

PCB AND PAH FUGACITIES IN SEDIMENT, WATER, AND LAKE TROUT OR RAINBOW TROUT AT MULTIPLE SITES THROUGHOUT THE LAURENTIAN GREAT LAKES BASIN

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Introduction

Contaminant fugacity ratios can be used as a tool to assess contaminant dynamics in biotic and abiotic media because at equilibrium, fugacities in adjacent environmental compartments should be equal.¹ Therefore, the extent of disequilibrium can be readily quantified and compared for different compounds, media, and systems.

Fugacities, or concentration ratios, have been used previously to evaluate mechanisms controlling contaminant dynamics. For example, Gobas and Maclean² calculated sediment:water fugacity ratios using literature data for Lakes Superior, Erie, St. Clair, and the Green Bay of Lake Michigan. They found that, for the most part, chemical fugacities in sediment were greater than in water. They argued that disequilibrium between sediment and water occurred because of organic carbon mineralization during deposition of settling particles. Using a modeling approach, they suggested that this process was similar to that of biomagnification in the intestines of fish as a result of digestion of organic matter, and that a substantial amount of magnification can occur even before chemicals enter the benthic food chain. As a second example, Burkhard et al.³ calculated biota:sediment accumulation factors (BSAFs) for PCBs, PCDDs, and PCDFs in southern Lake Michigan lake trout and argued that differences among compounds were due, in part, to differences in net metabolism in the food chain.

The first objective of this study was to calculate sediment:water, fish:sediment, and fish:water fugacity ratios for PCBs and PAHs at multiple sampling locations throughout the Laurentian Great Lakes Basin. The second objective was to use these ratios as a tool to evaluate and compare processes influencing contaminant trends throughout these lakes. To our knowledge, this study is among the largest multi-media data sets for the Laurentian Great Lakes.

Methods

The raw PCB and PAH data were obtained from the Ontario Ministry of the Environment (fish) and Environment Canada (sediment and water). Sample collection and analysis methods have been described elsewhere.^{4,5} Briefly, surficial sediment samples from Lakes Ontario (1998), Erie (1997), Huron (2002), and Superior (2000) were collected aboard the Canadian Coast Guard Ship *Limnos* using a mini box core sampling procedure. PCBs were extracted from sediment using dichloromethane followed by an open-column Florisil procedure. Analysis was performed using gas chromatography with electron capture detection (GC-ECD). PAHs were extracted similarly to the PCBs but were analyzed using GC equipped with a mass selective detector (MSD). Surface water samples were collected aboard the *Limnos* in the spring of 2004 (Ontario, Erie, Huron) or 2005 (Superior). The samples were stabilized with DCM in the field and then extracted using a large-column continuous-flow Goulden extractor in an ultra-trace clean laboratory. Water samples were analyzed by GC-MSD. Lake trout (Ontario, Huron, Superior) or rainbow trout (Erie) were collected between 1997 and 2003 by the Ontario Ministry of Natural Resources using nets or by electro fishing. Boneless fillet of the dorsal muscle of each fish were extracted with diethyl-ether/hexane and concentrations were measured by GC-ECD.

Sediment:water fugacity ratios were calculated as follows:

$$(1) \quad \frac{f_{\text{sediment}}}{f_{\text{water}}} = \frac{C_{\text{sediment}}/Z_{\text{sediment}}}{C_{\text{water}}/Z_{\text{water}}} = \frac{C_{\text{sediment}}H/K_{\text{oc}} \cdot \rho_{\text{sediment}}}{C_{\text{water}} \cdot H} = \frac{C_{\text{sediment}}/0.35K_{\text{ow}} \cdot \rho_{\text{sediment}}}{C_{\text{water}}}$$

where f_{sediment} and f_{water} are the chemical fugacities (Pa) in sediment and water, respectively, C_{sediment} is the concentration in sediment (ng/g organic carbon), C_{water} is the freely dissolved concentration in water (ng/g water, which was derived from measured units of ng/L assuming a density of water of 1 kg/L), Z_{sediment} and Z_{water} are the fugacity capacities of sediment and water, respectively ($\text{mol}/\text{m}^3 \cdot \text{Pa}$), H is Henry's law constant ($\text{Pa} \cdot \text{m}^3/\text{mol}$), K_{oc} is the organic carbon water partition coefficient (calculated as $0.35K_{\text{ow}}^6$), and ρ_{sediment} is the density of sediment, assumed to be 1.5 kg/L. Freely dissolved water concentrations were derived from measured dissolved water concentrations using a relationship developed by Burkhard⁷, and described by Borga et al.⁸ as $C_{\text{water}} = C_{\text{waterMeasured}}/(1+\text{DOC} \cdot 0.08K_{\text{ow}})$, where DOC concentrations (kg/L) were either measured as part of this study (Lake Ontario) or estimated from Anderson et al.⁹

Fish:sediment fugacity ratios were calculated as follows:

$$(2) \quad \frac{f_{\text{fish}}}{f_{\text{sediment}}} = \frac{C_{\text{fish}}/Z_{\text{fish}}}{C_{\text{sediment}}/Z_{\text{sediment}}} = \frac{C_{\text{fish}}H/K_{\text{ow}}}{C_{\text{sediment}}H/(0.35K_{\text{ow}} \cdot 1.5)} = \frac{0.615C_{\text{fish}}}{C_{\text{sediment}}}$$

where f_{fish} is the fugacity in fish (Pa) and C_{fish} is the concentration in fish (ng/g lipid).

Finally, fish:water fugacity ratios were calculated as follows:

$$(3) \quad \frac{f_{\text{fish}}}{f_{\text{water}}} = \frac{C_{\text{fish}}/Z_{\text{fish}}}{C_{\text{water}}/Z_{\text{water}}} = \frac{C_{\text{fish}}H/K_{\text{ow}}}{C_{\text{water}} \cdot H} = \frac{C_{\text{fish}}/K_{\text{ow}}}{C_{\text{water}}}$$

For sediment:water fugacity ratios, values were calculated at locations where both sediment and water measurements were available. Using this criterion, sediment:water fugacity ratios were calculated at 52 stations throughout the 4 lakes. Fish were not collected at discrete stations but rather were obtained from larger block areas¹⁰, which represent approximate fish home ranges. Therefore, in order to compare sediment and water measurements to fish, we calculated the average sediment or water concentrations at all stations within each specific block area.

Results and Discussion

For the most part, sediment:water fugacity ratios were greater than 1, which corresponds to the results of Gobas and Maclean² and which is hypothesized to be due to organic carbon mineralization. Gobas and Maclean² found, through an examination of 5 sites/data sets in large lakes, that the extent of chemical magnification occurring in sediment (i.e. the extent of sediment water disequilibrium) was greater in deeper lakes, because these lakes tend to have longer deposition times, which allow for a higher degree of organic carbon decomposition to occur. In contrast, when we calculated sediment:water fugacity ratios over a wider depth range, we found that sediment:water fugacity ratios tended to decrease with lake depth (Figure 1) and in general the degree of chemical magnification was greatest in shallow Lake Erie, and lowest in deep Lake Superior. However, sediment:water fugacity ratios also tended to increase with total organic carbon concentrations in the water column, estimated from Anderson et al.⁹ (Figure 2). These results suggest that primary production, estimated by total organic carbon in the water column, has a greater influence on the degree in which contaminants are magnified in sediment compared with lake depth.

At approximately 50% of the sites, PAH sediment:water fugacity ratios were orders of magnitude greater than for PCBs. This likely occurred because of enhanced sorption of PAHs to soot carbon.¹¹ At the other sites, there were minimal differences in the sediment:water fugacity ratios between these two classes of compounds. The contribution of soot carbon to the total organic carbon pool of sediment can have a large range¹² and the later sites likely contained relatively small amounts of soot carbon.

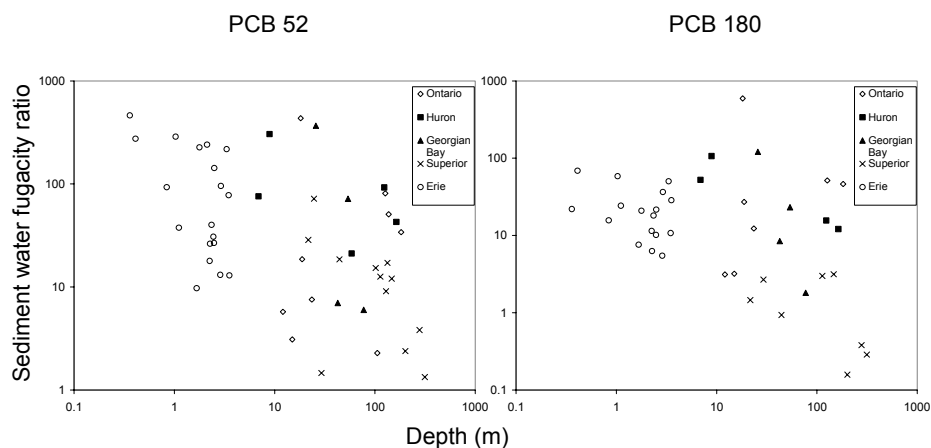


Figure 1: Sediment:water fugacity ratios versus lake depth at multiple sampling points in Lakes Ontario, Huron (and Georgian Bay), Superior, and Erie. Data for PCB 52 and PCB 180 are shown as representative lower chlorinated and higher chlorinated PCB congeners, respectively.

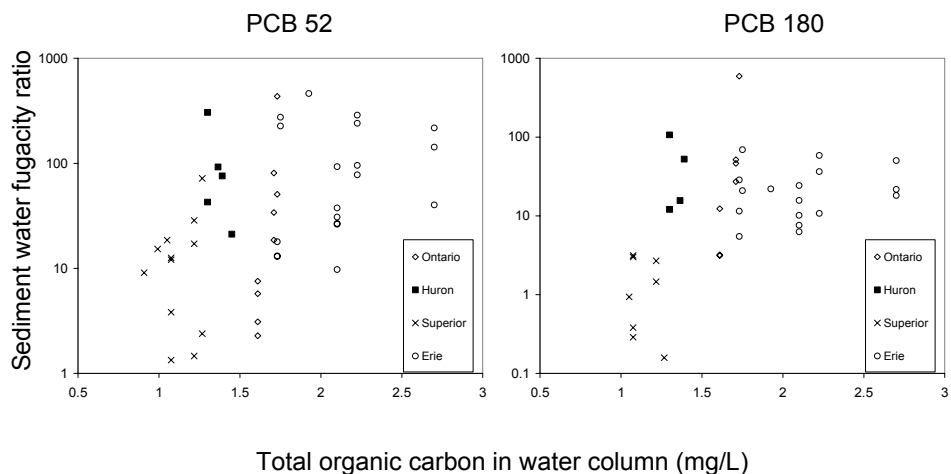


Figure 2: Sediment:water fugacity ratios versus total organic carbon in water at multiple sampling points in Lakes Ontario, Huron (and Georgian Bay), Superior, and Erie. Data for PCB 52 and PCB 180 are shown as representative lower chlorinated and higher chlorinated PCB congeners, respectively.

For the most part, PAHs were not detected in the lake trout or rainbow trout, which likely occurred because fish are known to rapidly biotransform PAHs to more toxic metabolites.¹³ In contrast, fish:sediment and fish:water fugacity ratios for PCBs were, for the most part, greater than 1 (Figure 3), since PCBs are biotransformed at a much slower rate and are subjected to biomagnification through the food web.¹⁴ The relative ranking of the fugacity ratios among areas were similar among PCB congeners, which corresponds to the results of Burkard et al.¹⁵ and is likely due to area-specific differences in food web processes. Surprisingly, both fish:sediment and fish:water fugacity ratios were consistently greater in Lake Superior trout from areas 5 and 7, which are located in the central north part of the lake, compared with other sites. Although trout from area 7 tended to be larger than those from other locations, trout from area 5 were smaller compared to all other sites, suggesting that age is not contributing to these elevated concentrations. Work is currently underway to determine possible reasons for these patterns.

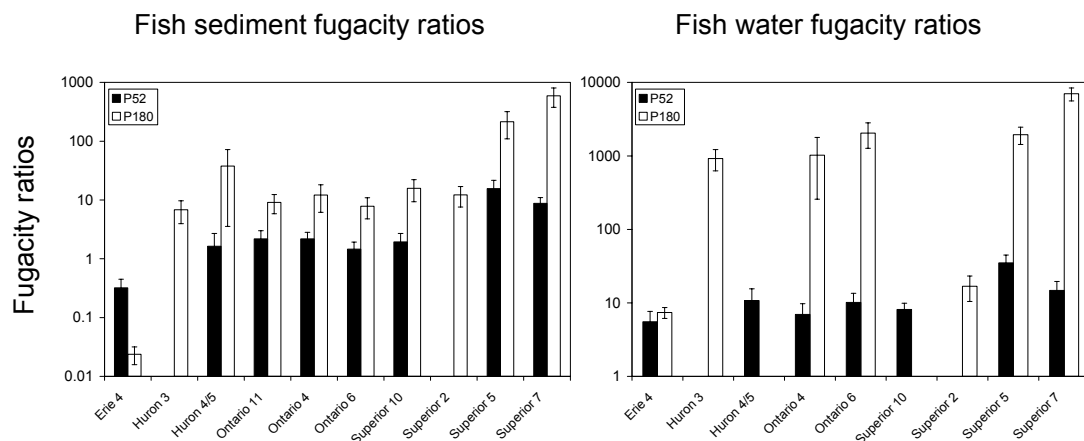


Figure 3: Fish:sediment and fish:water fugacity ratios at 10 areas throughout the Great Lakes Basin. Data are shown for PCB 52 and PCB 180 which are representative lower chlorinated and higher chlorinated PCB congeners, respectively.

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