Dry Deposition of Particulate Polychlorinated Biphenyls and Polycyclic Aromatic Hydrocarbons to Lake Michigan

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Dry deposition was collected from November 1993 to October 1995 at multiple sites within the Lake Michigan basin to estimate fluxes of particulate polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) as part of the Lake Michigan Mass Balance Study (LMMBS). Samples were also collected during the Atmospheric Exchange over Lakes and Oceans (AEOLOS) project to estimate fluxes to coastal waters adjacent to the Chicago urban area. Fluxes of particulate PCBs and PAHs were higher in Chicago than <15 km offshore and at rural sites. Geometric mean dry deposition fluxes across the Lake Michigan basin ranged from 3.6 to 65 mg/m²-day for particle mass, 0.06 to 0.21 μg/m²-day for Σ-PCBs, and 0.25 to 18 μg/m²-day for Σ-PAHs. Similarities in both the distribution pattern of PCB congeners and PAHs and the magnitude of their fluxes between dry deposition and surficial sediment suggest that dry deposition may dominate loadings to the lake. Conservative estimates of loadings to Lake Michigan through particle dry deposition are estimated to be 1100 kg/yr for PCBs and 5000 kg/yr for PAHs. These loadings are more than 3× greater than loadings by wet deposition and, for PCBs, are similar to inputs by air/water exchange.

Introduction

Wet deposition (rain, snow, fog), dry particle deposition, air/water, and air/terrestrial exchange link atmospheric contaminants with their aquatic/terrestrial reservoirs. Precipitation inputs of semivolatile organic chemicals (SOCs) are routinely measured in the Great Lakes region (*1–3*). Within the past decade, our understanding of air/water and air/terrestrial exchange has dramatically improved (*4–14*). However, few measurements of dry particle deposition of SOCs are available in the Great Lakes region (*15–17*), primarily because of the difficulty in making these measurements for SOCs with low atmospheric particle concentrations.

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Estimates of the dry depositional flux of SOCs to the Great Lakes have relied on calculations based on measured atmospheric particle concentrations ($C_{a,p}$) and a selected deposition velocity (V_d) (*2, 18–22*)

$$\text{flux } (\mu g/m^2\text{-day}) = C_{a,p} \text{ (ng/m}^3) \times V_d \text{ (cm/s)} \times 0.864 \tag{1}$$

where the last term is a unit conversion factor. However, estimates that assume constant values for V_d and $C_{a,p}$ result in large uncertainties (*23*) and underestimate the contribution of large (>10 μm) particles (*17, 24*). Spatial and temporal variability in V_d depends on meteorological parameters (wind speed, atmospheric stability, relative humidity) and physical characteristics of both the pollutant (particle size, shape) and receptor surface (type of surface, roughness). Consequently, V_d can range over 2 orders of magnitude (*25*).

The scarcity of dry deposition measurements results from the difficulty in constructing a representative surrogate surface. Since dry deposition has been described in terms of resistance to transfer across boundaries, each surface has a unique resistance or roughness (*26–30*). By default then, a surrogate surface cannot accurately mimic a natural plant or lake surface. Nevertheless, surrogate collection devices have been deployed to estimate dry deposition to various ecosystems. Such devices include wet/dry collectors of various configurations (*31–36*), moss bags (*37*), glass fiber filters (*16, 32, 38, 39*), Petri dishes (*39, 40*), water surfaces (*41, 42*), "Frisbee"-shaped air foils (*43–46*), and aluminum, glass, or Mylar plates coated with grease, glycerin, mineral oil, or other material to prevent bounce-off (*15–17, 47–51*). Surrogate surfaces are reproducible and can be deployed in large spatial arrays to estimate particle deposition (*40*) and to evaluate regional and temporal trends. The difficulty lies in extrapolating deposition to surrogate surfaces to that experienced by natural surfaces. Generally, particle deposition to rough plant and water surfaces is greater than that to smooth deposition plates (*25–27*) under similar conditions.

In this study, dry deposition was collected with a grease-coated smooth plate with a sharp leading edge similar to those used in wind tunnel studies (*52, 53*). Since the knife-edge provides minimal air flow disruption, a lower limit for dry deposition is measured (*17, 54*). A network of such devices was deployed at multiple sites in the Lake Michigan basin from November 1993 to October 1995 as part of the *L*ake *M*ichigan *M*ass *B*alance *S*tudy (LMMBS) and during July 1994 as part of the *A*tmospheric *E*xchange *o*ver *L*akes and *O*cean*s* (AEOLOS) project. The hypothesis of the AEOLOS project was that emissions of anthropogenic chemicals in the urban/industrial atmosphere of Chicago, IL/Gary, IN, result in enhanced depositional fluxes to proximate southern Lake Michigan waters. Simcik et al. (*55*) have shown that atmospheric levels of PCBs and PAHs in the Chicago urban area exceed those downwind over the water <15 km offshore by factors of 4–20. Offenberg and Baker (*56*) have confirmed that southern Lake Michigan is impacted by precipitation enriched with contaminants, such that wet loadings are greater than estimated from regional precipitation measurements. Atmospheric particle concentrations and dry depositional fluxes of trace metals were also elevated over the lake when winds were from the Chicago/Gary corridor (*46, 57, 58*). Here, spatial trends in the dry deposition flux of PCBs and PAHs from both the LMMBS and AEOLOS projects are presented and annual loadings to Lake Michigan estimated. Dry deposition fluxes are also compared to atmospheric particle concentrations during AEOLOS to
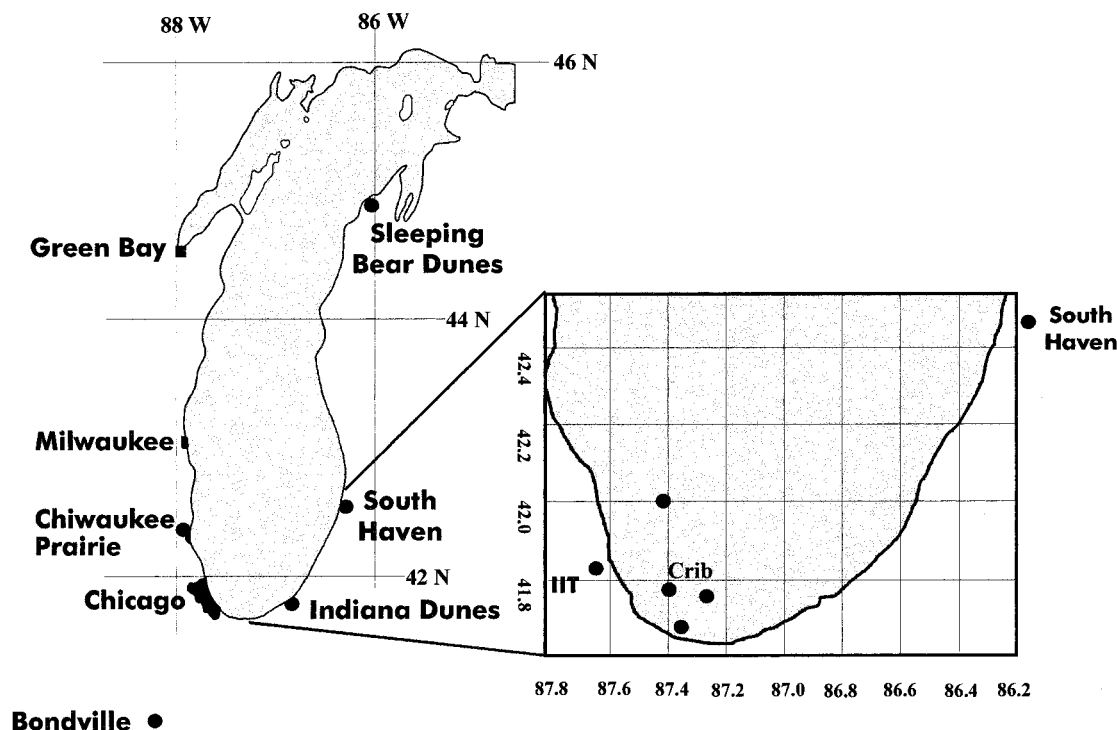
FIGURE 1. Location of dry deposition sites within Lake Michigan basin during the LMMBS and AEOLOS.

examine similarities in the distribution of PCB congeners and PAHs and to calculate deposition velocities.

Experimental Section

Sampling. Particle dry deposition was collected on Mylar strips (5.7 cm × 1.8 cm exposed surface area) coated with Apezion L grease (~5 μm thick, 1.4 mg mass) and attached to smooth poly(vinyl chloride) (PVC) plates. The PVC plates, containing a sharp leading edge (<10° angle), were pointed into the wind by a wind vane. The sharp leading edge provides laminar air flow over the strips that minimizes turbulent deposition. The greased surface eliminates particle bounce while collecting particles of all sizes. Potential artifacts associated with this technique include sorption of gas phase SOCs by the grease and volatilization losses of SOCs from deposited material during deployment. The impact of these artifacts are believed to be small. In one study with similar deposition plates, PCB fluxes from long-term exposures were not statistically different from short-term samples during the summer when evaporative losses from deposited material were expected to be at a maximum (*59*). In another study, greased deposition plates exposed to gas-phase PAHs in a PVC pipe under laminar flow conditions for periods of up to 400 h did not reach equilibrium (*60*). Thus, partitioning may be envisioned as a two-step process with rapid surface adsorption to the grease followed by a much slower absorption process that is limited by mass transfer within the bulk liquid. According to this scenario, field blanks exposed for even short periods may accumulate gas-phase SOCs at the grease surface very effectively. Subtracting this sorption to the field blank on a surface-area normalized or deposition basis from that measured on a field sample could then minimize sorption artifacts encountered during all stages of sample handling.

Deposition plates were mounted on Eagle II automatic dry deposition collectors at the following sites (Figure 1): Sleeping Bear Dunes, MI (SBD), 44° 44′ 30″ latitude, 86° 03′ 31″ longitude; South Haven, MI (SH), 42° 27′ 51″ latitude, 86° 10′ 12″ longitude; 68th St. and Harrison St. water intake cribs off-shore of Chicago; Chiwaukee Prairie, WI (CP), 42°

30′ 17″ latitude, 86° 48′ 33″ longitude; Indiana Dunes, IN (ID), 41° 37′ 54″ latitude, 87° 05′ 15″ longitude; Bondville, IL, 40° 03′ 09″ latitude, 88° 22′ 17″ longitude. The Eagle II collector contains two deposition plates mounted on arms that are pointed into the wind by a wind vane. A moisture sensor activates motors that cover the plates when it begins to rain or snow. When the sensor dries, the covers are retracted, and the plates are again exposed to the atmosphere. A timer monitors total exposure times. At locations with on-site operators, deposition plates were attached to manual samplers (*17, 24*) [Illinois Institute of Technology (IIT), Chicago, IL 41° 50′ 04″ latitude, 87° 37′ 29″ longitude, and aboard the R/V *Lake Guardian* at station number 5 (42° 00′ 00″ latitude, 87° 25′ 00″ longitude), station number 1 (41° 46′ 00″ latitude, 87° 20′ 00″ longitude, and station number 0 (41° 40′ 00″ latitude, 87° 22′ 00″ longitude)]. Preparation of the dry deposition strips and standard field operating procedures are described elsewhere (*61*).

Exposure times varied from 4 to 97 days for individual samples or sample composites and covered 20% to 30% of the total LMMBS period. Longer exposure times were necessary at rural/remote sites where particle deposition was low. After determining the final weight of the samples, the deposition strips were placed in clean amber wide-mouth bottles, frozen, and shipped to the University of Minnesota where they were again frozen until analyzed. A relative error of 3.7% in the weight of the deposition strips was determined from repeated weighings.

Analysis. Analytical methods are described elsewhere (*62*). Briefly, the deposition strips from any one site (or composite of concurrent exposure periods) were placed in amber vials, spiked with PCB and PAH analytical surrogates, and sequentially extracted with dichloromethane and hexane in a sonication water bath. Extracts were cleaned with 3% deactivated silica gel (0.6 g) and 5% deactivated alumina (1.0 g) using 0.5 cm i.d. × 20 cm glass columns. This method removed most of the Apezion L grease. However, upon final volume reduction to <100 μL prior to injection, extracts exhibited residual grease. To aid instrumental analysis, a 1 m glass capillary precolumn (0.25 mm i.d.) was attached to

TABLE 1. Particle Dry Deposition Flux of Particle Mass, PAHs, PCBs, and t-Nonachlor in the Lake Michigan Basin

sampling sites	mass flux (mg/m²-day)			Σ-PAHs (17 parent) flux (µg/m²-day)			Σ-PCBs[a] flux (µg/m²-day)		
	range	geometric mean	time-wgtd mean[b]	range	geometric mean	time-wgtd mean	range	geometric mean	time-wgtd mean
Chicago, IL ($n = 12$)	34–200	65	66	3.4–140	18	29	0.037–0.61	0.21	0.24
Over-Lake[c] ($n = 11$)	2.8–49	12	14	0.28–3.3	0.71	1.1	0.017–0.30	0.079	0.081
South Haven, MI ($n = 12$)	3.5–28	10	9	0.029–1.6	0.17	0.38	0.036–1.0	0.14	0.21
Sleeping Bear Dunes, MI ($n = 9$)	1.2–17	3.6	3.5	0.042–2.1	0.25	0.51	0.026–0.16	0.057	0.065

[a] Flux without dichlorobiphenyl congeners no. 4/10, 6, 7/9, 8/5. [b] Time-weighted mean flux = sum of field blank-corrected deposition (mass/m²)/sum of exposure time (days). [c] Sites include 68th Street crib ($n = 9$), Harrison Street crib ($n = 1$) and R/V *Lake Guardian* ($n = 1$).

the primary capillary column prior to injection. The precolumns were cut in half after 3–5 sample injections and replaced after 6–10 injections. Glass inserts on the inlet end of the gas chromatograph were changed daily. This preventative maintenance minimized degradation of the primary glass capillary column by the residual grease and maintained chromatographic resolution required for chemical identification and quantification. PCBs were analyzed on an HP 5890A GC equipped with a ^{63}Ni electron capture detector. Injection was splitless with detector and inlet temperatures at 300 °C. Initial temperature was 100 °C, held 1 min, ramped at 10 °C/min to 175 °C, ramped at 0.5 °C/min to 215 °C and at 2.0 °C/min to 280 °C, and held 15 min. PAHs were analyzed on an HP 5890A GC equipped with a mass selective detector (HP 5970) operated in the single ion monitoring mode. Injection was splitless with detector and interface temperatures of 300 °C, while the inlet temperature was 290 °C. Initial temperature was 50 °C, held one minute, ramped at 25 °C/min to 160 °C, ramped at 8.5 °C/min to 290 °C, held 7 min, ramped at 10 °C/min to 300 °C and held 14 min.

Quality Assurance/Quality Control. Strict quality assurance and quality control guidelines were developed and adhered to during the course of both the LMMBS and AEOLOS project. Surrogate recoveries ($n = 115$) were 88 ± 22% for 2,3,5,6-tetrachlorobiphenyl, IUPAC no. 65; 96 ± 23% for 2,3,4,4′,5,6-hexachlorobiphenyl, IUPAC no. 166; 69 ± 7% for d_{10}-fluorene; 89 ± 5% for d_{10}-fluoranthene, and 85 ± 8% for d_{12}-perylene. Procedural recoveries from solvent blanks spiked with a complete set of target compounds were 87% for Σ-PCBs ($n = 1$) and ranged from 77 to 120% ($n = 4$) for individual PAHs. Laboratory matrix spike recoveries ($n = 5$) averaged 136 ± 13% for Σ-PCBs (71 ± 12% when corrected for laboratory matrix blank levels) and ranged from 61 to 172% for PAHs (60–103%, blank corrected). Method detection limits (MDLs) were defined as the 95% confidence interval about the standard deviation of the mean mass determined from the analysis of seven laboratory matrix blanks spiked with target compounds at ∼5× instrument detection limits. MDLs ranged from 0.03 to 1.0 ng for PCB congeners and from 1.4 to 12 ng for individual PAHs. Instrument detection limits (IDLs), determined from the minimum area observed in standard chromatograms of peaks with S:N ratios of ∼3, were about an order of magnitude less than MDLs.

Procedural solvent blanks ($n = 4$) averaged 4.7 ng for Σ-PCBs and not detected (nd) to 0.83 ng for PAHs (1.6 ng for Σ-PAHs). Laboratory matrix blanks ($n = 5$), consisting of two dry deposition strips, averaged 6.4 ng for Σ-PCBs (3.1 µg/m², expressed on a surface area normalized basis) and ranged from 0.07 to 18 ng for individual PAHs and 41 ng for Σ-PAHs (0.036 to 9.0 µg/m² for PAHs and 20 µg/m² for Σ-PAHs).

Field matrix blanks were collected with each sample and exposed to ambient conditions only for the length of time (<30 min) required to set up the routine dry deposition samples. Generally, higher masses were observed in field blanks containing a greater number of strips. Normalized

to exposed surface area, field blanks for land sites ($n = 35$) averaged 5.1 µg/m² for Σ-PCBs and ranged from 0.069 to 5.2 µg/m² for PAHs (11 µg/m² for Σ-PAHs). At over-water sites, field blanks ($n = 11$) averaged 4.7 µg/m² for Σ-PCBs and ranged from 0.063 to 4.3 µg/m² for PAHs (9.4 µg/m² for Σ-PAHs). Since each sample had an associated field blank, the surface area normalized deposition of PCBs and PAHs from each field blank was subtracted from its corresponding field sample to minimize artifacts associated with sorption of gas-phase SOCs to the grease. None of the results were surrogate recovery corrected.

Results

Particle Mass. Particle dry deposition fluxes are listed in Table 1. As expected, geometric mean mass fluxes were much higher in Chicago (65 mg/m²-day) than observed <15 km offshore (12 mg/m²-day) or at the rural sites. Particle mass and elemental fluxes during LMMBS were 2–10 times higher in Chicago than measured over Lake Michigan and 5–30 times higher than rural fluxes (*63*). The high fluxes in Chicago reflect not only the greater degree of anthropogenic activity within the metropolitan area but also the greater atmospheric burden, and subsequent deposition, of large particles generated within the area. The mean flux of particles in Chicago during LMMBS is half the flux reported for 1989 to 1991 which averaged 130 mg/m²-day (*17, 64*). Similarly, the mass fluxes in Table 1 are less than the averages measured over the lake (27 mg/m²-day), at SH (40 mg/m²-day), and at SBD (23 mg/m²-day) during the Lake Michigan Urban Air Toxics Study (LMUATS) during the summer of 1991 (*64, 65*).

The area influenced by urban emissions depends on wind speed, emission height, the stability of the atmospheric boundary layer over the lake, and the size of the particles (*66*). Although southwesterly wind patterns occur ∼40–50% of the year (*66*), coastal meteorological conditions may inhibit particle deposition from the urban plume to the near-shore lake surface.

When air temperatures are warmer than surface water temperatures in spring and early summer, a cool, stable boundary layer forms near the lake surface under low wind conditions. This stratified air profile restricts atmospheric mixing to the lowest 50–100 m above the lake surface and prevents mixing with air above the thermal layer (*67*). In effect, the boundary layer caps vertical mixing near the surface at heights lower than predicted by the mixed layer which typically ranges in height from ∼1400 m in the warm season to ∼850 m in the cold season (*66*). In addition, afternoon lake breeze circulation patterns, which occur ∼5% of days during cold weather and ∼35% of days during warm months (*66*), causes a portion of the urban aerosols to be carried inland and transported aloft along the frontal convergence zone with the predominant westerly winds (*68*). Particles carried aloft may either continue out over Lake Michigan at elevated heights and eventually fumigated to the lake surface or along the eastern shore or be reentrained within the lake breeze inland return flow (*68*). Vertical air motions within

TABLE 2. Particle Dry Deposition Fluxes of Σ-PCBs Reported at Various Locations

flux (μg/m²-day)	year	location	sampling method[a]	ref
<0.05−3.8	1972−1973	La Jolla, CA	glass plates, mineral oil	(48)
0.05−0.15	1973−1974	Southern California Bight	glass plates, mineral oil	(47)
0.05−1.7	1974	Los Angeles basin	glass plates, mineral oil	(47)
0.25	1974	Los Angeles basin	glass plates, mineral oil	(49)
<0.3−0.42	1973−1975	Kingston, RI	aluminum pans, glycerin−water	(50)
<0.035−0.45	1976−1979	Columbia, SC	aluminum pans, glycerin−water	(50)
<0.006−0.095	1977−1979	North Inlet Estuary, SC	aluminum pans, glycerin−water	(50)
0.08	1977	Navarre, MN	glass plates, glycerol	(15)
0.26	1977	Ely, MN	glass plates, glycerol	(15)
0.78	1977−1979	Minneapolis, MN	glass plates, glycerol	(15)
0.018 ± 0.011	1977−1979	sites around Saginaw Bay, MI	filters, wetted with propane/butanediols	(16)
0.12	1979−1980	Waukegan, IL	filters, wetted with propane/butanediols	(16)
0.63	1979	Chicago, IL	filters, wetted with propane/butanediols	(16)
0.04	1985	southern France	glass wool in stainless steel funnels	(35)
4.5	1989−1990	Chicago, IL	Mylar strips, Apezion L grease	(17)
0.87	1992	Door Co., WI	Mylar strips, Apezion L grease	(60)
0.23	1992	Sleeping Bear Dunes, MI	Mylar strips, Apezion L grease	(60)
3.5−6.8	1994	Taiwan	aluminum strips, silicone grease	(51)
0.21	1993−1995	Chicago, IL	Mylar strips, Apezion L grease	this study
0.08	1993−1995	offshore Chicago, IL	Mylar strips, Apezion L grease	this study
0.14	1993−1995	South Haven, MI	Mylar strips, Apezion L grease	this study
0.06	1993−1995	Sleeping Bear Dunes, MI	Mylar strips, Apezion L grease	this study

[a] Sampling method includes support and coating, if any.

lake breeze and heated land circulations result in the sorting of particles from the urban plume according to size and terminal velocities (66). Large particles (>~10 μm) tend to be deposited within a few kilometers of their source, while small particles (<~2 μm) may remain suspended in the air currents becoming dispersed throughout the mixed layer with minimal deposition. Thus, complex atmospheric concentration and deposition patterns exist near coastal zones.

Particle deposition velocities (V_d) can be estimated for total suspended particulates (TSP) from the measured mass flux using eq 1 (with TSP substituted for $C_{a,p}$), assuming that similar particle size fractions are collected by the TSP and dry deposition collectors. During AEOLOS, the geometric mean TSP concentration in Chicago, measured with dichotomous air samplers, was 27 μg/m³ ($n = 18$) in July 1994 and 28 μg/m³ ($n = 4$) during January 1995 and was 15 μg/m³ over the lake ($n = 18$, July values only) (69). The over-lake TSP concentration was approximately half of that measured in 1977 over southern Lake Michigan (35 ± 23 μg/m³) (70). Although the July 1994 and January 1995 urban TSP concentrations were similar, the summer flux of particle mass (45 mg/m²-day) was half the winter flux (85 mg/m²-day). From eq 1, V_d is estimated to be 1.9 cm/s for TSP during the summer in Chicago and 3.6 cm/s during the winter. The corresponding summer flux of particulate matter over the lake was 11.5 mg/m²-day, with a resulting V_d of 0.9 cm/s. The decrease in V_d over the lake suggests that the median diameter of particles impacting the deposition plate over the lake is smaller than in Chicago. Thus, a substantial fraction of large particles are deposited close to their urban source.

PCBs. The flux of total PCBs (sum of all congeners, Σ-PCBs) is listed in Table 1. The geometric mean dry deposition flux diminishes from ~0.2 μg/m²-day in Chicago to 0.06 μg/m²-day at SBD. The lower fluxes at the rural sites and over the lake results from both the removal of large particles from the atmosphere close to their source and the low atmospheric concentration of PCBs relative to the urban site (55). The dry deposition flux in Chicago is more than an order of magnitude less than the 4.5 μg/m²-day previously reported for PCBs from the metropolitan area using the same sampling technique in 1989−1990 (17), even though the mass fluxes were a factor of 2 less (mean 65 mg/m²-day, this study; 130 mg/m²-day (17)). One reason may be the blank
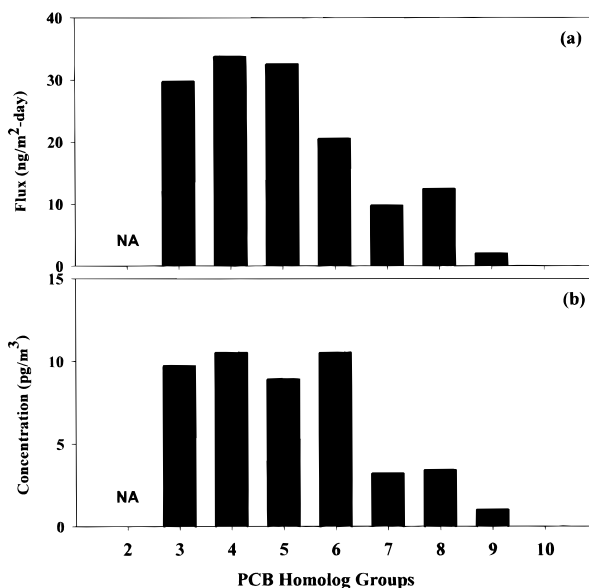

FIGURE 2. Comparison of the geometric mean (a) summer dry deposition flux of PCB homologue groups and (b) atmospheric particle concentration in July 1994 (55) in Chicago, IL.

correction employed in this study, which attempts to correct for gas partitioning to the greased collection plates. Dry deposition of PCBs in Chicago during this study is ~3× less than measured in 1979 (16) (Table 2). At rural sites, the flux of PCBs is also ~5−10× less than summer 1992 samples taken in Door Co., WI (0.87 μg/m²-day) and SBD (0.23 μg/m²-day) (65). Nevertheless, dry deposition of particulate PCBs in the Lake Michigan basin generally agree with measurements from other regions of the world (Table 2).

PCB congeners observed in dry deposition (Figure 2a) are similar to the pattern observed on atmospheric particulate matter collected by high volume air samplers (55) (Figure 2b). Hi-vols generally collect atmospheric particles ≤~100 μm depending on flowrate and ambient wind speed (Graseby-General Metal Works, personal communication). Thus, the particle size spectrum collected by the deposition strips and hi-vols are similar. However, the number distribution of

various particle sizes collected by the hi-vol may be different from those collected by the deposition strips. In some dry deposition samples, significant contributions were made by a few trichlorobiphenyls. The presence of these congeners, which have high atmospheric gas-phase concentrations, in the deposition samples may be due to (1) their association with large atmospheric particles, foliar debris, bacteria, or pollen that are collected by the deposition plates, (2) their sorption to large surface dust aggregates that become suspended during high wind conditions, or (3) their gas-phase sorption to the grease in excess of blank levels.

Regression analysis of the congener distributions indicated a significant correlation ($r = 0.71$, $p < 0.05$) between the geometric mean flux observed in Chicago and over the lake. This indicates that even though particle fluxes are greatly reduced over the lake, the distribution of PCBs on the settling particles impacting both sites is similar. There is also a weak, yet significant correlation ($r = 0.44$, $p < 0.05$) between the overall geometric mean summertime dry deposition flux and the July 1994 atmospheric particle concentration (55) in Chicago. Considering the differences in time, 2 years of deposition measurements versus 2 weeks of continuous air monitoring, the correlation demonstrates that PCBs collected by the dry deposition plates reflect PCBs associated with atmospheric particles.

These dry depositional fluxes can be compared to model estimates from the upper Great Lakes region for PCBs which range from ~0.001 to 0.01 $\mu g/m^2$-day (2, 18, 20, 22, 71, 72). Model calculations underestimate dry deposition to Lake Michigan by approximately an order of magnitude. Interestingly, the magnitude of dry deposition fluxes in this study are very similar to Lake Michigan surficial sediment accumulation rates which range from 0.05 to 0.08 $\mu g/m^2$-day (73). A strong correlation ($r = 0.82$, $p < 0.05$) in the PCB congener profile between the Lake Michigan surficial sediment accumulation rate (73) and the July 1994 AEOLOS atmospheric particle concentration in Chicago (55) indicates that the surficial sediment reflects atmospheric particles. Another correlation ($r = 0.56$, $p < 0.05$) in the distribution of PCB congeners between the surficial sediment and dry deposition in Chicago suggests that dry deposition may account for most of the particulate PCBs accumulating in the sediments of Lake Michigan.

The approach used to calculate V_d for TSP was applied to PCB congeners with detection rates of ≥50% in both dry deposition and the atmospheric particle phase during summer and winter months in Chicago. The geometric mean particle concentration of Σ-PCBs without the dichlorobiphenyls ($C_{a,p}$ in eq 1) was 48.5 pg/m^3 during July 1994 and 31.3 pg/m^3 in January 1995 (55). The corresponding dry flux was 0.19 $\mu g/m^2$-day in summer and 0.20 $\mu g/m^2$-day during winter. The resulting V_d for Σ-PCBs in warm months was 4.4 and 7.2 cm/s during the winter. These estimates are reasonable for deposition of particles >10 μm (26, 28, 30). The higher V_d in winter may partially result from the few air samples ($n = 3$) taken in January 1995 which do not accurately characterize atmospheric conditions over the winter. In contrast, the 17 air samples collected in July 1994 can adequately characterize summer air burdens since a greater variety of meteorological conditions were encountered. Over-lake estimates of V_d were not made since the particulate PCB content of the air samples was low (5.7 pg/m^3) and near detection limits.

PAHs. Similar observations and conclusions were found for PAHs as for PCBs. The geometric mean dry deposition of Σ-PAHs (17 parent PAHs) from 1993 to 1995 ranged from ~18 $\mu g/m^2$-day in Chicago to 0.2 $\mu g/m^2$-day at SH (Table 1). The near-shore region of southern Lake Michigan experienced intermediate deposition rates of 0.7 $\mu g/m^2$-day. The rapid decrease in the deposition flux with distance from
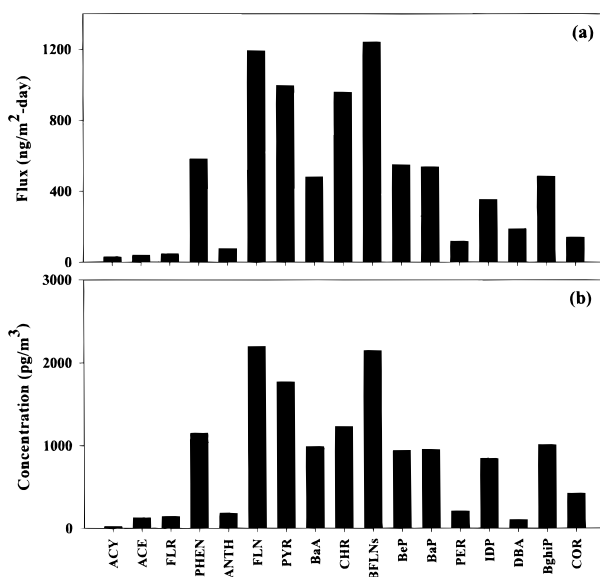

FIGURE 3. Comparison of the geometric mean (a) summer dry deposition flux of PAHs and (b) atmospheric particle concentration in July 1994 (55) in Chicago, IL (see Table 3 for PAH acronyms).

Chicago again supports the hypothesis that large particles are efficiently removed from the urban plume in the coastal zone (<15 km). Small particles are also being deposited, but coarse particles with large settling velocities (>0.5 cm/s) contribute most of the deposited mass.

The blank-corrected distribution of Σ-PAHs measured in summer dry deposition and on atmospheric particles during AEOLOS (55) is illustrated in Figure 3. The patterns are remarkably similar ($r = 0.98$, $p < 0.05$) verifying that dry deposition to the surrogate surface reflects atmospheric particulate matter.

No previous measurements of PAH dry deposition in the Great Lakes region are available for comparison. However, the over-water and rural fluxes are similar in magnitude to dry deposition fluxes measured near Boston, MA (Σ-PAHs ~0.2−1.5 $\mu g/m^2$-day) (36). In addition, the rural dry fluxes from this study are similar to model calculations based on particulate air concentrations in the upper Great Lakes region. These estimates (Table 3) range from 0.02 to 0.6 $\mu g/m^2$-day for Σ-PAHs (19, 22, 74−76). The estimates of Eisenreich and Strachan (22) are an order of magnitude less than other reported values. An estimate of dry deposition in Chicago of ~0.6 $\mu g/m^2$-day, based on particle size distributions <10 μm (75), is ~30× less than fluxes measured in this study. This low estimate results from not accounting for the deposition of particles >10 μm.

The dry deposition flux of PAHs offshore of Chicago is about half the surficial sediment accumulation rate of PAHs in southern Lake Michigan (~1.5−2 $\mu g/m^2$-day) (77). Strong correlations were found in the distribution of PAHs between the surficial sediment accumulation rate and both the geometric mean atmospheric particle concentrations in Chicago during AEOLOS in July 1994 ($r = 0.92$, $p < 0.05$) and the geometric mean dry deposition flux in Chicago ($r = 0.91$, $p < 0.05$). Thus, particle deposition of PAHs contributes significantly to the PAH burden of Lake Michigan waters and sediments.

The geometric mean atmospheric particle concentrations of Σ-PAHs in Chicago was 14.4 ng/m^3 in July 1994 and 16.3 ng/m^3 in January 1995 (55). The corresponding geometric mean dry flux of Σ-PAHs was 8.0 $\mu g/m^2$-day during warm months and 31 $\mu g/m^2$-day in winter. The resulting V_d for individual PAHs ranged from 0.4 to 2.1 cm/s (summer) and from 1.0 to 3.7 cm/s (winter), while for Σ-PAHs the deposition

TABLE 3. Particle Dry Deposition Flux (μg/m^2-day) of PAHs within the Lake Michigan Region

PAH	model predictions					direct deposition measurements			
	Lake Michigan (74)[a]	Lake Superior (19)[b]	Lake Michigan (22)[c]	Chicago (75)[d]	Lake Michigan (76)[e]	this study Chicago[f]	this study Over-lake[f]	this study SH[f]	this study SBD[f]
acenaphthylene (ACY)						0.03	0.004	0.003	0.001
acenaphthene (ACE)						0.12	0.012	0.009	0.002
fluorene (FLR)	0.022		0.00001		0.0001	0.11	0.005	0.009	0.003
phenanthrene (PHEN)	0.013	0.079	0.0010	0.019		1.56	0.060	0.107	0.051
anthracene (ANTH)	0.013	0.005				0.19	0.008	0.005	0.008
fluoranthene (FLN)	0.020	0.090	0.0007	0.040	0.005	2.71	0.106	0.041	0.045
pyrene (PYR)	0.022	0.075	0.0005	0.043	0.001	2.24	0.077	0.019	0.042
benzo[*a*]anthracene (BaA)	0.018	0.018	0.0008	0.030	0.004	1.09	0.025	0.005	0.025
chrysene (CHR)		0.057	0.0036	0.061	0.017	1.88	0.094	0.018	0.021
benzo[*b+k*]fluoranthenes (BFLNs)			0.0047	0.127		2.91	0.114	0.013	0.044
benzo[*e*]pyrene (BeP)		0.038	0.0008	0.052	0.032	1.18	0.055	0.014	0.023
benzo[*a*]pyrene (BaP)	0.022	0.019	0.0008	0.046	0.043	1.10	0.049	0.011	0.020
perylene (PER)	0.013			0.009		0.26	0.008	0.006	0.010
indeno[*c,d*]pyrene (IDP)		0.053	0.0030	0.055	0.056	0.77	0.031	0.008	0.010
dibenzoanthracene (DBA)				0.004		0.33	0.017	0.005	0.002
benzo[*g,h,i*]perylene (BGHIP)	0.036	0.027	0.0033	0.074	0.045	0.99	0.048	0.013	0.014
coronene (COR)				0.034		0.28	0.016	0.004	0.004
Σ-PAHs[g]	0.18	0.46	0.019	0.59	0.20	17.8	0.73	0.29	0.32

[a] Calculated here from reported loadings in kg/yr, surface area of Lake Michigan and 0.9 as fraction of year without precipitation. [b] Calculated using a deposition velocity of 0.99 cm/s. [c] Calculated using a deposition velocity of 0.2 cm/s. [d] Calculated from size distributions of particulate PAHs (<10 μm). [e] Calculated using a hybrid-receptor deposition model. [f] Geometric means. [g] Sum of listed PAHs.

velocity was 0.64 cm/s (summer) and 2.2 cm/s (winter). These V_d values are reasonable for coarse size particles >2.5 μm. Deposition velocities for PAHs were higher during the winter than in summer, similar to the results for TSP and PCBs. The increased flux during the winter may be due to the higher wind speeds that resuspended more soil and road dust than during the summer in Chicago. During LMMBS, dry deposition of metals was generally low during the winter (*63*), although high metal fluxes were observed in January 1995 during AEOLOS (*46, 58*). Typically, dry deposition is thought to be less during the winter due to frozen or snow covered soil (*78*), but there was no snow cover in Chicago during the January 1995 sampling period.

Over the near-shore area of southern Lake Michigan, the geometric mean atmospheric particle concentration of Σ-PAHs in July 1994 was 1.6 ng/m^3 (*55*), which is ~10× less than the urban signal during July. The summer dry flux over the lake was 0.86 μg/m^2-day, again an order of magnitude less than in Chicago. The resulting V_d estimate ranged from 0.24 to 4.3 cm/s for individual PAHs and was 0.61 cm/s for Σ-PAHs. For Σ-PAHs, the deposition velocity was the same in Chicago as a short distance offshore. This suggests that PAHs impacting the deposition plates at both sites were associated with similar particle sizes. However, fewer particles over the lake resulted in less deposition.

AEOLOS Results. The long-term measurements during LMMBS can be compared to short term "snapshots" of dry deposition obtained during AEOLOS. Figure 4 summarizes individual dry deposition measurements during July 1994 from all sites (see Figure 1), except in Chicago which is represented by the LMMBS August 1994 sample.

The flux of particle mass was about twice as high in Chicago as at the other sites, which had rather uniform depositions (Figure 4a). The majority of large particles generated within the urban corridor are deposited within a distance bounded by the ship's location < 15 km offshore. Elevated fluxes of PCBs were found in Chicago and Chiwaukee Prairie (Figure 4b). PCB deposition is lower offshore and at SBD. Slightly higher fluxes were observed along the eastern shore of southern Lake Michigan at SH and ID.

Figure 4c illustrates that dry deposition of PAHs is greatly reduced away from sources. Anthropogenic activity along
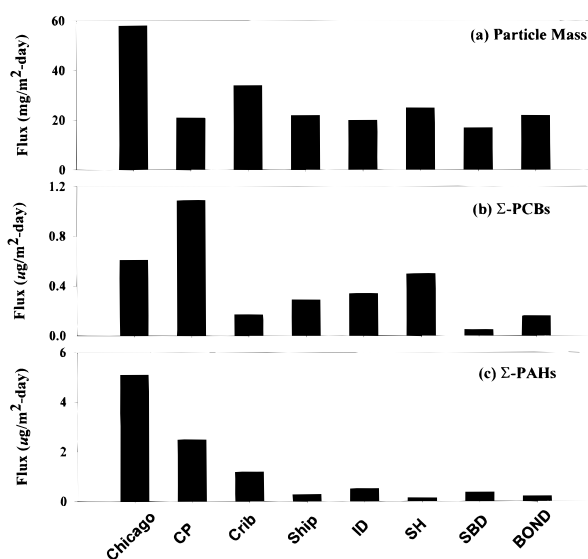

FIGURE 4. Dry deposition flux of (a) particle mass, (b) PCBs, and (c) PAHs during AEOLOS July 1994 (CP = Chiwaukee Prairie; Crib = 68th St. water-intake crib; Ship = R/V *Lake Guardian* at sites 5, 1, and 0; ID = Indiana Dunes; SH = South Haven; SBD = Sleeping Bear Dunes; Bond = Bondville).

the urbanized western shore significantly influences local atmospheric inputs, but fluxes dramatically decrease away from major emission sources. The dry deposition gradient with distance from Chicago is supported by metals data during AEOLOS. Average measured dry fluxes of Pb, Cu, and Zn in Chicago were approximately 70, 60, and 200 μg/m^2-day, respectively, but only 3, 10, and 10 μg/m^2-day offshore (*58*). Since large particles dominate dry deposition, the generation of these particles during anthropogenic activities or resuspension of soil and road dust increases local atmospheric loading over background levels that are dependent on the deposition of fewer large particles.

Loadings to Lake Michigan. The Chicago site was complimented by three off-shore sites (the 68th St. and Harrison St. water-intake cribs and the R/V *Lake Guardian*

TABLE 4. Particle Dry Deposition Loadings to Lake Michigan

PCB Congeners		PAHs	
chemical	loading[a] (kg/yr)	chemical	loading[a] (kg/yr)
17, 15	34	acenaphthylene	23
16, 32	12	acenaphthene	44
28, 31	23	fluorene	53
33, 53, 21	44	phenanthrene	971
52, 43	23	anthracene	149
44	60	fluoranthene	889
37, 42	24	pyrene	807
41, 71, 64	37	benzo[a]anthracene	467
70, 76	25	chrysene	429
66, 95	23	benzo(b+k)fluoranthenes	871
56, 60	17	benzo[e]pyrene	445
101	78	benzo[a]pyrene	394
110, 77	34	perylene	197
149, 123	7	indeno[c,d]pyrene	207
153, 132, 105	38	dibenzoanthracene	53
163, 138	7	benzo[g,h,i]perylene	280
187, 182	14	coronene	80
174	20		
170, 190	15	Σ-PAH	5030
201	19		
203, 196	26		
195, 208	16	Particle Mass	72×10^6
194	13		
total PCBs[b]	1090[c]		

[a] Calculated from data in Table 1 with geometric mean dry deposition flux at over-lake site impacting 2.6% of lake and flux at SBD influencing the remaining 97.4%. [b] Sum of congeners without dichlorobiphenyls. [c] Listed congeners represent approximately 55% of total PCB loading.

during AEOLOS) to evaluate the magnitude of dry deposition impacting the lake adjacent to the metropolitan area. The Sleeping Bear Dunes (SBD) site was chosen to characterize deposition to the remainder of the lake beyond direct urban influences.

Conservative dry deposition loadings to Lake Michigan were calculated assuming that the fluxes measured offshore of Chicago (Table 1) apply to an area 15 km × 100 km (~2.6% of Lake Michigan surface area) adjacent to the urban/industrial corridor and that the fraction of the year without precipitation is 0.9. Fluxes at SBD were applied to the remainder of the lake (5.63×10^{10} m^2). Inputs of PCBs are estimated to be ~1100 kg/yr by particle dry deposition (Table 4). This is of the same order of magnitude as inputs by air/water exchange (~880 kg/yr) (9, 11) and about 4–20× greater than estimated loadings by wet deposition, ~50–250 kg/yr (2, 18, 22, 56). Previous estimates for the dry deposition of PCBs ranged from ~16 to 170 kg/yr (2, 18, 22, 71). The estimated dry deposition loading of Σ-PAHs to Lake Michigan is ~5000 kg/yr. This compares with previous dry deposition loadings which range from 360 kg/yr (22) to 4000 kg/yr (74). Wet deposition loadings of PAHs are estimated to be ~1600 kg/yr (22).

In summary, lower limits of dry deposition result from measurements to a smooth plate with a sharp leading edge relative to a rough lake surface. Although the hydrophobic grease surface is susceptible to gas partitioning, correcting deposition to the exposed plates by individual field blanks resulted in distributions of PCBs and PAHs in this study that were very similar to patterns observed on atmospheric particles. Thus, surrogate surfaces are capable of providing reasonable dry deposition flux estimates in large spatial arrays.

Dry deposition will be elevated over background levels downwind of any area, whether agricultural farm field, dry lake bed, or urban/industrial center, where significant numbers of large particles are generated. The impact zone will depend on the size of the particles generated, their emission height, and ambient wind speed. In this study, we noted that dry deposition of PCBs and PAHs was reduced to near background levels within ~15 km offshore of Chicago but still dominanted by a few large particles. Deposition velocities ranging from ~0.8 to 3.5 cm/s for a variety of trace metals over the lake during July 1994 (46) are similar to the 0.6–0.9 cm/s velocities for PAHs and TSP, respectively, reported here. Thus, an approriate V_d for modeling dry deposition may range from ~0.5 to 2 cm/s to reflect the ability of a few large particles to dominate deposition even at locations distant from major sources.

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