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ARTICLE *in* ENVIRONMENTAL SCIENCE AND TECHNOLOGY · APRIL 1997

Impact Factor: 5.33 · DOI: 10.1021/es960798f

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Article

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Environ. Sci. Technol., **1997**, 31 (5), 1534-1538• DOI: 10.1021/es960798f • Publication Date (Web): 29 April 1997

Polychlorinated Biphenyls in Chicago Precipitation: Enhanced Wet Deposition to Near-Shore Lake Michigan

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To determine if elevated levels of atmospheric contaminants in urban areas enhance atmospheric deposition to adjacent surface waters, precipitation was sampled at three stations along a transect from Chicago, IL, across southern Lake Michigan. Rainwater was collected during several storms in July 1994 and January 1995 in southern Chicago aboard the R/V *Lake Guardian* positioned 15 km east of downtown Chicago and at a rural site along the southeastern shore of the lake as part of the study Atmospheric Exchange Over Lakes and Oceans (AEOLOS). Total PCB concentrations in Chicago precipitation ranged from 4.1 ng/L (January 19, 1995) to 189 ng/L (July 21, 1994) and were 2–3 orders of magnitude higher than the measured regional background concentrations. Concentrations of PCBs in urban precipitation were dominated by particle-bound congeners, implying PCB enrichment in rainwater due to efficient scavenging of highly contaminated particulate matter from the urban atmosphere. PCB levels in precipitation falling over southern Lake Michigan were from two to as much as 400 times greater than the measured regional background concentration, indicating that the "urban plume" of Chicago increases atmospheric deposition of contaminants to Lake Michigan over spatial scales of tens of kilometers. Enriched urban precipitation extending out over Lake Michigan provides 50–400% greater PCB wet deposition loadings than background precipitation.

Introduction

Inputs of toxic anthropogenic organic compounds, such as polychlorinated biphenyls (PCBs), have severely impacted the Great Lakes. Consequently, the magnitude of various PCB sources and internal cycling processes has been the focus of much research, with the relative significance of each process varying among the Great Lakes. Atmospheric deposition, both wet and dry, plays a strong role in contaminant cycling in Lakes Superior, Michigan, and Huron (*1*). Though airborne concentrations of PCBs are relatively constant throughout the entire Great Lakes airshed (*2*), atmospheric deposition provides 90%, 58%, and 78%, respectively, of the PCBs to the upper Great Lakes and only 13% and 7% to Lakes Erie and Ontario (*1*). Differences in relative importance depend greatly on hydraulic residence times, surface area to volume ratios, lake surface area to drainage basin area ratios, and relative strength of emission sources.

Recent studies suggest that elevated atmospheric concentrations of PCBs in the heavily developed greater Chicago area enhance PCB loadings to southern Lake Michigan (*3*–*5*). The elevated atmospheric concentrations in Chicago lead to large dry deposition fluxes of 3.8 –6.0 μg m^{-2} day^{-1} due to PCBs bound to extremely large (supermicrometer) aerosols (*6*). However, PCBs are also known to be effectively removed from the atmosphere by precipitation (*7*–*9*). Away from urban areas, dry deposition is not the major deposition mechanism delivering PCBs to Lake Michigan; wet deposition provides 80% of the total atmospheric deposition of PCBs to the surface of Lake Michigan (*10*).

The relation between atmospheric and precipitation concentrations has led to studies of both wet and dry deposition in such ecosystems as the Great Lakes (IADN; *2*) and the Chesapeake Bay (CBADS; *11*). These field studies utilized few sample sites operating continuously over long periods of time to determine seasonal trends in the regional contaminant concentrations and depositional fluxes. Yet, such field studies fail to address mesoscale influences (e.g., elevated urban concentrations) on deposition to coastal waters (*11*). Large wet deposition fluxes of PCBs (*12*) and inorganic contaminants (*13*) have been found in samples taken in Chicago, IL. Additionally, Capel *et al.* (*14*) reported highly enriched concentrations of organic contaminants in urban fogwaters of Dübendorf, Switzerland. Although fluxes of contaminants are known to be high in urban areas, the relation of urban fluxes measured over land to those deposited to coastal waters has previously not been investigated. Prior to this field study, decreasing wet deposition fluxes with distance from the urban center were expected. However, the prediction of high urban over-land fluxes extending out over southern Lake Michigan was highly uncertain. While rural overwater vs over-land airborne PCB concentrations have been shown to differ (*16*), extrapolation of such differences to concentrations in precipitation over near-shore urban waters was, at best, tentative.

The objective of this research was to quantify the concentrations and speciations of selected compounds in wet deposition over and around southern Lake Michigan. In this paper, we present concentrations (filter retained and nonfilter retained) of PCB congeners in discrete rain events around southern Lake Michigan in 1994. Large urban wet deposition fluxes of particle-bound PCBs extend from Chicago, IL, over, but not across, southern Lake Michigan.

Methods

As part of the Atmospheric Exchange Over Lakes and Oceans (AEOLOS) study, gradients in atmospheric deposition fluxes to Lake Michigan adjacent to Chicago, IL, were quantified. The lack of historical information available to anticipate the subregional scale variations in deposition rates led us to establish one mobile and two stationary sampling platforms covering a projected trajectory from Chicago out across Lake Michigan (Figure 1). This anticipated air mass trajectory was based on regionally prevailing southwesterly winds. In 1994 and 1995, precipitation samples were collected at these three sites to assess the impact of Chicago's urban contaminant plume on neighboring Lake Michigan. Precipitation was collected on an event basis and analyzed for organic contaminants. Automated precipitation samplers (1 m^2; *12*) were deployed at both the Chicago, IL, and South Haven, MI, sampling sites (41°50′04″ N by 87°39′29″ W and 42°27′52″ N

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S0013-936X(96)00798-5 CCC: $14.00

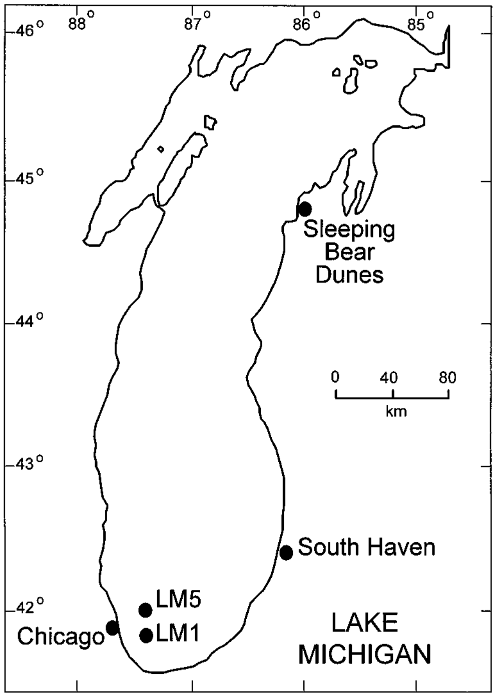

FIGURE 1. Location of precipitation sampling sites around southern Lake Michigan.

by 86°10′09″ W, respectively). Two manual sampling funnels were located aboard the U.S. EPA R/V *Lake Guardian* stationed on anchor at two water quality monitoring stations in southern Lake Michigan, LM5 and LM1 (42°00′00″ N by 87°25′00″ W and 41°46′00″ N by 87°20′00″ W, respectively), approximately 15 km east of downtown Chicago. Though these sampling locations are close to major shipping channels, no ships passed within 2 km during the sampling periods. During all sampling, the ship remained on a single anchor, allowing the wind to pass directly over the bow of the ship, thus the roll of the ship was minimized, keeping the funnel nearly level during sampling. During all precipitation events collected, wind speed, direction, air temperature, and relative humidity were recorded with commercially available sensors.

Details of the automated precipitation sampling method are presented elsewhere (*8, 9, 12, 16*). Precipitation was collected by means of an automated wet-only collector equipped with a 1 m^2 stainless steel collection funnel connected to an *in situ* filtration system consisting of a glass fiber filter (GFF; 90 mm diameter, Schleicher & Schuell No. 25), followed by a column of Amberlite XAD-2 resin. A visually small fraction of particles washed out during precipitation events adhered to the funnel surface rather than being washed onto the filter. To include these particles in a sample, the funnel was manually scrubbed with clean glass wool wetted with deionized water after each precipitation event. This funnel wipe sample was combined with the filter sample for analysis. Previous results (*17*) indicated that the funnel wash contained an important portion of the total particulate PCBs in rural areas and largely consisted of particles.

While rural, automated precipitation sampling has been performed with consistency and accuracy (*2, 8, 9, 12*), urban sampling suffers from unique problems not seen in rural studies. Automated rain sampling in an urban area, such as Chicago, can be plagued with problems related to the high ambient air concentrations and subsequently high field blanks. The high aerosol concentrations are the likely source of contamination to field blanks. Event-based precipitation sampling can help avoid such problems, with the cleaning and servicing of the sampler just prior to and immediately after an event. During setup and precleaning of the urban automated sampler, the funnel was washed and then wiped with glass wool. It was not uncommon to see particles collecting on the funnel in the short time it took to wipe the entire funnel. The presence of visibly large particles on the funnel may be verification of dry deposition of supermicrometer particles. These particles were not individually analyzed, and thus determination of whether they were of local (i.e., rooftop) or ambient atmospheric origin is not possible. The use of positive lock lids or positive pressure sampling trains during interevent periods might help solve the problem of high precipitation field blanks in urban areas.

Shipboard sampling was performed manually with two funnels (1 m^2 aluminum and 0.78 m^2 stainless steel) located atop the bridge on the R/V *Lake Guardian*. Prior to a rain event, the funnels were cleaned, and an 18-L stainless steel collection can (*Challenger VI*, Spartansburg Steel Products, Spartansburg, SC) was connected to the bottom of the funnels with 0.5 m of 0.5 cm i.d. Teflon tubing, allowing gravity transfer to the canister. After collection, pressurized clean air was used to push the collected rain water through a GFF (47 mm diameter; Schleicher & Schuell No. 25) and upward vertically through an XAD-2 column identical to those used in the automated samplers. Flow through the resin column was maintained at ∼200 mL/min by manual adjustment of the pressure in the collection container. When the filter became clogged, filtration was momentarily halted, the filter was replaced, and the process was resumed. Multiple filters for a single event were combined for analysis. In an attempt to collect particles that had settled or stuck to the side of the can during the filtration process, the collection can was rinsed three times with deionized water after processing all rainwater, and the resulting can washes were filtered and passed through the resin. After the rain event ended, the shipboard funnels were wiped in an identical manner as the automated rain samplers. All filter and wipe samples were stored frozen, and all resin samples were stored refrigerated in the dark.

Analysis. Concentrations of approximately 85 PCB congeners were measured in precipitation samples collected at three sites around and over southern Lake Michigan. Resin samples were Soxhlet extracted in 1:1 acetone/hexane for 24 h. Combined filter and wipe samples were Soxhlet extracted for 24 h in methanol followed by 24 h in dichloromethane. After extraction, all samples underwent liquid/liquid back-extraction with slightly salted deionized water to remove inorganic salts and other water-soluble compounds. The samples were then fractionated into two eluents on a Florisil (60−100 mesh; J. T. Baker Co., Phillipsburg, NJ) column (*18*) to remove interferences. Laboratory spike analysis revealed that the first Florisil fraction contained 95.6 ± 1.0% of the total PCBs, and the second fraction contained 4.9 ± 0.9% (average ± standard error), and as such only the first Florisil fraction was analyzed. Concentrations of PCB congeners were determined by capillary gas chromatography and electron capture detection using a Hewlett-Packard 5980 GC equipped with a ^{63}Ni electron capture detector and a 60 m DB-5 capillary column (0.32 mm i.d and 0.25 mm film thickness). Following the procedure of Mullin (*19*), a 610 ng/mL PCB solution was made, and congeners were identified based on relative retention times. A single calibration standard was used to generate daily response factors for each congener relative to two non-industrially synthesized PCB internal standards (*20*). In instances where congeners were not chromatographically resolved, their combined concentrations were calculated. Total PCB concentrations in each phase were calculated as the sum of 36 resolved congeners and 23 unresolved pairs.

High contaminant levels in filter samples collected in Chicago, IL, caused some analytical difficulties. After extraction and liquid/liquid back-extraction, red solids precipitated upon transfer from dichloromethane to hexane. This precipitate was removed by filtration through a clean sodium sulfate column packed under glass wool. Furthermore, due to the extremely high concentrations in filter samples and to

TABLE 1. Meteorological Conditions during Precipitation Events around Southern Lake Michigan

date	location	rain (mm)	wind dir[a]	air temp[b] (°C)	wind speed[c] (m/s)	start time (CST)	duration (h:mm)	Σ-PCB concn (ng/L)	% on filter	storm type
7/19/94	Chicago	13.10	176	24	2.9	06:00	1:30	13.3	94	localized thunderstorm
	LM5	1.37	210	21	10.3	06:30	1:35	0.37	92	localized thunderstorm
7/20/94	Chicago	7.39	261	22	3.6	20:35	1:25	189	83	convective thunderstorm
	LM5	6.35	240	22	17.9	21:05	1:25	0.34	44	convective thunderstorm
	S. Haven	12.18	189	19	2.3	20:40	10:05	0.17	66	convective thunderstorm
7/21/94	Chicago	18.00	241	19	2.6	20:00	12:00	8.2	72	cold front
	LM1	13.11	245	19	2.2	21:00	13:00	7.2	98	cold front
	S. Haven	3.00	208	19	2.2	23:00	8:15	0.02	100	cold front
1/19/95	Chicago	22.55	226	3	5.4	22:00	17:50	4.1	79	cold front

[a] Mean wind direction during rain event. [b] Mean air temperature during rain event. [c] Mean wind speed during rain event; see Figure 1 for locations.

ensure reliable chromatography only one-tenth of the total raw extract was cleaned on the Florisil column. The subsamples were analyzed in the same manner as all other samples and blanks, with the resulting analyte masses appropriately corrected.

Quality Assurance. Average recoveries of analytical surrogates spiked into each sample prior to analysis (resins, 83% ± 5%; 76% ± 6%; 72% ± 4%; filters, 91% ± 2%; 74% ± 8%; 83% ± 4%; congener nos. 14, 65, and 166, respectively; av ± se) indicated no correction for laboratory biases was necessary. At each site during each of the sampling intensives, field blanks were taken in an identical manner as samples by passing 500 mL of deionized water through the sampler. The masses of individual congeners in samples were compared to those found in the phase-specific field blank. A blank-based limit of detection was calculated for every congener in each sample as three times the respective field blank. Blank filtering was performed when the measured mass of a congener did not exceed the respective blank-based limit of detection. Congeners that were not above the sampling site specific, blank-based limit of detection are not reported in the following results. Therefore, the respective field blanks contained less than one-third of the level of analyte in all samples presented here.

Results

Storm Descriptions. All precipitation events during May 17–19 and July 17–28, 1994 were collected at each of the three locations described above. Furthermore, a single event was collected on January 19, 1995, at the Chicago sampling site. During the May 1994 sampling period, no precipitation fell at any of the sites. Though 14 discrete precipitation events were collected and analyzed, with a wide range of rain volumes and PCB concentrations, those storms that did not deliver rain to more than one sampling location are not described here in detail. However, the single January 19, 1995, rain event collected in Chicago has been included due to the unique sampling conditions. During three consecutive storms on July 19, July 20, and July 21, 1994, precipitation fell sequentially on multiple sampling locations. The first of these three storms was a localized thunderstorm, which did not carry across the lake. The storm on July 20 was a convective thunderstorm associated with an advancing warm front. This storm stalled over the eastern edge of Lake Michigan, producing a longer duration precipitation event at South Haven than at the other two locations. The third event was a slower moving storm associated with an advancing cold front. Lowest precipitation rates were measured during this storm, yet highest precipitation amounts were collected. Rainfall intensities ranged from 0.4 mm/h (July 21, 1994, in South Haven, MI) to 8.7 mm/h (July 19, 1994, in Chicago). Further details of the events are presented in Table 1.

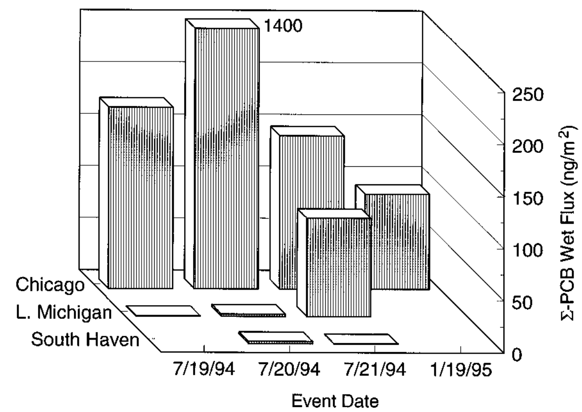

FIGURE 2. Total PCB wet fluxes by storm event at locations around southern Lake Michigan.

PCBs in Rainwater. Wet deposition total PCB fluxes (resin + filter) by event ranged from 0.05 ng/m^2 at South Haven on July 21, 1994, to 1400 ng/m^2 in Chicago on July 20, 1994 (Figure 2). Highest fluxes were measured in Chicago rainwaters, with single event fluxes of 174, 1400, and 147 ng/m^2 during three consecutive storms during July 1994 and 91 ng/m^2 in January 1995. Fluxes to southern Lake Michigan were 0.50, 2.2, and 94 ng/m^2 during the same three consecutive storms. The wet deposition fluxes over Lake Michigan were from 1 to 1800 times greater than the fluxes measured at South Haven, MI, which were 2.0 and 0.05 ng/m^2 (July 20 and 21, 1994, respectively). Among the three sampling locations, total PCB concentrations ranged from 0.02 to 189 ng/L. Highest concentrations were measured in Chicago, with concentrations of 13, 189, and 8.2 ng/L during three consecutive storms in July 1994 and of 4.1 ng/L in January 1995. Concentrations in precipitation collected over southern Lake Michigan were 0.37, 0.34, and 7.2 ng/L during the three consecutive storms in July 1994. PCB concentrations in precipitation falling over Lake Michigan were two to as much as 400 times greater than the regional background concentrations measured at South Haven, MI (0.17 and 0.02 ng/L, July 20 and 21, 1994). Concentrations of total PCBs in rainwater from the rural site were lower than the volume-weighted mean PCB concentration measured by the IADN network at Sleeping Bear Dunes, MI (1.05 ± 0.23 ng/L; 1992 annual average; *2*), suggesting that the regional background signal was sampled at South Haven.

Volume-weighted mean (VWM) concentrations at the three locations were 29.3, 5.8, and 0.1 ng/L (Chicago, IL, $n = 6$; Lake Michigan, $n = 5$; South Haven, MI, $n = 3$, respectively; Figure 3). The standard error of the weighted mean (SEM_w) was calculated for each sampling location as an approximate ratio variance as expressed by Endlich *et al.* (*21*). The following formula used to calculate the SEM_w was given in an IADN data report by Gatz *et al.* (*2*):

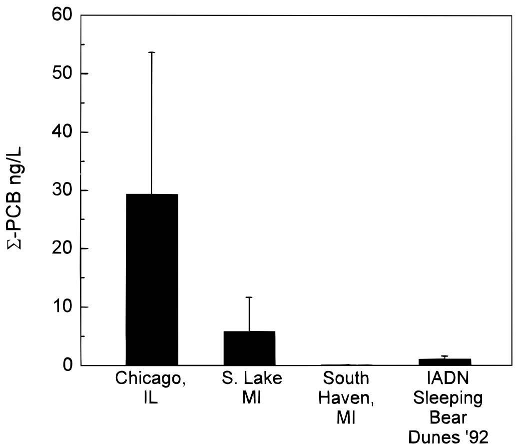

FIGURE 3. Concentrations and speciations of PCB homologs in precipitation around southern Lake Michigan precipitation. All concentrations are in nanograms per liter. Note the scale differences between samples.

$$(\mathrm{SEM_w})^2 = \frac{n}{(n-1)(\sum P_i)^2}\left[\sum(P_iX_i - \overline{PX_w})^2 - 2\overline{X_w}\sum(P_i - \bar{P})(P_iX_i - \overline{PX_w}) + \overline{X_w}^2\sum(P_i - \bar{P})^2\right]$$

where P_i is the precipitation amount of sample i, X_i is the concentration in sample i, $\bar{P}$ is the mean precipitation amount for samples 1 to n, and $\overline{X_w}$ is the precipitation weighted mean concentration. The $\mathrm{SEM_w}$ for the volume-weighted mean concentrations at each location were determined to be ±24.0, ±5.7, and ±0.04 ng/L (Chicago, Lake Michigan, and South Haven, respectively). A combined volume-weighted concentration for "urban-influenced" precipitation, calculated by including all over water samples ($n = 5$) with all urban precipitation samples ($n = 6$), is 23.2 ± 15.3 ng/L (VWM ± $\mathrm{SEM_w}$). This urban-influenced VWM concentration is strongly dominated by the high concentration event in Chicago on July 20, 1994.

Discussion

Highest VWM PCB concentrations were measured in Chicago, with the concentration decreasing across the lake to background levels at South Haven, MI. The measured concentrations gradients are indicative of the Chicago urban plume depositing PCBs to Lake Michigan over spatial scales of tens of kilometers. Low volume samples collected had little effect on the site-specific volume-weighted mean concentrations, with the VWM concentration at Chicago decreasing from 29.7 to 29.3 ng/L upon inclusion of two low volume (~1 L) independent storms collected in Chicago.

In two successive storms (July 20 and 21, 1994), concentration ratios of total PCBs changed dramatically from 1128:2:1 to 470:416:1 (Chicago:Lake Michigan:South Haven). While the meteorological conditions changed significantly (strongly convective thunderstorm associated with a warm front vs cold front), these storms both exhibited decreasing PCB rainwater concentrations with distance from Chicago. Such decreases suggest sequential washing out as the air mass progressed from Chicago across Lake Michigan to South Haven.

In general, higher PCB precipitation concentrations occurred when the fraction of PCBs retained on the filter was greater (Figure 4). Additionally, events that had the highest concentrations at the urban and overwater sites were distinguished by homolog distributions dominated by particle-bound tetrachlorinated biphenyls. In both the July 19 and 20, 1994, storms, total PCB concentrations were much higher in Chicago than over Lake Michigan. However, in the storm on July 21,1994, in which total PCB concentrations measured in Chicago were low (8.2 ng/L) relative to the previous events (13 and 190 ng/L), concentrations over the lake were the highest measured (7.2 ng/L). The lower concentration in Chicago rainwater collected on July 21, 1994 is indicative of less efficient scavenging of the urban air during this storm. The higher concentrations deposited to southern Lake Michigan on July 21, 1994, may be due to incomplete washout of aerosol-bound PCBs while the storm was over Chicago and subsequent transport out over the lake before deposition. However, this sample was collected at a different site from the other over water samples presented in detail here, and the high concentration observed may be due to collection of rainwater that fell through a higher concentration plume existing within the Chicago urban atmosphere. In all samples presented here, urban and overwater precipitation contained significant amounts of particle-bound PCBs implying enrichment due to efficient scavenging of highly contaminated particulate matter from the urban atmosphere.

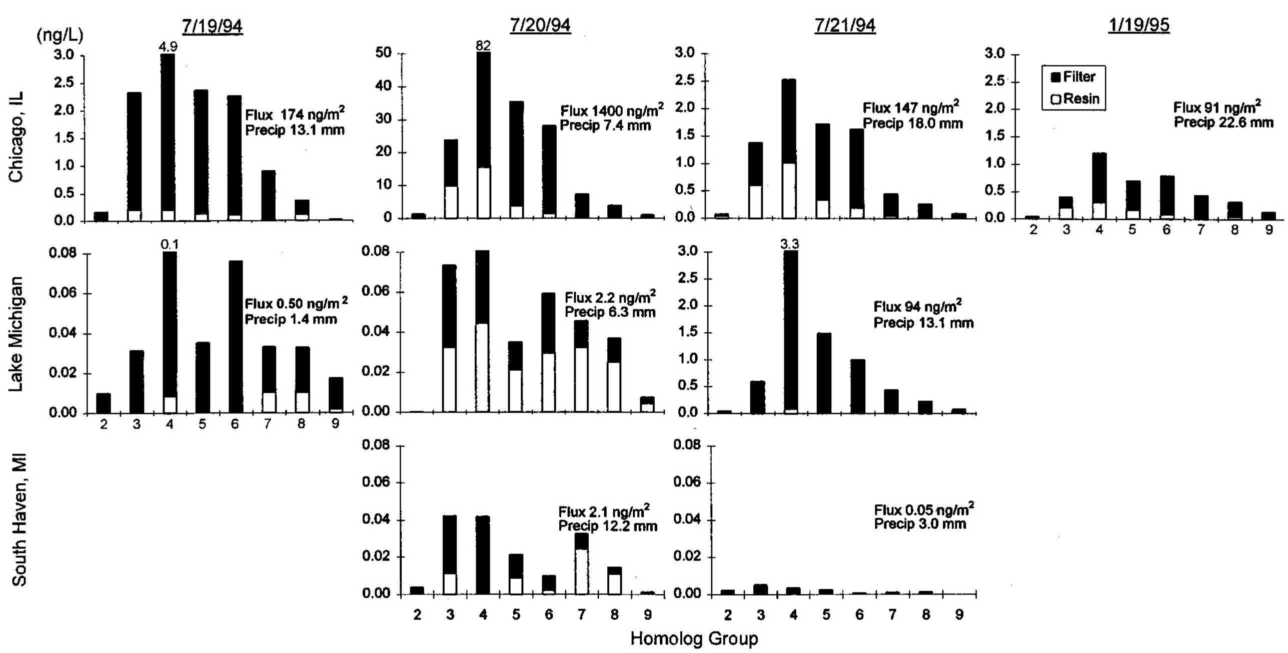

FIGURE 4. Volume weighted mean concentrations of Σ-PCBs in precipitation around southern Lake Michigan (VWM ± $\mathrm{SEM_w}$).

Total PCB concentrations measured in precipitation at South Haven, MI, are comparable to those measured at Sleeping Bear Dunes, MI, as part of the Integrated Atmospheric Deposition Network (IADN; *2*). Different quantification and more stringent blank filtering methods performed in this study account for the difference. Approximately 85 congeners were quantified in this study, with the 35 congeners quantified in IADN accounting for >90% of PCBs in all samples presented here. Likewise, a comparison to concentrations found earlier in Chicago precipitation (104 ± 78 ng/L, $n = 22$; *13*), shows comparable results for urban precipitation.

A demonstrative calculation of current annual lakewide PCB wet deposition flux was performed using the simple equation:

$$\text{lakewide annual wet deposition} = [B(1 - f) + (Uf)]PA$$

where P is the yearly rain (lakewide 90 year average) − 0.795 m/yr (*22*); B is the background Σ-PCB concentration in rainwater 1.05×10^{-9} kg/m^3 − IADN 1992 annual average Sleeping Bear Dunes, MI (*2*); U is the urban-influenced Σ-PCB rain concentration $= 23.2 \times 10^{-9}$ kg/m^3—(this study); f is the fraction of lake with urban-influenced precipitation; A is the area of lake − 5.775×10^{10} m^2.

With wet deposition at background concentrations only, 50 kg of PCBs are input into Lake Michigan by wet deposition annually. This simplified calculation of background wet deposition loading to Lake Michigan agrees well with the loading of 52 ± 13 kg/yr determined by Hoff *et al.* (*23*). Inclusion of the urban-influenced wet deposition over 5% of Lake Michigan's surface area increases annual lakewide PCB wet deposition to 100 kg. Enriched urban precipitation extending over a greater fraction of the lake's surface area increases lakewide wet deposition even further, with 10% and 20% of the lake influenced translating into 150 and 250 kg of PCBs deposited, respectively. Thus, a small area of the lake influenced by enriched precipitation strongly influences lakewide wet deposition to Lake Michigan. With such high Σ-PCB concentrations in urban precipitation, not much of the lake area needs to be influenced to greatly increase the yearly lakewide wet deposition loading. From the samples collected here, the urban influence clearly extends out from Chicago, sometimes only a few kilometers, and sometimes tens of kilometers out over Lake Michigan. With the limited number of samples collected, we estimate that between 5 and 20% of the lake is influenced by the enriched urban precipitation. This initial calculation indicates that highly enriched rainwater in and near Chicago is a significant input of PCBs to Lake Michigan in relation to "background" wet deposition to the rest of the lake.

In summary, Σ-PCB wet fluxes and concentrations in Chicago rainwaters are extremely high. The concentrations and distributions of PCBs in precipitation collected from urban, over water, and rural locations support the hypothesis that washout of urban atmospheric PCBs is a major source to coastal Lake Michigan near Chicago. Filter retained congeners provide, on average, 82% of the PCB mass deposited during urban rain events. High wet deposition fluxes of up to 94 ng/m^2/event extend out over Lake Michigan on the order of tens of kilometers, yet do not extend completely across the lake. Urban and over water total PCB fluxes are highly variable, suggesting meteorology plays a significant role in controlling the magnitude of the urban wet deposition flux to Lake Michigan. Estimation of yearly average wet deposition fluxes to Lake Michigan shows a strong urban influence on the lakewide wet deposition of PCBs. This calculation indicates that highly enriched rainwater in and near Chicago increases the lakewide PCB wet deposition inputs to Lake Michigan, accounting for 50 to 400% greater loadings than lakewide background wet deposition.

Acknowledgments

We wish to express our appreciation to Steve Eisenreich for guiding the AEOLOS project, to Captain Ronald Ingram and crew of the EPA R/V *Lake Guardian* for assistance in collection of samples, to Tom Holson of Illinois Institute of Technology for access to the Chicago sampling site and laboratory space, to George S. Vadas and Mike C. Granger for field collection and sampler maintenance, and to Bernard S. Crimmins and Cheryl A. Clark for laboratory assistance. The AEOLOS project was funded by a grant from the U.S. Environmental Protection Agency, AREAL (EPA CR 822046-01-0), Project Officer Alan Hoffman. This is the University of Maryland Center for Environmental and Estuarine Studies Contribution No. 2789.

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Received for review September 16, 1996. Revised manuscript received December 30, 1996. Accepted January 7, 1997.⊗

ES960798F

⊗ Abstract published in *Advance ACS Abstracts,* March 1, 1997.