Sediment Trap Fluxes and Benthic Recycling of Organic Carbon, Polycyclic Aromatic Hydrocarbons, and Polychlorobiphenyl Congeners in Lake Superior

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Sediment trap fluxes of solids, organic carbon, polycyclic aromatic hydrocarbons (PAHs), and polychlorinated biphenyls (PCBs) were measured in Lake Superior in 1984 and 1985. Mass fluxes from surface waters ranged from 0.14 to 1.1 g/m²-day and increased near the lake floor due to resuspension of surficial sediment and horizontal transport in the benthic nepheloid layer. Organic matter fluxes from surface waters ranged from 60 to 90 mg of C/m²-day, with ~5% of organic carbon settling from surface waters accumulating in bottom sediments. Concentrations of PCBs and PAHs are enriched 10–100 times on settling particles relative to those on suspended particles. Resultant settling fluxes are 10–100 times greater for several PCB and PAH compounds than net accumulation rates in bottom sediments, indicating the effective and rapid recycling in the benthic region. Biological packaging of organic pollutants into rapidly settling particles is an efficient pathway for the transport of contaminants from surface waters to benthic regions of large lakes.

Introduction
Cycling of many chemical species in natural waters is intimately linked to the production, transport, and loss of particles within the water column. Associations with settling particles control the water column residence times of hydrophobic organic contaminants (HOCs) such as polychlorobiphenyls (1) as well as many trace metals (2–6). In the long term, burial of contaminants in bottom sediments serves as an important self-purification mechanism in lakes, estuaries, and oceans. On shorter time scales, however, the dynamics of particle formation and transport drive spatial and temporal variations in the water column inventories of particle-associated species. Such fluctuations may increase net contaminant residence times and dampen the water column response to decreased loadings. In this study, we report on the intertwined cycles of particulate matter, organic carbon, and hydrophobic organic contaminants in oligotrophic Lake Superior.

Processes controlling the type and quantity of suspended solids in the water column of the Laurentian Great Lakes include shoreline erosion, resuspension of surficial sediments, primary production, and calcite precipitation (3). Each of these sources varies in response to changes in hydrodynamics, weather, and season. In large lakes and in the oceans, degradation of organic particles is very efficient and only a small fraction of primary production is incorporated into sediments (7–9).

The chemical composition of particles suspended in the water column also varies spatially and temporally. During
stratification, surface waters of the Great Lakes are dominated by biogenic particles, including bacteria, algae, zooplankton, and their remains, while bottom waters throughout the year contain relatively more inorganic solids derived from resuspension and deep-water turbidity currents (3). Temporal and spatial variations in the aquatic cycling and residence times of HOCs are largely controlled by their associations with suspended and settling solids. These associations result primarily by partitioning into the organic surface coating of the particles (10, 11) and are therefore closely linked to the production, transport, and degradation of organic-rich biotic solids in the water column.

A mass balance approach has been used to describe the important components of HOC cycling in the Great Lakes (1). Inputs of HOCs to Lake Superior are dominated by atmospheric deposition while burial in sediments and volatilization are major removal mechanisms. The net residence time of PCBs in Lake Superior ranges between 3 and 9 years while the residence times of particles are estimated to be approximately 1 year (1). Several recent studies have found, however, substantial short-term variations in water column burdens of HOCs. In the summers of 1978, 1979, and 1980, the estimated PCB inventory in Lake Superior varied from 16,000 to 40,000 to 11,000 kg, respectively (12). Elevated levels in 1979 were attributed to increased sediment resuspension throughout the lake following an especially severe winter and late spring in 1978-1979. Substantial decreases in PCB levels in the 14 months between sample collection in 1979 and 1980 suggest efficient removal of HOCs from the water column. Rapid HOC removal was also noted during stratification in 1983 in western Lake Superior (13). Inventories of the heavier PCB congeners (approximated by the mixture Aroclor 1254) decreased rapidly with a first-order half-life of 17-28 days, presumably due to loss by sedimentation during stratification. A net settling velocity of 7.5-11.5 m/day is required to support this observed loss rate (13). Interestingly, lower molecular weight PCB congeners were not effectively removed from the water column during this study, indicating that losses via sedimentation are selective as well as rapid.

Episodic resuspension of fine-grained sediments in near-shore areas of the Great Lakes increases near-bottom suspended solids concentrations and reentrains sediment-bound contaminants into overlying waters (9, 13-16). The benthic nepheloid layer (BNL) serves as a pool of contaminants available for mixing throughout the water column during poorly stratified periods. Eadie et al. (17) estimated that 14% of the particulate PCB inventory in Lake Michigan results from sediment resuspension during nonstratified periods.

We hypothesize that the short-term cycling and net residence times of hydrophobic organic contaminants in large lakes and the oceans are controlled by their associations with particles. Further, particle dynamics are dominated by production of biomass in surface waters, by resuspension of surficial sediments, and by degradation of organic particles during settling (Figure 1). In this study, sediment traps were deployed at several depths at four locations in Lake Superior during both stratified (July-September) and nonstratified (September-July) conditions. Settling particles collected were analyzed for organic carbon, nitrogen, and a suite of HOCs, including 35 polychlorobiphenyl (PCB) congeners and 13 polycyclic aromatic hydrocarbons (PAHs). The resulting mass, organic carbon, and HOC fluxes allow compound-specific settling velocities and water column residence times to be estimated. This study identifies the role of large, rapidly settling particles in selectively removing contaminants from surface waters and establishes the importance of benthic recycling in the aquatic geochemistry of particle-associated contaminants.

**Experimental Section**

**Site Description.** Lake Superior is a large (8.21 X 10^10 m^2, mean depth 145 m, maximum depth 405 m), dimictic lake located in a subarctic temperate zone in midlatitude North America. The lake stratifies in May or early June, overturns in November or December, and experiences partial ice cover for 4-5 months each year, and full ice cover approximately 1 in 10 years. Episodic benthic currents during poorly stratified periods redistribute sediments throughout the lake (18). Suspended solids concentrations average 0.1-0.5 mg/L during the summer (12, 19) and the total organic carbon concentrations average 1.6 mg/L in the open areas of this oligotrophic lake (19). Lake Superior has a small watershed to lake area ratio and receives more than half of its hydrologic, nutrient, and contaminant inputs from direct precipitation (20).

**Sampling.** Settling solids were collected by sediment traps deployed at several depths at four locations in Lake Superior.
Superior in 1984–1985 (Table I). The first deployment was during stratified conditions (15 July–11 September 1984) and the second deployment covered the poorly stratified winter conditions as well as spring and early summer (10 September 1984–17 July 1985). The 10-cm-diameter traps are Plexiglass cylinders with a 5:1 height to diameter ratio (9, 21). Each trap has a powder funnel at the bottom connected to a 500-mL linear polyethylene bottle. Chloroform (20 mL) was added to each bottle and the entire trap filled with filtered lake water prior to deployment to limit biological activity. Upon retrieval, approximately 400 mL of overlying water was siphoned off, and the residue was then air-dried in the collection bottle at 60 °C, weighed to the nearest 0.01 g, and stored frozen. Mass collection efficiencies for this trap design are estimated to be >90% (22–24).

Suspended solids and sediment cores were collected at several sites in Lake Superior in 1986 (Table I, ref 19). Sampling techniques are described elsewhere (13, 19) and summarized here. Surface water particles were collected from both the epilimnion (10 m) and in or just below the metalimnion (25 m) by pumping 300–500 L of water at 10 L/min from depth with a submersible pump through a precompressed 293-mm glass fiber filter and into a pre-cleaned stainless steel holding tank. Sixty-seven liters of filtrate was pumped through a 2.5 cm i.d. × 20 cm column of cleaned Amberlite XAD-2 resin (Rohm and Haas) at 100 mL/min to isolate hydrophobic organic compounds.

**Sample Analysis.** All samples were analyzed for 14 PAHs and 35 PCB congeners. The extraction, preparation, and analysis previously described for the suspended solids and sediment samples (19) was modified for the small sediment trap samples as follows. Between 0.05 and 2.5 g of dried sediment trap material was sonicated in a 50-mL Teflon centrifuge tube with 10 mL of methanol for 90 s and centrifuged at 10,000 rpm and the supernatant decanted. The sample was further sonicated with a second 10-mL aliquot of methanol and two 10-mL aliquots of dichloromethane. All four extracts were combined, concentrated, and then processed by the same procedure used for the suspended solids and sediments (19). Extraction using sonication recovered 87.3 ± 11.3% (N = 72) of PCB congeners relative to Soxhlet extraction.

Sample extracts were analyzed for PAHs by gas chromatography with isotope dilution selected-ion mass spectrometry (SIM). The remaining hexane extract was eluted from a 13-g Florisil column (1.25% water deactivated) with 50 mL of hexane followed by 60 mL of 10% (v/v) diethyl ether in hexane to remove interfering compounds. The hexane eluent containing all PCB congeners was concentrated by solvent reduction prior to analysis. PCBs were identified and quantified by capillary gas chromatography with electron capture detection as described by Baker and Eisenreich (19). Mirex and chrysenes-d$_{12}$ were added to all samples as surrogates prior to extraction to monitor overall procedural recovery. Mirex recoveries averaged 86 ± 23% (N = 81) for water samples collected in 1986 and 68 ± 18% (N = 38) for sediment trap samples. Recoveries of perchlorinated chrysene averaged 79 ± 15% (N = 37) and 100 ± 25% (N = 38) for the two sample sets. Reported concentrations are not corrected for recovery. Recovery of PAHs and PCBs from spiked sediment samples averaged 88% and 86%, respectively.

Sediment trap solids were analyzed for organic carbon and total nitrogen by high-temperature oxidation using a Perkin-Elmer CHN analyzer. Particulate organic carbon was measured on bulk suspended and accumulated sediments by the method of Parsons et al. (25) with minor modifications, in which samples were refluxed at 70 °C for 4 h with excess chromate ion to oxidize the particulate organic matter, and the remaining chromate ion was measured spectrophotometrically.

**Results and Discussion**

**Mass Fluxes.** Mass settling fluxes determined by sediment traps in Lake Superior are shown in Figure 2. Surface water (10 m) fluxes ranged from 0.14 to 0.89 g/m$^2$-day and were slightly higher, at the 90% confidence level, during the unstratified period. Settling fluxes are considerably lower than those measured in the other Laurentian Great Lakes (3, 9, 27–30) and are comparable to fluxes in the North Atlantic (31, 32) and the Panama Basin (33–35). The three open-lake sites (1–3) are quite similar, having mass fluxes of 0.14–0.19 g/m$^2$-day, and constant with depth to within 5–25 m of the lake floor, where they increase approximately 2-fold during stratification and 5-fold during the unstratified deployment (Figure 2). Increased benthic fluxes result from resuspension of local sediments and downslope sediment transport in turbidity currents (14, 36). The profiles of mass flux in surface and middepth waters are similar between the two deployment periods, suggesting that seasonal variations in particle sources are relatively small, that sediments from episodic resuspension events are limited to the nearshore and deep waters of the lake, and that a rather constant supply of particles reaches the bottom waters throughout the year. More frequent trap deployments are required to assess short-term variations in vertical fluxes in the water column.

The surface water mass flux at site 4, the site shallowest and closest to shore, is higher than those at the open-water sites and is similar to fluxes measured in Lake Michigan (26). Mixing of resuspended surficial sediments throughout the water column, shoreline erosion, and perhaps greater primary productivity result in higher settling fluxes at this site.

Rates of particle recycling and degradation may be estimated by comparing settling fluxes through the water column to net rates of sediment accumulation. Sediment cores collected near the trap deployments were analyzed for $^{210}$Pb to determine net sediment accumulation rates (37–39). Sediment accumulation rates range from 26 to 48 g/m$^2$-year in the three open lake cores and 190 g/m$^2$-year in the nearshore core (39). Annual settling fluxes from surface waters are 20–130% greater than sediment accumulation rates, indicating that only a fraction of settling solids are incorporated into bottom sediments.
Table II. Concentrations of PAHs, PCBs, and Organic Carbon Associated with Suspended, Settling, and Accumulating Sediments in Lake Superior

<table>
<thead>
<tr>
<th>compd</th>
<th>surficial sediments</th>
<th>surface water sediment traps</th>
<th>surface water suspended solids</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mean ± SD (number)</td>
<td>stratified</td>
<td>unstratified</td>
</tr>
<tr>
<td></td>
<td>(ng/g)</td>
<td>2006 (352)</td>
<td>287 (50)</td>
</tr>
</tbody>
</table>

Mean particle settling velocities (Sv) and water column residence times (tR) can be calculated from settling fluxes and standing crop particle concentrations as follows:

\[ S_v = \frac{J_z}{C_z} \]  

\[ t_R = \frac{C_z Z}{J_z} = Z / S_V \]

where \( J_z \) is the settling flux (g/m²-day), \( C_z \) is the solids concentration (g/m²), and \( Z \) is the depth of the water column. During summer months, suspended solids concentrations in central and eastern Lake Superior average 0.4 g/m² (19). Based on settling fluxes from 35 m, settling velocities during stratification were 0.46, 0.29, 0.27, and 0.46 m/day at sites 1-4, respectively. These estimated settling velocities correspond to the terminal settling velocity of a 12-µm particle of density 1.05 g/cm³, which is larger than the mean particle size of standing crop particles measured in the western arm of Lake Superior (5 µm, ref 36), but comparable in size to many phytoplankton species. Resulting particle residence times in the photic zone (35 m) and the water column (280 m) are 100 days and 2.5 years, respectively. This calculation may underestimate the \( S_v \) of large, rare (e.g., 1/µm³) particles, which are not likely to be sampled during water filtration for suspended solids measurement.

Organic Carbon Fluxes. Solids settling from surface waters during stratification contain significantly more organic carbon than do suspended solids collected during the same season (Table II) and have similar carbon contents as algae (40). Lower carbon contents of settling solids during unstratified conditions likely result from a larger contribution from eroded clays and resuspended sediments to the settling flux at that time. Both settling and suspended solids are significantly enriched in organic carbon relative to surficial sediments (Table II). Sediment trap solids are depleted in nitrogen (molar C/N ratios 14-45), suggesting that the organic matter is partially degraded. Grazing by zooplankton and subsequent production of fecal pellets, as well as formation of large aggregates (“marine snow”), are thought to control vertical fluxes of...
many species in the oceans (e.g., ref 41). Our data suggest that these processes are also important in large freshwater systems. We have observed large, amorphous aggregates in increasing concentrations within 5 m of the lake floor during submersible dives throughout central and eastern Lake Superior.

Organic carbon fluxes from the surface waters of Lake Superior range from 60 to 90 ng of C/m²-day (Figure 3). These values are similar to those of the other Great Lakes (26, 27, 29, 30) and are greater than found in the open ocean (e.g., ref 34). Organic carbon settling velocities calculated from settling fluxes at 35 m during stratification and a standing crop particulate OC concentration of 0.09 g of C/m² (19) average 0.76 m/day, approximately twice the mean particle settling velocity, suggesting that settling solids are enriched in organic carbon. Organic carbon fluxes from surface waters are remarkably constant among all four sites and between deployment periods. With the exception of the deepest traps at sites 3 and 4, OC fluxes increase only slightly near the lake floor, indicating that the sources contributing to benthic mass fluxes are relatively deficient in organic matter.

In situ degradation during settling decreases OC fluxes with depth at the three open lake sites (Figure 3). The rate of OC decomposition can be estimated from the decrease in OC flux between surface water and middepth traps at these sites by using the OC transit time determined from the settling velocities calculated above. Assuming that the decreased flux is due solely to degradation of organic matter, the resulting first-order rate constant and half-life average 7.8 x 10⁻² day⁻¹ and 104 days, respectively (Table III). This degradation rate agrees well with rates determined in sediment trap incubations and surficial sediments but is as much as 25 times slower than those measured on suspended solids. Total PCB (t-PCB) concentrations on particles collected by near-bottom sediment traps exhibit inorganic fluxes comparable to net sediment accumulation rates. We propose that the settling flux consists of organic matter dominated vertical settling and a primarily inorganic lateral flux along the lake floor (Figure 1). The vertical flux of organic matter is balanced by degradation as particles settle through the water column, followed by mixing of solubilized components throughout the water column during unstratified periods. Only a small fraction of materials carried by settling organic matter are incorporated into bottom sediments. Conversely, movement of eroded clays downslope from nearshore areas by turbidity currents and episodic sediment resuspension supply the clays that are incorporated into bottom sediments (14, 38). Near-bottom traps collect solids from both sources, yielding high benthic mass fluxes.

PCB and PAH Concentrations on Settling Solids. A most significant finding of this study is the elevated PCB and PAH concentrations measured on solids settling through the water column of Lake Superior relative to those on suspended solids. Total PCB (t-PCB) concentrations (sum of 35 congeners) on particles collected by near-bottom sediment traps at the three open lake sites averaged 2020 ± 1240 and 810 ± 660 ng/g during stratified and unstratified deployments, respectively (Table II). These t-PCB concentrations in the trapped material are higher than those reported for suspended particulate or surficial sediment samples collected from Lake Superior during the past decade (1). Higher contaminant concentrations during stratification may reflect larger loadings from the atmosphere or a greater sorptive capacity and scavenging efficiency during the summer months. In general, PCB and PAH concentrations on settling solids decrease with depth in the water column, perhaps due to dilution by less contaminated resuspended sediments and contaminant release during in situ organic matter degradation (see below).

Concentrations of PCBs and some PAHs associated with settling solids are often 1–3 orders of magnitude greater than those measured on suspended solids and surficial
sediments collected from Lake Superior (Figure 4). Although the sediment traps were deployed during stratification from July to September 1984 and the waters and sediments sampled in August 1986, HOC concentrations probably did not differ by more than 2-fold between these periods (19). The more soluble di-, tri-, and tetrachlorobiphenyl congeners, fluorene, and phenanthrene are most enriched on settling solids while the higher molecular weight PAHs are depleted on settling solids relative to suspended and accumulating sediments. Qualitatively, the relative amounts of PCB congeners and PAHs on solids settling through the water column are remarkably similar to those dissolved in Lake Superior surface waters (Figure 5), suggesting a direct uptake of contaminants from the dissolved phase, independent of contaminant solubility or hydrophobicity.

The highest concentrations of PCB congeners and lower molecular weight PAHs (e.g., phenanthrene) found in this study were measured on solids settling from the photic zone at site 4 during stratification. The total PCB concentration of solids collected in the 10-m trap was 11.3 μg/g, more than 5 times greater than t-PCB levels in open lake traps. These higher concentrations at site 4 may reflect localized sources of HOCs from nearby populated areas (i.e., Marquette, MI). It is conceivable that the chloroform used as a trap poison may have extracted dissolved HOCs from the lake water during trap deployment, leading to the apparent HOC enrichment in the trap samples. However, calculated HOC concentrations resulting from equilibrium partitioning between the chloroform poison and the ambient dissolved HOC concentrations are much higher than HOC levels measured in the trap samples. In addition, such a partitioning would result in enrichment of the more hydrophobic HOCs, in contrast to the observed enrichment of more soluble species. Further, similar total PCB concentrations were found in samples collected by unpoisoned traps codeployed with our traps (43). We conclude, therefore, that elevated contaminant concentrations in the sediment trap samples were not an artifact of the chloroform poisoning.

Partitioning of PCBs and PAHs to Settling Solids. Contaminant associations with aquatic solids are thought to result from partitioning of HOCs between dissolved and particulate phases. The extent of partitioning is quantified by an equilibrium distribution coefficient ($K_d$), the ratio of particle-associated and dissolved contaminant concentrations. The magnitude of $K_d$ depends on properties of both the solid phase and the organic contaminant (see refs 11 and 44). Karickhoff et al. (45) observed that $K_d$s of a series of HOCs on several sediments depended directly on the fractional organic carbon content ($f_c$) of the solids and introduced the organic carbon normalized distribution

\[
K_d^{OCN} = K_d \times f_c
\]

Figure 4. Concentration of PCBs and PAHs on suspended, settling, and accumulating sediments in central Lake Superior. Asterisks denote analytical detection limits for compounds not detected.
The dependence of $K_d$ on $f_{oc}$ supports partitioning of contaminants into organic matter as the dominant mechanism of HOC–particle associations. Numerous investigators have reported linear relationships between $K_d$ and $K_{ow}$ (e.g., refs 11 and 46).

Sediment trap $K_d$s of PCB congeners and PAHs were calculated by dividing the HOC concentration of trap material collected during stratification at site 1 by the dissolved (e.g., nonfilterable) HOC concentration in surface water collected from the central basin of Lake Superior in August 1986. As noted previously, HOC concentrations likely did not vary more than 2-fold between deployment of sediment traps in 1984 and collection of surface waters in 1986. As has been reported for distribution coefficients of PCBs to suspended solids in Lake Superior (47), $K_d$s of all compounds studied were weakly correlated with organic content of the settling particles. Observed $K_{oc}$ values for PCB congeners on settling particles are higher than those for PCBs on suspended solids in surface waters ($\log K_{oc} = 6.37 \pm 0.36$ vs $5.16 \pm 0.43$ L/kg) and are independent of $K_{ow}$. The $K_d$s of these compounds were comparable to those measured by using radiolabeled HOCs spiked into ambient lake water (48). PAH distribution coefficients are also quite variable for both suspended and settling solids samples and appear independent of $K_{ow}$ (Figure 6). Large $K_{oc}$ values independent of $K_{ow}$ argue against simple adsorption or partitioning as the dominant mechanism by which settling particles obtain hydrophobic contaminants.

Distribution coefficients of HOCs in predator fishes (i.e., bioconcentration factors) greater than $K_{ow}$ have been interpreted by Connolly and Pedersen (49) as evidence of uptake of contaminant through the food web. Vertical particle fluxes in the oceans are dominated by zooplankton fecal pellets and amorphous “marine snow” (e.g., refs 41 and 50). Elder and Fowler (51) measured a total PCB distribution coefficient to zooplankton fecal pellets in the Ligurian Sea of $6.4 \times 10^6$ L/kg, which agrees very well with PCB distribution coefficients of sediment trap solids reported in this study. Rapidly settling zooplankton fecal pellets are thought to be important in the vertical transport of $^{210}$Po and $^{210}$Pb (52), diatom frustules (53, 54), and organic contaminants, including PAHs (55) and PCBs (51). Both the magnitude of organic contaminant concentrations and the partitioning behavior indicate that rapidly settling particles collected in sediment traps in Lake Superior are biogenic solids that have acquired organic contaminants through the process of biomagnification.

**PCB and PAH Fluxes.** Total PCB (sum of 35 congeners) settling fluxes from open-lake waters averaged 0.37 $\pm 0.25$ and 0.16 $\pm 0.08$ $\mu g/m^2$-day during stratified and unstratified deployments, respectively. Phenanthrene fluxes averaged 1.02 $\pm 0.71$ and 0.56 $\pm 0.17$ $\mu g/m^2$-day during the same periods. Surface water HOC fluxes at site 1 were very similar between deployments, while stratified HOC fluxes were significantly greater at the other sites (Figures 7 and 8). Higher contaminant fluxes during stratification despite lower mass fluxes imply either higher HOC levels in surface waters or more efficient scavenging by settling particles during summer months. It is unclear why fluxes at site 1 did not increase during stratification. PCB fluxes are remarkably constant with depth during unstratified deployments but decrease during stratification (Figure 7). Between 67% and 83% of the total PCB flux settling from surface water is not delivered to near-bottom traps. At site 4, the large decrease in PCB flux between the 10-, 35-, and 75-m traps results primarily from significantly lower fluxes of hexachlorobiphenyl congeners. PCBs may be released from settling solids during degradation of organic matter during transit. Although particles collected by surface water traps during summer months are greatly enriched in PCBs and phenanthrene, these compounds are apparently readily released during settling.

Chemical specific settling velocities at site 1 are shown in Figure 9. Settling velocities at the other two open-lake sites are similar to those at site 1. As no water column HOC data near site 4 are available, HOC settling velocities cannot be calculated for this site. PCB congener settling velocities range from 1.3 to 71 m/day, with a mean t-PCB velocity of 14 m/day. PAHs generally have smaller settling velocities than PCB congeners except phenanthrene, which settles at 65 m/day. Higher settling velocities of the more soluble di- and trichlorobiphenyls and phenanthrene result both from their enrichment in settling solids and their depletion in standing crop solids (Figure 4). HOC settling velocities are significantly higher than mean mass settling rates (0.34 m/day), which is consistent with the hypothesis.
that contaminants settle from the water column incorporated into large, rapidly settling particles.

Large HOC fluxes and rapid settling velocities imply very short residence times in surface waters. The mean annual t-PCB flux from the epilimnion of Lake Superior is 71 g/m²-year and the t-PCB concentration in surface waters averages 0.5 g/m³ (19), resulting in a t½ of 0.25 year in the photic zone and 1.5 years in the entire water column. Estimates of the net, long-term PCB t½ in Lake Superior range from 1 to 9 years (7), indicating that much of the PCB flux measured in sediment traps results from recycling within the water column. Without such recycling, the water column would become depleted in those species with the highest settling velocities (e.g., di- and tri-chlorobiphenyls and phenanthrene). In fact, the opposite is true as these compounds dominate the HOC pool in the lake's waters (19).

Further evidence of intense internal recycling of HOCs in the water column is provided by a comparison of HOC settling fluxes with net HOC burial rates in bottom sediments. In the central basin near site 1, the surficial sediment accumulation rate is 73 g/m²-year (0.2 g/m²-day) and the upper 2 cm is partially mixed, as determined by ²¹⁰Pb radiodating (38). HOC accumulation rates calculated by multiplying the surficial (0.5 cm) sediment HOC concentration and the mass accumulation rate represent the net HOC burial flux averaged over 8–9 years. HOC recycle ratios were calculated by dividing the annual settling flux at 35 m from site 1 by the HOC accumulation rate in the nearby core (Figure 10). Although shallow traps and sediment cores integrate fluxes over different time scales, which may complicate this analysis, these recycle ratios estimate the relative rates of benthic recycling of HOCs.

Recycle ratios are much greater than 1 for all PCB congeners, fluorene, and phenanthrene, indicating that significant amounts of these compounds are recycled near the sediment–water interface. Less than 1% of the t-PCB flux at 35 m accumulates in underlying sediments. HOCs that are most enriched in settling solids are also those recycled to the greatest degree. That is, chlorobiphenyls containing two to four chlorines, fluorene, and phenanthrene are present in high concentrations on settling particles but are released during settling through the hypolimnion and near the lake floor. These more soluble HOCs may be associated with labile organic matter, which is easily degraded. In contrast, fluxes of higher molecular weight PAHs from the photic zone are less than their net accumulation rates (i.e., recycle ratios <1), inferring the existence of other sources. Lateral, downslope transport of recently eroded clays may supply these PAHs from nearshore areas. Alternatively, mixing of surface sediments with sediments from below may increase PAH levels in surficial sediments. PAH concentrations are higher in underlying sediments that were deposited more than 10 years ago (38).

Figure 10 shows that HOC recycle ratios depend directly on their aqueous solubilities. More soluble compounds have high fluxes but very low accumulation rates and are efficiently recycled. More hydrophobic HOCs are efficiently incorporated into sediments. Recycle ratios are largely invariant with location and depth in the water column. An interesting feature of Figure 10 is that PCBs have consistently higher recycle ratios than PAHs. If associations between HOCs and particles were controlled exclusively by partitioning, PCBs and PAHs should have similar aqueous behaviors. We propose that this difference may result from the way in which PCBs and PAHs are introduced into the water column. PCB congeners are emitted to the atmosphere primarily in the gas phase by volatilization from terrestrial and aquatic reservoirs. Once in the atmosphere, the absorption of gas phase onto ambient aerosols depends on the congener vapor pressure, the air temperature, and the aerosol concentration and composition. Conversely, combustion of fossil fuels emits PAHs into the atmosphere either adsorbed to or incorporated into coemitted aerosols. PAHs with sufficient vapor pressures may volatilize from the aerosol but most, particularly higher molecular weight compounds, remain bound to aerosols. Transport of both classes of HOCs from the atmosphere to surface waters is dominated by aerosol washout during precipitation events. Once deposited in surface waters, PCBs and low molecular weight PAHs desorb and dissolve into the bulk liquid. Higher molecular weight PAHs are trapped within particles and do not partition into the dissolved phase. Those compounds that dissolve in surface waters are available for enrichment in rapidly settling particles, while those HOCs that enter the lake on and remain attached to particles do not participate in this enrichment and settle more slowly. In support of this scenario, PCB and PAH patterns in settling solids are similar to those of the dissolved phase in surface waters (Figure 5), suggesting that these solids obtain their HOCs from the dissolved phase.

**Conclusions**

This study has found that many organic contaminants undergo significant recycling with the water column of Lake Superior. Lower chlorinated PCB congeners and the PAHs fluorene and phenanthrene are rapidly removed from surface waters and settle through the water column to the sediment–water interface. At the lake floor, a large fraction of the recently settled HOCs are released and

![Figure 9. Settling velocities of PCB congeners and PAHs.](image)

![Figure 10. Recycling ratios of PCB congeners and PAHs vs their aqueous solubilities.](image)
mixed back into the water column. In contrast, settling fluxes of higher molecular weight PAHs from surface waters are low but those compounds are efficiently buried in surficial sediments with little benthic recycling.

Removal of HOCs from surface waters by rapidly settling particles limits volatilization, thereby increasing net HOC residence times in the water column. In addition, rapid settling provides a direct pathway linking the surface and benthic waters of Lake Superior. This process is similar to that observed in the Sargasso Sea, where seasonal fluxes of particles and organic carbon transport organochlorines into the deep waters (56). In the Great Lakes, Eadie et al. (57) reported rapid water column transport and uptake in benthic organisms of phenanthrene, but not other PAHs, which they attributed to the settling of the spring diatom bloom. The lake floor is a highly productive area with large populations of micro- and macrofauna, which depend on the rain of reduced organic carbon settling from above. This study has shown that these settling particles are greatly enriched in hydrocarbon organic chemicals. We suggest that the benthic food web is an important entry point for these pollutants into the whole-lake food chain.

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