Accumulation of Atmospheric and Sedimentary PCBs and Toxaphene in a Lake Michigan Food Web

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Seston, sediment, settling organic matter, and food web members were collected from Grand Traverse Bay, Lake Michigan, between April 1997 and September 1998 to examine PCB and toxaphene biomagnification. Stable isotopes of nitrogen and carbon were analyzed in samples and used to establish trophic structure of the food web and to determine the importance of atmospheric versus sedimentary sources in delivering PCBs to the food web. Nitrogen isotopes were confounded by multiple variables in this system, particularly seasonal variation, and did not display a simple pattern of enrichment among trophic levels. However, δ13C displayed little seasonal variation and was positively correlated with PCB concentrations among food web members (r² = 0.69). Plots of δ13C vs PCBs separate food web members into three distinct groupings comprised of invertebrates, primary forage fish, and predatory fish. Stable isotope values of the primary organic sources indicate that the atmosphere, and not the sediment, is the most likely source of PCBs to the food web of Lake Michigan. Additionally, we suggest that seston may be important in delivering PCBs to pelagic food web members and species that receive a majority of their nutrition through pelagic sources. In contrast, settling particles are implicated in delivering PCBs to benthic organisms and Mysis relicta.

Introduction

Polychlorinated biphenyls (PCBs) and toxaphene are organochlorine contaminants that have been studied frequently in aquatic systems due to their bioaccumulative and toxic nature (1–3). Since the ban on PCB and toxaphene use and production, concentrations have decreased significantly in the atmosphere and water column surrounding the Great Lakes area (4, 5). PCB concentrations in fish tissue also decreased (6) until the mid-1980s when an apparent stabil-

ization in lake trout PCB body burdens was observed (7). It is unclear as to what processes are supporting this trend, but several theories implicate continued atmospheric deposition and/or efficient recycling from sediments (8). Yet others contend that this is a natural consequence of non-steady-state responses of internal reservoirs (9, 10).

The atmosphere is believed to be a primary source of PCBs and toxaphene to the surface waters of the Great Lakes. Through air–water exchange processes, the levels of these contaminants are sustained in the dissolved phase, which lead to their exposure in the plankton community (11–13). Sediments are a sink for hydrophobic contaminants such as PCBs as they become sorbed to settling particles and are buried. However, several studies have indicated that this is an inefficient process for PCB burial and that a large percentage of these contaminants are recycled within the benthic environment (4, 8). Evidence suggests that recycling of contaminated sediment through benthic infraunal organisms may be supplying PCBs to top predators of the food web such as lake trout (14, 15). The motivation behind this study was to evaluate the influence of atmospheric versus sedimentary sources of PCBs and toxaphene to the top fish predators, primarily lake trout, using stable isotope correlations.

This research was conducted as part of an extensive study on contaminant dynamics in Grand Traverse Bay (GTB), Lake Michigan, and data have already been published describing biogeochemical cycling of seston in the water column (16). The goal of this project was to determine the predominant pathways by which PCBs are transferred from the atmosphere, water, and sediment to the upper trophic level biota using stable isotopes as tracers. In this paper, we present our findings on PCB and toxaphene burdens within the biotic compartments and correlate these burdens to their size, lipid content, and isotopic values to determine the primary variables influencing contaminant biomagnification.

Experimental Section

Sample Collection. Sampling was conducted in Grand Traverse Bay (GTB), Lake Michigan, from April 1997 through September 1998. Benthic invertebrates, Diporeia aestivalis (amphipoda) and Mysis relicta, were sampled along with both an inner bay track, GT1 (44°50.0 N, 85°37.4 W to 44°52.0 N, 85°37.4 W), and an outer bay track, GT3 (44°58.5 N, 85°24.5 W to 44°58.6 N, 85°24.5 W), and during daylight hours monthly from April through September of both years. Invertebrates were collected with trawls and adjustable benthic sled deployments. Benthic invertebrate taxa were separated, and a subset was frozen for isotope and contaminant analyses. Plankton samples were collected between 0 and 80 m using oblique tows with a 1 m diameter plankton net with a 153-mm mesh at two sites in GTB during April through September of both years. Planktonic samples were filtered onto glass fiber filters and frozen until analysis.

Alewife (Alosa pseudoharengus), bloater (Coregonus hoyi), and deepwater sculpin (Myoxocephalus thompsoni) were collected from their pelagic, demersal, and benthic habitats, respectively, along with their potential invertebrate prey. Alewife and bloater were collected primarily by use of two 100-ft panels of bottom-set 1–3-in. stretched mesh gill nets fished for variable periods of time between 6 and 24 h at both sites. Deepwater sculpin were collected with a benthic sled fitted with a 750-μm mesh net with a 90 cm × 60 cm mouth along the inner track and outer bay benthic sled track in April and May, and with an otter trawl (5-mm mesh cod

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analyses. Additional fishes collected included rainbow smelt (Osmerus mordax), round whitefish (Prosopium cylindraceum), lake trout (Salvelinus namaycush), salmon (Salmo solar sebago), and burbot (Lotida lota). All fish collected were composited by size classes (their lengths and mass recorded) and then wrapped in aluminum foil and frozen for contaminant and isotope analyses.

Extraction and Analysis. In the field, invertebrates were sorted into large and small size classes when possible. Fish samples were composited according to species, month of collection, and size class when sufficient numbers were available. All biota samples were homogenized whole, extracted, and analyzed for a suite of PCBs as reported in Stapleton (17). Toxaphene was quantified using a GC/ECNI method reported in Glassmeyer et al. (18). Briefly, wet homogenized tissue was ground with sulfuric acid using a mortar and pestle and Soxhlet extracted for 24 h using dichloromethane. PCB surrogates (3,5-dichlorobiphenyl, IUPAC congener 14, and 2,3,4,4′,5,6-hexachlorobiphenyl, IUPAC congener 146) were added previously to Soxhlet extraction for quality assurance. Lipid content was measured using a gravimetric method as reported in Kucklick et al. 

Laboratory extraction of this material resulted in PCB levels averaging 101 \pm 27\% of the certified levels. Laboratory matrix blanks consisted of approximately 30 g of granulated Na2SO4 spiked with surrogate PCB and toxaphene levels for each species sampled are listed in the Supporting Information (Table 1) in addition to their sample size and average lipid content. Despite sampling for plankton at two different locales within GTB, no statistically significant differences in our measurements were evident between the sites. Therefore, all plankton samples were assumed to be collected from the same area, and sample site was not a variable in our analyses. Additionally, fish caught at various locations around our sampling sites of GT1 and GT3 were composited together, and again sampling site was not a variable in our analyses.

PCB and toxaphene concentrations, 1800 and 1200 ng/g wet weight (ww), respectively, were highest in the one individual burbot (L. lota) sampled (Figure 1). The lowest concentrations observed were found in M. relicta, 12 \pm 4.4 and 5.0 \pm 2.3 ng/g ww (n = 8), for PCBs and toxaphene, respectively. Lake trout had relatively high concentrations of both contaminants, averaging 1200 \pm 460 ng/g ww in PCBs and 440 \pm 160 ng/g ww in toxaphene. These values are comparable to recently reported values (approximately 1400 ng/g ww) on Lake Michigan lake trout from the USGS contaminant monitoring program that has surveyed all five of the Great Lakes (22) and are lower than historical values of lake trout PCB burdens in the Great Lakes (6). Generally, species were enriched in PCBs relative to toxaphene with one exception, deepwater sculpin (M. thompsoni). Average PCB concentrations in sculpin were 120 \pm 54.2 ng/g ww, in contrast to the toxaphene burdens that averaged 230 \pm 105 ng/g ww. Using a standard nonpaired t-test statistic, the mean toxaphene and PCB concentrations are significantly different (p < 0.01) in sculpin.

Compared to recently reported values of PCB concentrations in Lake Superior’s food web (2), PCB levels in GTB are 2–10 times higher among species. Historically, Lake Michigan biota have possessed higher concentrations of PCBs (6) despite the comparable levels of PCBs in the dissolved and particulate phases of the water column (4, 23). This disparity may reflect differences in both the physical dimensions of these lakes and the local loadings (13).

Toxaphene levels in Lake Superior’s biota (2) are higher than those measured here, especially within bloater (C. hoyi) tissue. Bloater in Lake Superior are among the most highly contaminated species with respect to toxaphene (1100 \pm 260 ng/g ww), while the same size bloater population in GTB display very low toxaphene concentrations (92 \pm 32 ng/g ww). Toxaphene levels in Lake Superior have been notoriously high relative to the other Great Lakes, reflecting either differences in limnological processes within the lake or indicating nonatmospheric sources of toxaphene to Superior

Results and Discussion

PCB and Toxaphene Concentrations. Average PCB and toxaphene levels for each species sampled are listed in the Supporting Information (Table 1) in addition to their sample size and average lipid content. Despite sampling for plankton at two different locales within GTB, no statistically significant differences in our measurements were evident between the sites. Therefore, all plankton samples were assumed to be collected from the same area, and sample site was not a variable in our analyses. Additionally, fish caught at various locations around our sampling sites of GT1 and GT3 were composited together, and again sampling site was not a variable in our analyses.

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![FIGURE 1. Average PCB and toxaphene concentrations within species sampled over the 1997–1998 sampling season.](image-url)
The disparity in toxaphene biota burdens between these two closely related systems may reflect differences in loadings and cycling of toxaphene within the water column or be indicative of different feeding habits of the bloater between the two systems.

Factors Affecting Bioaccumulation. Many variables including size, age, lipid content, length, and trophic position affect contaminant biomagnification. In this study, we were able to monitor the size, lipid content, and trophic position of the food web in GTB and will discuss their influence on PCB and toxaphene body burdens. A companion paper is in preparation describing the seasonal effects observed through this study (26).

Size or Age. The influence of age on the biomagnification of hydrophobic contaminants in fish can be significant considering the long environmental half-lives of these compounds, some of which are estimated to be as high as 20–30 yr (5, 13, 27). Through extensive sampling efforts in this project, we were able to collect a large number of deepwater sculpin ranging in size from approximately 60 to 190 mm that could be separated into five distinct size classes. As seen in Figure 2, both PCB and toxaphene burdens are correlated with size class of sculpin ($r^2 = 0.83$ and 0.64 for PCBs and toxaphene, respectively; Figure 2). PCB burdens in sculpin $<100$ mm are $60 \pm 19$ ng/g ww and increase to $190 \pm 25$ ng/g ww in fish $>161$ mm. Toxaphene concentrations range from $94 \pm 42$ in sculpin $<100$ mm and increase to $340 \pm 121$ ng/g in fish $>161$ mm. Deepwater sculpin $<100$ mm have comparable levels of both PCBs and toxaphene; however, large sculpin have significantly higher toxaphene burdens ($p < 0.01$) as compared to PCBs. This may indicate that the half-lives of toxaphene in fish tissue are greater than for PCBs since fish length is typically correlated to age.

Lipid Content. Figure 3 displays the relationship observed between $\Sigma$PCB and toxaphene concentrations correlated to lipid content among species. The observed correlation and slope is greater for $\Sigma$PCBs as compared to toxaphene, and as much as 60% of the variability in $\Sigma$PCB body burdens can be attributed to changes in lipid content based upon the regression analysis. This is comparable to trends observed in Lake Ontario (3), Lake Baikal (19), and Lake Superior (2), where as much as 82%, 99%, and 81% of the variability in $\Sigma$PCB burdens was associated with lipid content, respectively. However, lipid normalization does not remove the variability in contaminant body burdens among species, indicating that other factors are important.

Monitoring of contaminant residues in bloater (C. hoyi) in Lake Michigan over the past 30 yr has revealed a reduction in both the contaminant levels and the average lipid content of the species (28). Within Lake Michigan, the average lipid content of whole fish in comparable size bloater was measured at 22% in 1969; it was measured at 11.9% in 1986; and in our study, the average lipid content observed was 2.4%. This reduction may be a consequence of dietary shifts, competition for resources, or changes in the productivity of the system; all of which can influence contaminant assimilation by food web members (29).

Trophic Position. Nitrogen isotopes are useful indicators of trophic position and are therefore often employed in bioaccumulation studies (19, 30–32). As seen in Figure 4, the range in both $\delta^{15}N$ and $\delta^{13}C$ is approximately $6-7\%$o among the food web members, indicating comparable fractionation in both carbon and nitrogen. Other studies have observed similar trends, although the range in $\delta^{13}C$ fractionation displayed in GTB is greater than most studies (33, 34). The high correlation between these stable isotopes, in
addition to the C:N ratios reported in McCusker et al. (16), indicate that this system is less influenced by external factors such as terrestrial nutrient input (allochthonous production).

The observed relationship between ln PCB and $\delta^{13}$C values is provided by the regression equation ln PCB = 0.39 $\delta^{13}$C + 0.089 ($r^2 = 0.29$, Figure SA). The relationship between these two variables is weaker than found in previous studies on Lake Superior (2), Lake Ontario (3), and Lake Baikal (19). However, the slope of the regression analyses in this food web is greater than the slopes calculated in Lake Superior and Lake Ontario and equivalent to the study in Lake Baikal, indicating greater biomagnification in the food web with each trophic level. Regression analysis between toxaphene and $\delta^{15}$N revealed a similar correlation with respect to $\delta^{15}$N.

Our study encompassed seasonal sampling, and there was a seasonal trend in the nitrogen isotope signals of alewife, zooplankton, and D. hoyi. For example, zooplankton collected in April had a $\delta^{15}$N signal of 14% which decreased to a value of 8% by September. Seasonal shifts in $\delta^{15}$N within a species confounded the use of $\delta^{15}$N to estimate trophic position.

In contrast, carbon isotopes within a species displayed very little seasonal variation over the sampling period. A significant relationship was observed between ln PCBs and the $\delta^{13}$C content of food web members ($r^2 = 0.69$, $p = 0.001$; Figure 5B). This correlation separated organisms into three distinct groupings, which supported the parallel stomach content analyses. Invertebrate species represent an important link in the transfer of contaminants from phytoplankton and particulate material within the water column to forage and predatory fish. The carbon isotope values of the three invertebrate species were within a narrow range (~28.3 to ~26.0%), and all were relatively low in PCBs and toxaphene. We classify them as trophic level 2 species since they feed predominantly upon phytoplankton and particulate organic matter, which have been found to have $\delta^{13}$C values in GTB ranging from ~30 to ~25% (16). The $\delta^{13}$C values of the forage fish bloater, alewife, and deepwater sculpin range from ~25.0 to ~23.2%. These fishes were more enriched in PCB burdens, and we classify them as trophic level 3. Finally, the top predators in our system (burbot, salmon, lake trout, and our largest whitefish possess $\delta^{13}$C values ranging from ~22.1 to ~21.2%) are classified as trophic level 4 and are very enriched in contaminants. Carbon isotopes have previously been of little use in defining trophic levels in aquatic systems due to little fractionation of the isotopes between predator and prey in laboratory studies (35) and the substantially different $\delta^{13}$C values of terrestrial versus aquatic organic matter (36). However, in this study, we have shown that carbon isotopes do fractionate through the food web and can be used to assess biomagnification.

The correlation between $\delta^{13}$C and PCB burdens has an inherent problem in the interpretation due to the covariance between lipid and $\delta^{13}$C. With each increase in trophic level ($\delta^{13}$C), there is a direct increase in contaminants related to trophic transfer and an indirect rise in contaminants related to an increasing lipid content with increasing trophic level. From this relationship, it seems apparent that some of the variability in the contaminant burdens among trophic levels is driven by differences in lipid content. To deduce the relative importance of these direct and indirect effects of trophic level on contaminant burdens, path analysis was performed using the values from the PCB food web regressions.

In using path analysis, we assume that trophic level (as estimated by $\delta^{13}$C) controls PCB levels in biota through two paths. Through one path, trophic level influences lipid content, and lipid in turn controls PCB levels. Through a second path, trophic level has a direct influence on PCB levels through trophic transfer. Using this technique, we can estimate the relative contributions of these two paths to the observed correlation between PCB burden and trophic level. Path analysis calculates path coefficients from the correlation matrix among variables and quantifies the relative importance of the two different pathways (37). The correlations ($r$) between $\delta^{13}$C and PCBs, PCBs and lipid, and lipid and $\delta^{13}$C are 0.64, 0.79, and 0.58, respectively. The direct and indirect control of trophic level ($\delta^{13}$C) on PCB burdens is given by

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**FIGURE 4.** Biplot of the average carbon and nitrogen isotope values of the food web members, seston, and sediment.

**FIGURE 5.** Log natural $\Sigma$PCB burdens among species correlated to their respective (A) $\delta^{15}$N and (B) $\delta^{13}$C signature. ZP, zooplankton; DP, Diporeia hoyi; MY, Mysis relicta; SC, Myoxocephalus thompsoni; SM, Osmerus mordax; AL, Alosa pseudoharengus; BT, Coregonus hoyi; WF, Prosopium cylindraceum; LT, Salvelinus namaycush; SA, Salmo solar sebago; BB, Lota lota.
correlation between \( \delta^{13}C \) and \( \sum \text{PCBs} \) = 
\[ \delta^{13}C \rightarrow \sum \text{PCBs} \] 
\[ (\delta^{13}C \rightarrow \text{lipid}) \times (\text{lipid} \rightarrow \text{PCBs}) \] 
coefficient

The path coefficients are \( (\delta^{13}C \rightarrow \sum \text{PCBs}) = 0.27, (\delta^{13}C \rightarrow \text{lipid}) = 0.64, \) and \( (\text{lipid} \rightarrow \sum \text{PCBs}) = 0.58. \) From this, the coincident increase in lipid content with trophic level (the indirect path, \( 0.64 \times 0.58 = 0.37 \) ) exerts more influence on \( \sum \text{PCBs} \) than does the increase due solely to trophic level (the direct path = 0.27). Therefore, the increase in \( \sum \text{PCB} \) body burdens with increasing \( \delta^{13}C \) is influenced by increases in lipid content.

**Pelagic and Benthic Transfer of PCBs.** The primary objective of this study was to assess the relative importance of atmospheric versus sedimentary assimilation of PCBs into the food web of Lake Michigan. To examine this, the relationship between isotopes and contaminant levels was assessed among food web members and the organic matter sources. The primary sources of organic matter and contaminants in this study were seston, settling organic matter, and sediment. (Settling particulate matter collected using sediment traps 38 and seston collected by filtration 16 were both collected as part of this study and analyzed for stable isotopes and PCBs.) PCB levels in seston collected from a depth of 5 m averaged 28.5 ± 16.0 ng/g dry weight (dw) between April and September 1997 and possessed \( \delta^{15}N \) values ranging from 3.5 to 6.5%. \( \delta^{13}C \) values ranging from -31.0 to -27.0% (16). PCB levels in sediment trap material averaged 31 ± 32 ng/g dw in traps deployed beneath the photic zone (approximately 30 m) and have higher average \( \delta^{15}N \) values ranging from 5.7 to 10.97%o (\( \delta^{13}C \) values are not available for sediment trap material). Material collected from sediment cores in GTB possess average PCB content of 33 ± 5 ng/g dw, and the isotope values were 5.4 ± 0.4 and -24.8 ± 1.1% for \( \delta^{15}N \) and \( \delta^{13}C \), respectively. Lipid contents in the seston and settling organic matter was 4.7 ± 2% (16).

From the data presented in Figure 4, we conclude that sediment cannot be a primary source of contaminants to the food web. While the nitrogen isotopes in sediment are comparable to seston and settling particulate matter, the carbon isotope values of sediment are distinctly different. The sediment is clearly enriched in \( \delta^{13}C \) relative to the invertebrates sampled, indicating that the sediment is not a primary source of their organic matter. The invertebrates sampled in this study are the primary dietary items of the forage fish sampled and were verified through stomach content analyses (39). Therefore, it seems unlikely that there are any missing sources of carbon to this food web that were not considered in this study. Additionally, it is unlikely that zooplankton are receiving a source of organic matter from the sediment due to their position in the water column. As mentioned previously, carbon isotopes could not be calculated for the settling particulate matter collected in the sediment traps and are therefore not plotted in Figure 5. However, from other studies, we expect the \( \delta^{13}C \) values of the settling organic matter to be comparable or depleted relative to the sediment (40).

We conclude, therefore, that seston and settling organic matter are the primary vectors of PCB incorporation into the Lake Michigan food web. To determine the relative importance of seston versus settling organic matter supplying PCBs to the food web, we applied regression analyses to all the data. Because path analysis indicated that lipid content exerted an influence over contaminant burdens with increasing trophic level, we normalized PCB burdens to lipid content and correlated these values to their respective carbon and nitrogen isotope signatures. Correlations observed using carbon isotopes and lipid-normalized PCB burdens were of little use due to the lack of carbon isotope data in setting

![FIGURE 6. Natural log lipid-normalized \( \sum \text{PCB} \) burdens among species correlated to their respective \( \delta^{15}N \) signature. Plots represent average values, and error bars represent standard deviation.](image-url)
zooplankton indicate that either zooplankton are not their primary source of organic matter, the Mysis populations we analyzed are not feeding up the zooplankton we collected in our plankton tow, or there is differential assimilation of organic matter and contaminants in this species. We hypothesize that Mysis are feeding heavily upon settling detrital and refractory particles within the water column that are lower in lipid-normalized PCBs. Lake trout inhabit both the pelagic and the benthic realms and feed upon fish in both zones (45, 46). This suggests that there is an input of PCBs from both seston and settling particles in Grand Traverse Bay and explains their position along the regression line of Figure 6. Burbot feed heavily on plankton tows, or there is differential assimilation of contaminants from seston and settling particulate material that supply PCBs to the food web of Lake Michigan. Suspended seston and settling particles in the water column may be supplying a second route to the benthic inhabitants. This material is available free of charge via the Internet at http://pubs.acs.org.

Supporting Information Available

One table giving a summary of samples collected, lengths, and calculated measurements of the lipid content (1 page). This material is available free of charge via the Internet. This is the University of Maryland Center for Environmental Science Contribution No. 3475.

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