodium azide in 1987. A high percentage of the large fraction consisted of fecal material while the small fraction was dominated by diatoms in most cases.  $\Sigma\text{PCB}$  concentrations ranged from 92 to  $447 \text{ ng}/\text{g}$  in the sodium azide traps.

**Mass Fluxes.** Mass fluxes (Figure 3) in surface water traps (10–35 m) averaged  $0.12 \pm 0.06 \text{ g}/\text{m}^2\cdot\text{d}$  ( $n = 11$ ) in 1987 and  $0.14 \pm 0.06 \text{ g}/\text{m}^2\cdot\text{d}$  ( $n = 12$ ) in 1991. At a total suspended matter (TSM) concentration of  $0.2 \text{ g}/\text{m}^3$  (20), the average mass settling velocity ( $S_v$ ) was calculated as

$$S_v = \text{mass flux}/\text{TSM} \quad (1)$$

Settling velocities averaged  $0.6 \text{ m}/\text{d}$  in 1987 and  $0.7 \text{ m}/\text{d}$  in 1991. Mass fluxes were generally constant to within 25 m of the lake floor in 1991. Average mass fluxes in bottom traps (<25 m from the bottom) increased to  $0.60 \pm 0.40 \text{ g}/\text{m}^2\cdot\text{d}$  ( $n = 10$ ) in 1991 and  $1.05 \pm 1.09 \text{ g}/\text{m}^2\cdot\text{d}$  ( $n = 10$ ) in 1987. Lateral particle transport by bottom currents and focusing or possibly resuspension explains the higher bottom fluxes (37, 38). Sediment resuspension cannot account for bottom settling particle fluxes during the stratified period in Lake Ontario (39) and is unlikely at these deep sites in Lake Superior. Similar mass fluxes were reported for traps deployed during stratification in 1984 (3).

Focus-corrected surficial mass accumulation rates in sediment cores collected near the trap sites ranged from  $0.20$  to  $0.80 \text{ g}/\text{m}^2\cdot\text{d}$  (40, 41). Using an atmospheric derived  $^{210}\text{Pb}$  inventory of  $15.5 \text{ pCi}/\text{cm}^2$  (42, 43) to correct sedimentation rates for focusing as reported by Klump et al. (44), an average sedimentation rate of  $0.43 \text{ g}/\text{m}^2\cdot\text{d}$  ( $n = 10$ ) was determined for Lake Superior. Surface trap mass fluxes during stratification in 1987 and 1991 are approximately one-third sediment accumulation rates, which is not surprising since bank erosion dominates sediment input (45). Furthermore, organic carbon content of bottom sediments is low (0.01–5%) as compared to settling solids (20–50%)

indicative of dilution by inorganic solids and decomposition (35, 44, 46, 47).

Organic carbon content in near-surface traps averaged  $480 \pm 170 \text{ mg}/\text{g}$  ( $n = 6$ ) in traps poisoned with chloroform in 1987 and  $260 \pm 100 \text{ mg}/\text{g}$  ( $n = 12$ ) in 1991. Surface traps spiked with sodium azide in 1987 averaged  $180 \pm 30 \text{ mg}/\text{g}$  ( $n = 5$ ). In 1984, organic carbon content of surface traps was  $410 \pm 100 \text{ mg}/\text{g}$  ( $n = 9$ ; 3). Organic carbon content was generally constant with depth to 25 m above the lake floor at the open lake sites (1–3). Bottom traps had lower organic carbon content due to laterally derived sediment and decomposition. The OC content of traps within 25 m of the lake bottom was  $95 \pm 53 \text{ mg}/\text{g}$  ( $n = 10$ ) in 1991 and  $95 \pm 59 \text{ mg}/\text{g}$  ( $n = 10$ ) in 1987. Surficial sediments in depositional areas of Lake Superior contain 20–50 mg/g organic carbon (3, 35, 44, 47). Assuming minimal OC decomposition occurs at depths 5 m off the lake floor and above and that laterally derived sediment of similar OC content to bottom sediment dilutes the OC content of bottom sediment trap material, the bottom traps consist of ~20% epilimnion-derived settling material and ~80% laterally derived sediment. This calculation was based on settling solids containing 350 mg/g of OC and bottom sediments containing 30 mg/g of OC. If recently settled material accounts for 20% of bottom trap fluxes, then total mass fluxes in the bottom traps would be ~ $0.7 \text{ g}/\text{m}^2\cdot\text{d}$ . Actual measured fluxes averaged 0.60 and  $1.05 \text{ g}/\text{m}^2\cdot\text{d}$  in 1991 and 1987, respectively.

**Organic Carbon Fluxes.** OC fluxes (Figure 4) were relatively constant with depth in the open lake (sites 1–3) to within about 25 m of the lake floor. Surficial traps averaged  $49 \pm 16 \text{ mg}/\text{m}^2\cdot\text{d}$  ( $n = 6$ ) in 1987 for chloroform-spiked traps and  $34 \pm 14 \text{ mg}/\text{m}^2\cdot\text{d}$  ( $n = 12$ ) in 1991. There was a significant increase in OC flux in 1991 at sites 2 and 3 between the 10 and 35 m traps. Material identified under microscope in these 35-m traps was depleted in diatoms and had more zooplankton and fecal remains relative to the overlying traps. At the shallower sites (4 and 5), OC flux generally increased with depth due to resuspension. During shorter time periods corresponding to trap deployment, OC fluxes may increase with depth due to the different time frames in which the settling particles originated. Organic carbon accumulation

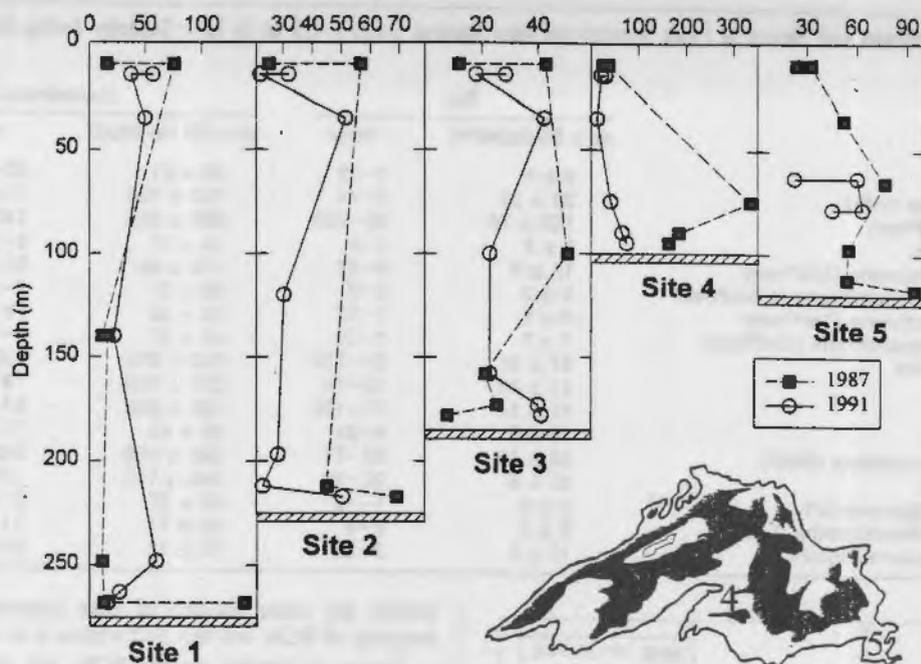


FIGURE 4. Organic carbon fluxes ( $\text{mg}/\text{m}^2\text{-d}$ ) in Lake Superior measured in sediment traps in 1987 and 1991.

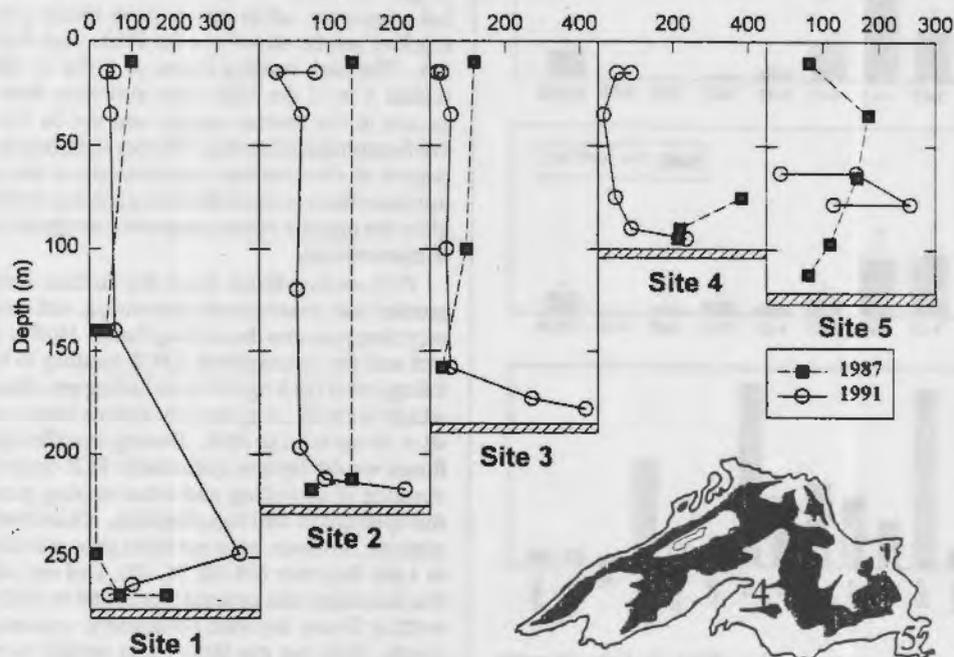


FIGURE 5.  $\Sigma\text{PCB}$  settling fluxes ( $\text{ng}/\text{m}^2\text{-d}$ ) in Lake Superior 1987 and 1991.

in surficial sediments in eastern and central Lake Superior is  $15 \pm 11 \text{ mg}/\text{m}^2\text{-d}$  ( $n = 12$ ; 44, 48), indicating that ~30–40% of organic carbon settling from the epilimnion accumulates in bottom sediments.

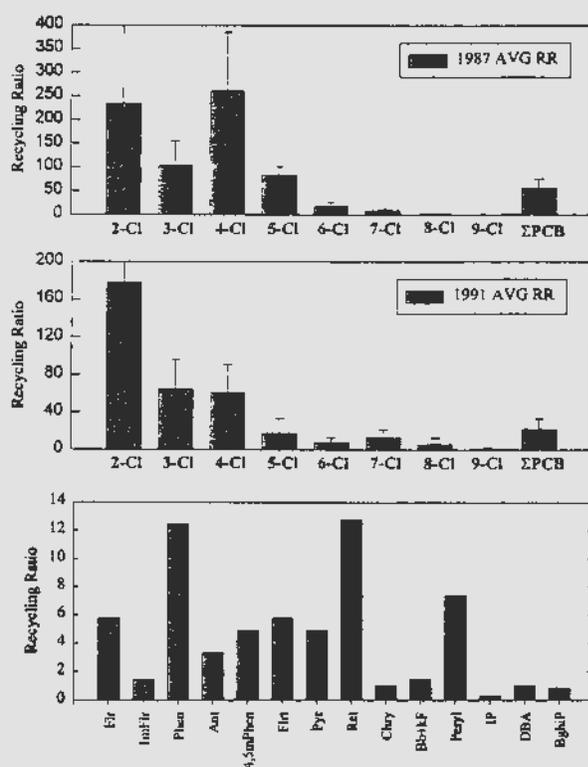
**PCB Fluxes.**  $\Sigma\text{PCB}$  settling fluxes (Figure 5) determined in surface traps averaged  $121 \pm 40 \text{ ng}/\text{m}^2\text{-d}$  ( $n = 5$ ) for traps poisoned with chloroform in 1987 and  $48 \pm 23 \text{ ng}/\text{m}^2\text{-d}$  ( $n = 12$ ) in 1991. Similar to OC,  $\Sigma\text{PCB}$  settling fluxes were relatively constant from the surface waters to within 25 m of the lake floor at sites 1–3. Within 25 m of the lake floor, fluxes increased in some cases and decreased in others. Resuspension of bottom sediments that contain ~10 ng/g of  $\Sigma\text{PCBs}$  (35, 40) cannot account for elevated bottom  $\Sigma\text{PCB}$  fluxes (e.g., sites 2–4 in 1991). At these sites, PCB recycling may have created higher concentrations in the benthic

nepheloid layer. Lower  $\Sigma\text{PCB}$  fluxes near the lake floor could be attributed to organic matter decomposition in the benthic nepheloid layer and surficial sediments and subsequent contaminant release into the water column.

Baker et al. (3) reported that less than 1% of PCBs settling from the epilimnion accumulate in the sediments. On the basis of  $\Sigma\text{PCB}$  settling fluxes determined from surface traps, 2–5% of settling PCBs accumulated in the sediments in 1987 and 1991. In 1984, PCB settling fluxes at site 1–35m were compared to accumulation rates from a nearby core yielding a recycling ratio. In this study, recycling ratios were determined using the average settling flux from the surface water traps relative to accumulation at a core from site 3 (40). Average  $\Sigma\text{PCB}$  recycling ratios (Figure 6) determined for 1987 and 1991 (~20–60) were 2–5 times lower than in

**TABLE 3. Concentrations and Fluxes of PAMs Determined from Surface Traps (<35 m) in Lake Superior during Stratification, 1991**

	flux		concentration		n
	av ± SD (ng/m <sup>2</sup> -d)	range	av ± SD dev (ng/g)	range	
fluorene (Flr)	6 ± 4	1-12	45 ± 21	22-91	9
1-methylfluorene (mflr)	23 ± 23	2-74	140 ± 150	11-482	9
phenanthrene (Phen)	130 ± 70	60-280	820 ± 350	340-1270	9
anthracene (Ant)	3 ± 2	1-6	14 ± 11	6-33	9
2-methylphenanthrene (2mPhen)	17 ± 9	9-37	110 ± 44	53-186	9
4,5-methylenephenanthrene (4,5mPhen)	5 ± 2	2-9	38 ± 21	9-64	9
1-methylphenanthrene (1mPhen)	8 ± 5	1-17	58 ± 22	25-92	9
3,6-dimethylphenanthrene (dmPhen)	7 ± 7	1-23	44 ± 37	5-113	9
fluoranthene (Flrt)	47 ± 31	21-120	320 ± 210	130-770	9
pyrene (Pyr)	31 ± 18	13-74	220 ± 130	79-480	9
retene (Ret)	37 ± 34	11-120	260 ± 230	57-790	9
chrysene (Chr)	10 ± 6	4-24	68 ± 43	17-160	9
benzo(b+k)fluoranthene (Bbkf)	53 ± 13	32-71	320 ± 100	200-460	6
perylene (Peryl)	33 ± 8	25-39	240 ± 110	130-360	3
indeno[1,2,3-cd]pyrene (IP)	6 ± 4	1-12	38 ± 27	6-75	5
dibenzo(a,c+a,h)anthracene (DBA)	3 ± 2	2-4	20 ± 11	11-28	2
benzo(g,h,i)perylene (BghiP)	11 ± 7	3-22	71 ± 42	37-150	5



**FIGURE 6. Average recycling ratios (RRs) in Lake Superior determined from surface traps and NOAA site 3 sediment core and PAH recycling ratios in 1991 from trap site 1-35m and NOAA site 3 sediment.**

1984. Recycling ratios decreased from 1984 to 1991 due to decreased PCB settling fluxes, but changes in  $\Sigma$ PCB accumulation rates in bottom sediment over a 7 year period cannot be accurately determined in Lake Superior. Mass accumulation in Lake Superior sediments is sufficiently low that contaminant accumulation rates are integrated over several years in the upper 0.25-0.50 cm of sediment. In the core used by Baker et al. (3), the top slice integrated 8-9 yr of accumulation, while the core used in the present study integrated 4-5 yr. Results from 1984 indicate that 67-83% of the  $\Sigma$ PCB flux from surface waters was recycled before reaching the bottom traps (3). The results from 1987 and 1991 do not give consistent evidence for recycling of PCBs

within the water column of Lake Superior. Rather, the majority of PCBs are recycled within 5 m of the lake floor.

Lower molecular weight PCBs are recycled in Lake Superior to a greater extent than higher chlorinated congeners (Figure 6). Baker et al. (3) observed the same behavior in Lake Superior, while others have found similar but not as marked results elsewhere for PCBs and PAHs (1, 2, 25, 49, 50). The high settling fluxes of PCBs in 1987 and 1991 to within 5 m of the lake floor indicates that most recycling occurs in the benthic region and not in the water column. We hypothesize that the PCB recycling ratios decrease as the degree of chlorination increases since less soluble species are more likely to repartition to particles in the benthic region after the organic matter they were originally associated with is mineralized.

PCB settling fluxes from the surface waters were much greater than atmospheric deposition, indicating that internal recycling supports the settling fluxes. Hoff et al. (21) predicted wet and dry atmospheric  $\Sigma$ PCB loading to Lake Superior of 2.8 ng/m<sup>2</sup>-d (13.5 ng/m<sup>2</sup>-d including gas absorption) in 1994, which is small compared to surface water settling fluxes of 48 ± 23 ng/m<sup>2</sup>-d in 1991. During stratification, PCB settling fluxes would deplete epilimnetic PCB concentrations in the absence of upwelling and other mixing processes between the epilimnion and hypolimnion. Dissolved  $\Sigma$ PCB concentrations, however, have not been shown to change seasonally in Lake Superior (20, 33, 51, 52), and net volatilization was the dominant loss process from 1980 to 1992 (20, 53). If PCB settling fluxes depleted epilimnetic concentrations significantly, then net gas absorption would increase, especially toward the end of the stratified period. But instantaneous net gas absorption fluxes have never been measured in Lake Superior (33, 53).

The magnitude of PCB settling fluxes reflects the dynamic PCB cycling in oligotrophic Lake Superior. In 1991, the  $\Sigma$ PCB burden in Lake Superior was ~2600 kg, with ~80% occurring in the dissolved phase (20). On the basis of a  $\Sigma$ PCB settling flux of 50 ng/m<sup>2</sup>-d to the benthic region in 1991, 1500 kg or ~60% of the  $\Sigma$ PCB burden was incorporated into settling particles and transported to the benthic region. Thus, PCBs that exist in the dissolved phase must be efficiently incorporated into settling solids and transported to the benthic region, but not buried in the sediments, rather released back into the dissolved phase (i.e., recycled).

**PAH Concentrations and Fluxes.** Unlike  $\Sigma$ PCB, most PAH concentrations on settling solids collected in surface traps have not changed significantly from 1984 to 1991.

Fluorene ( $310 \pm 86$  (3) to  $45 \pm 21$  ng/g) and phenanthrene ( $5500 \pm 3300$  (3) to  $820 \pm 350$  ng/g) concentrations decreased dramatically from 1984 to 1991, but no significant change occurred for any of the other PAHs. PAH profiles in sediment cores from Lake 227 in the Experimental Lakes Area, Ontario, Canada (51); Lake Superior (44); and Lake Michigan (24) suggest no recent decreases in PAH concentrations as well. It is unclear why fluorene and phenanthrene concentrations decreased.

PAH fluxes measured in surface traps were dominated by three- and four-ringed PAHs (Table 3). The magnitude of PAH settling fluxes were similar to those found in two small lakes in Ontario, Canada (54); the Alboran Sea (10); and the continental shelf off northeastern United States (55), but less than those found in the Baltic Sea (4); the northwestern Mediterranean Sea (2, 50); and a small lake in the United Kingdom (1). Fluxes of PAHs with three and four rings exhibited patterns with depth similar to  $\Sigma$ PCB. The similarity between three- and four-ringed PAHs and PCBs suggests that both sets of compounds are incorporated into settling solids by the same mechanism, specifically, partitioning from the dissolved to organic carbon-rich settling particles. PAHs with more than four rings were not found consistently in the surface traps (Table 3). Since they exist primarily in the particulate phase in both the atmosphere (56, 57) and water (25), they behave differently than PCBs and lower molecular weight PAHs.

PAH recycling ratios (Figure 6) were determined from settling fluxes in 1991 from site 1-35m and from PAH accumulation rates from NOAA site 3 (48). The PAH recycling ratios are lower than PCB ratios ( $\sim 20$ –50) and range from less than 1 to  $\sim 12$ . Sanders et al. (1) reported lower recycling ratios for PAHs relative to PCBs in Esthwaite Water, as did Jeremiason et al. (54) in two small lakes in northwestern Ontario, Canada. Baker et al. (3) reported fluorene and phenanthrene recycling ratios similar in magnitude to PCB ratios, but ratios lower than 1 were reported for many higher molecular weight PAHs. Lippiatou et al. (2, 50) also found higher recycling ratios for phenanthrene, fluoranthene, and pyrene relative to less soluble higher molecular weight PAHs. The higher molecular weight PAHs, except for retene and perylene, had lower recycling ratios in this study as well. Retene and perylene may be formed in Lake Superior from natural precursors (58, 59) and thus may not exhibit recycling behavior similar to other higher molecular weight PAHs that likely enter Lake Superior on soot particles (3).

The average settling flux of phenanthrene ( $130 \pm 71$  ng/m<sup>2</sup>-d) and pyrene ( $31 \pm 18$  ng/m<sup>2</sup>-d) from surface waters in Lake Superior was greater than estimated wet and dry depositional fluxes of 12 and 9.3 ng/m<sup>2</sup>-d for phenanthrene and pyrene, respectively (21). Hoff et al. (21) found the air-water fugacity gradient for phenanthrene to favor water to air exchange on an annual basis, but for pyrene the fugacity gradient suggested net air to water exchange. Thus, internal recycling appears to support, in part, phenanthrene settling fluxes. Incorporating net gas absorption for pyrene, the estimated annual atmospheric loading was 76 ng/m<sup>2</sup>-d (21), which is greater than particle settling fluxes.

PCB concentrations on particles settling from the surface waters of Lake Superior have declined at a first-order rate of  $0.26 \text{ yr}^{-1}$ , similar to the reported  $0.20 \text{ yr}^{-1}$  decline in surface waters from 1980 to 1992 (20). This concurrent decrease indicates that PCB exposure at the base of the food chain has decreased in response to lower atmospheric PCB loadings. PCB and organic carbon settling fluxes are generally constant or increase with depth to within 5 m of the lake floor. However, only 2–5% of settling PCBs and  $\sim 30$ –40% of settling organic carbon accumulate in bottom sediments as a result of benthic recycling, suggesting that recycled PCBs are associated with the labile organic carbon fraction. Further-

more, PCB settling fluxes are greater than atmospheric loading to the lake, indicating that the majority of settling PCBs are derived from in-lake recycling that occurs within 5 m of the lake floor. Fluxes of PAHs are dominated by PAHs with three and four rings that exhibit similar settling patterns to PCBs. Approximately 8–33% of settling PAHs with three and four rings accumulate in bottom sediments.

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