Polycyclic Aromatic Hydrocarbons in Sediments and Pore Waters of the Lower Great Lakes: Reconstruction of a Regional Benzo(a)pyrene Source Function

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INTRODUCTION

In the Great Lakes, as in most aquatic systems, the rapid and efficient processes of sorption and settling scavenge hydrophobic organic contaminants (HOC) from the water column, with the result that the largest fraction of persistent trace contaminant inventories presently resides in sediments. However, studies of the long-term behavior of certain fallout radionuclides and stable contaminants in the Great Lakes have shown that higher levels persist in the lakes than would be expected if settling and burial were the sole transport process. Toxic materials return from sediments due primarily to resuspension. Constituents initially transferred to sediments are homogenized via bioturbation, creating a mixed layer corresponding to a decade or more of accumulation. These are resuspended back into the water column during the isothermal period and are available for uptake by pelagic biota. A second, poorly quantified return pathway to pelagic biota is via the direct uptake of sediment-bound contaminants by benthos and food web transfer.

The processes of sorption, settling and resuspension, bioturbation, and burial together control the phase distribution, long-term behavior, and, to some degree, bioavailability of most trace contaminants in aquatic systems. The degree of partitioning of a constituent between particulate and dissolved phases, generally presented as the ratio \( K_d \), is a function of the compound's intrinsic properties and the composition (e.g., particle size, fraction organic carbon) of the substrate. Once the HOC is associated with particulate matter, its water column residence time is relatively short (ca. months in the 100-m deep Great Lakes). Mean particle settling velocities of approximately 1 m/day have been estimated for the period of thermal stratification in several large lakes in the world, and values during the isothermal period are greater. At a
depth of approximately 10–20 m above the bottom, particles enter the benthic nepheloid layer (BNL), a region of elevated particle concentration and mass flux. The BNL is a regular feature in all of the Great Lakes and appears to be composed primarily of resuspended sediments. The BNL is frequently recharged from a variety of sources in addition to the particles settling down from above. In shallow waters, surface and internal waves, and occasional strong currents, resuspend sediments, sorting the particles and transporting them horizontally as well as vertically. During the long period when the system is not thermally stratified, there appears to be local resuspension even in deeper regions, and the resuspended sediments are well mixed throughout the water column. With the onset of stratification, vertical turbulence is markedly reduced below the thermocline, and the bulk of resuspended materials resettle to the BNL and lake bottom. The long-term consequence of seasonal resuspension and redeposition is the eventual accumulation of particle-associated contaminants in least turbulent areas of the lakes. The resultant lateral inhomogeneity of sediment-associated trace constituents, called focusing, operates strongly in the Great Lakes system.

At the sediment surface, freshly deposited materials are mixed with older sediments as a result of the movement and feeding activities of organisms inhabiting the upper layers of sediment (1–10 cm thick). As a result of mixing, materials which would have been buried are reintroduced into the resuspendible pool. Several studies have shown that, in general, organisms occur in sufficient numbers throughout the Great Lakes to homogenize near-surface sediments, representing the input of years to decades. In the Great Lakes, the amphipod Diporeia sp. is the predominant benthic organism, constituting 65% of the macroinvertebrate population biomass. Note that Diporeia sp. is a new genus and was previously classified as Pontoporeia hoyi. Diporeia lives at the interface, although it does burrow down a few centimeters and mixes sediments in a dispersive manner. Diporeia can also swim up into the water column. Oligochaete worms are also major contributors to sediment mixing in the lakes. These animals characteristically burrow several centimeters down into the sediments and spend a significant amount of their time feeding in a head-down position while excreting from tails protruding through the sediment-water interface. This particle-selective conveyor-belt process has the effect of bringing buried materials back into the resuspendible pool and ultimately homogenizing near-surface deposits. This mixed layer zone has been shown to be directly related to the vertical distribution and numbers of organisms that can mix sediments at a given site. The reintroduction of homogenized materials from the sediment mixed layer into the water via resuspension allows constituents to move toward new sorption equilibria.

The polycyclic aromatic hydrocarbons (PAH) constitute a large class of compounds generally formed in the incomplete combustion of fossil fuels. At relatively low combustion temperatures, the multiringed PAH contain a large number of alkyl side chains. The abundance of these side chains decreases as combustion temperature increases, so that at temperatures above approxi-
mately 750°C, the unsubstituted parent ring structures predominate. Studies of several combustion sources and sediments have shown that several PAH are ubiquitous and relatively abundant. Among the most common and easily identified are phenanthrene, fluoranthene, pyrene, and benzo(a)pyrene (BAP). The structures of these PAH are given in Figure 9.1. In this chapter, we examine the distribution of these four PAH within the highly industrialized lower Great Lakes in well-characterized sediments going back to before 1800 in an attempt to (1) estimate the historical fluxes of PAH to these lakes and compare them to other lake systems and (2) use this information to reconstruct a historical source function for BAP for the lower Great Lakes.

METHODS

Sediment samples were collected aboard the Canadian RV Limnos with a 0.25-m² box corer at two sites in eastern Lake Ontario (described in detail in Eisenreich et al.¹⁰) and a high depositional site in eastern Lake Erie (42°31'00" N, 79°53'38" W). For the Lake Ontario samples, 3-in. diameter subcores were taken, extruded and sectioned at 1-cm intervals in the field, and stored frozen until extraction. Larger (5-in.) subcores were collected from the Lake Erie box core, and the extruded 2-cm sections were stored in refrigeration until centrifuged. Radionuclide analyses were performed on adjacent 3-in. subcores (from the same box core) sectioned at 0.5-to 1-cm intervals.

Pore waters were separated from the Lake Erie sediments by centrifugation; then 2-cm sections from two adjacent 5-in. subcores were combined. These large wet sediment samples (> 500 mL) were placed in precleaned 1-L high-density polyethylene bottles and spun at 2500 rpm for 20 min in an IEC Model K centrifuge. Small chunks of dry ice were placed inside the centrifuge to keep the temperature below ambient. Under these conditions, 290–375 mL of pore water was separated per 2-cm section. The water was decanted and immedi-

![Figure 9.1. Ring structure of the four combustion PAH discussed in this chapter.](image-url)
ately filtered through precombusted (4 hr at 400°C) Whatman GFF glass-fiber filters (nominal cutoff < 1 μM). Dissolved organic carbon (DOC) was analyzed from subsamples by the wet oxidation method. The remainder of the pore water was dosed with two radiolabeled PAH compounds as tracers for the analytical methodology and extracted three times with approximately 10% of the water volume using methylene chloride.

Sediments were Soxhlet extracted (wet) with 125 mL MeOH for approximately 4 hr. After cooling, 250 mL of CH₂Cl₂ was added and extraction continued overnight. The extracts were transferred to 500-mL separatory funnels and washed with 3 × 50 mL of CH₂Cl₂ extracted distilled water. The solvent portion of the extracts was then reduced in volume by rotary evaporation (equipped with a cold finger trap to increase efficiency) to approximately 5 mL, transferred to a 50-mL round-bottom flask, and 15 mL of pentane was added. Rotary evaporation was continued until the sample was reduced in volume to approximately 2 mL; then this step was repeated. The extract, now in pentane, was evaporated to approximately 0.5 mL with a stream of clean nitrogen gas. This was introduced onto a column (12 × 0.5 cm) that had been slurry packed with fully activated (8 hr at 200°C; stored at 120°C) silica gel. The upper 1 cm of the column was dry packed with precleaned sodium sulfate to trap any remaining water. The first elution, 12 mL of pentane, removed primarily the saturated hydrocarbons. The second elution, calibrated for each batch of silica gel, used 10-12 mL of 9-14% CH₂Cl₂ in pentane to elute the PAH. A 15-mL wash of CH₂Cl₂ recovered the remainder of the extract. These eluents were evaporated to 0.5 mL in a stream of dry nitrogen, and 50 μL was removed for counting of radiotracer. Extraction yields were based on the average of the recovery of spiked radiotracers. The radioactivity was measured on a Packard 460C liquid scintillation spectrometer. Sample quench was corrected using the external standards method after subtracting background.

Analysis was performed on a Hewlett Packard 5880 gas chromatograph equipped with an autoinjection system, programmed in a dual column mode. An injection was made into each 20-m capillary column (DB-1 and DB-5) at 100°C. The program was then automatically started (4°C/min to 280°C) with detection on a pair of HNU photoionization detectors (10.2 eV) optimized for PAH. These detectors are 20-50 times more sensitive than FID for the aromatic compounds. Compound identification was based on retention times on both columns being within 0.5% of mixed external standards run on the same day. Samples were quantified by running a set of three standards, covering an order of magnitude in concentration (responses were within linear range), at the beginning of each programmed autosample run. If the response of the sample fell outside of the standard runs, the sample concentration was altered by dilution or evaporation and rerun. Solvent blanks were run between each sample/standard to ensure that there was no memory. For 12 sets of three concentrations of the PAH standards, the measured standard deviation was less than 10% of the mean values for each compound.

A problem common to analyses of trace contaminants in the environment is
our ability to collect a representative sample and the quality of data achievable with existing technologies. We have previously reported on the precision of our analyses for PAH in sediments; coefficients of variation for extractions of a homogenized, split sediment sample for the PAH were 34% (Phen), 21% (Fl), 20% (Py), and 19% (BAP). Analysis of two other samples similarly collected on two subsequent cruises did not substantially change the means or coefficients of variation. For this study, we regard the precisions cited above to be realistic.

RESULTS AND DISCUSSION

Sediment Geochronology

The Lakes Erie and Ontario cores selected for analysis were collected as part of a more comprehensive evaluation of tracers in lake sediments. Core geochronology is based on the analysis of fallout $^{137}\text{Cs}$ and natural $^{210}\text{Pb}$. The geochronology of the two Lake Ontario cores is analyzed in detail elsewhere. The latter treatment includes a correction for the recent (past 80 years) increase in the concentration of organic carbon and CaCO$_3$, both related to nutrient-enhanced productivity. Both cores appear to have an uninterrupted record of deposition over their length, and their recent accumulation rates differ by a factor of 1.8. The first of these cores, designated E-30, has a base sediment accumulation rate of 0.040 g/cm$^2$ year until approximately 1900, after which it increased to a maximum of about 0.055 g/cm$^2$ year due to the carbon dilution mentioned above. The second core, G-32, had a base sedimentation rate of 0.090 g/cm$^2$ year, which began increasing at the same time to a maximum of about 0.115 g/cm$^2$ year.

The down-core distribution of the $^{137}\text{Cs}$ and $^{210}\text{Pb}$ for the eastern Lake Erie core is presented in Figure 9.2. The $^{137}\text{Cs}$ peak corresponds with the maximum load in 1963. The $^{137}\text{Cs}$ data were least-squares fitted to a rapid steady-state mixing (RSSM) model, from which the thickness of the sediment mixed layer (3.35 g/cm$^2$) and sediment accumulation rate (0.60 g/cm$^2$ year) are optimized. The solid line in Figure 9.2a is the fit to the measured $^{137}\text{Cs}$ points. Using these same parameters, the model was fit to the $^{210}\text{Pb}$ constant source function, with excellent results (Figure 9.2b), increasing our confidence in the parameter values. Thus, the sediment accumulation rate in the core from eastern Lake Erie is 5–10 times that of the Lake Ontario cores.

Combustion PAH in Sediments

The PAH concentrations measured in these three Great Lakes cores (Figure 9.3) fall within the range of measurements in other locations, and as is expected, they are more representative of highly populated, industrialized sites. Laflamme and Hites, in their analysis of sediments from around the
Figure 9.2. (a) The depth profile of $^{137}$Cs measured in the Lake Erie 1983 MS box core. The two lines represent the results of the rapid steady-state mixing (RSSM) model (solid) and an external integration model (dashed); the differences are negligible. Results from the RSSM are the mixed layer depth (3.35 g/cm$^2$) and sediment accumulation rate (0.60 g/cm$^2$ year). (b) The depth profile of excess $^{210}$Pb. The line represents the results of applying the RSSM with $^{137}$Cs-derived parameters to the $^{210}$Pb source function. The agreement with the Pb data increases our confidence in the RSSM parameters.

The surface and subsurface maximum concentration are also within the range already described in the literature. The Charles River (Boston, MA) and New
Figure 9.3. Depth profiles of the four combustion PAH in three sediment cores: Lake Erie 1983 MS data (asterisks), 1981 Lake Ontario G-32 core (open rectangles), and 1981 E-30 core (filled-in rectangles). All concentration data are plotted against $^{210}$Pb estimates of the date. Peak values were recorded in the 1950s and were approximately two to three times as large as present concentrations.
York Bight, for example, have higher reported concentrations,\textsuperscript{16} as do some of the cores from the Greifensee.\textsuperscript{18} These sites are in highly industrialized areas and most likely receive localized inputs. More surprising is the high surface sediment concentration in remote Adirondack lakes,\textsuperscript{17} whose source of PAH is predominantly atmospheric (from combustion-related activities in the Great Lakes region). Furlong et al. also found very high concentrations and fluxes of combustion PAH in Adirondack lakes.\textsuperscript{19} If the source assumption is correct, then these findings imply a relatively long-range (hundreds of kilometers) transport of large amounts of the combustion PAH.

The PAH profiles that we measured in Lake Ontario exhibit a clear subsurface maximum (Figure 9.3). In many recently collected sediments, the maximum reported value for the combustion-related PAH is at the surface.\textsuperscript{17,18,20} Undoubtedly, the primary source of these compounds is incomplete combustion of fossil fuels. In the Great Lakes region, the major industrial energy source (coal) and home heating (coal and wood) were being replaced by cleaner-burning oil and natural gas by the late 1950s. These changes, plus emission controls subsequently imposed by environmental legislation, have resulted in an observable decrease in the concentration of BAP in regional air and in the delivery of PAH to Lake Ontario. Profiles of PAH with subsurface maxima have been reported for Puget Sound\textsuperscript{21} and some small lakes in the northeast United States.\textsuperscript{19,22} Concentration maxima in these systems occurred between 1940 and 1955, similar to those described in this chapter, and subsequent reductions have also been attributed to changes to cleaner fuels and emission controls.

Surface concentrations of PAH in the Lake Erie core (Figure 9.4) were low relative to other (near-shore) sediments reported for Lake Erie,\textsuperscript{13,23} but well within the range reported for the other open Great Lakes. Based on the radionuclide interpretation, the core covers the period of approximately 1959 (38–40 cm) to the collection date of 1983; thus, each 2-cm section represents less than 2 years of accumulation. Peak PAH concentrations (approximately two times the surface concentrations) were observed between 20 and 30 cm (approximately 1964–1970). In Figure 9.3 the sediment PAH are presented as concentration versus radionuclide model estimated date. This allows the two Lake Ontario cores to be superimposed and presented along with the Lake Erie core described above. It is clear from this figure that the Lake Erie core was too short to reach the peak concentrations of PAH. These values occurred in the mid-1950s (Table 9.1); the error in the time estimate is approximately ±5 years. Since the Lake Erie core did not reach PAH background, it is not included in Table 9.1.

Concentrations of the four PAH show background levels of a few tens of ng/g, presumably produced by natural forest fires, until the middle of the 19th century. The subsequent increase in PAH concentration, presumably anthropogenic in origin, corresponds to the growth of population and industrial development in the region.\textsuperscript{24} Surface sediment concentration of these PAH were higher in the Ontario cores than in the Erie core. This is mainly due to the
Figure 9.4. Combustion PAH measured in the 1983 Lake Erie MS box core. Each line represents the concentration of phenanthrene, fluoranthene, pyrene, or benzo(a)pyrene as identified in the legend. The core spans the period of approximately 1959 to the time of collection, 1983. The reduction near the surface is significant, a factor of 2–3 less than the peak.

Table 9.1. PAH Concentrations (ng/g sed) in Lake Ontario Sediments

<table>
<thead>
<tr>
<th>Core 81E–30</th>
<th>PAH Max</th>
<th>Year</th>
<th>PAH</th>
<th>Max/1981</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenanthrene</td>
<td>812</td>
<td>1953</td>
<td>307</td>
<td>2.6</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>1145</td>
<td>1953</td>
<td>349</td>
<td>3.7</td>
</tr>
<tr>
<td>Pyrene</td>
<td>839</td>
<td>1959</td>
<td>249</td>
<td>3.3</td>
</tr>
<tr>
<td>Benzo(a)pyrene</td>
<td>809</td>
<td>1959</td>
<td>425</td>
<td>1.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Core 81G–32</th>
<th>PAH Max</th>
<th>Year</th>
<th>PAH</th>
<th>Max/1981</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenanthrene</td>
<td>854</td>
<td>1954</td>
<td>301</td>
<td>2.8</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>909</td>
<td>1954</td>
<td>466</td>
<td>1.9</td>
</tr>
<tr>
<td>Pyrene</td>
<td>773</td>
<td>1954</td>
<td>418</td>
<td>1.8</td>
</tr>
<tr>
<td>Benzo(a)pyrene</td>
<td>494</td>
<td>1957</td>
<td>300</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Accumulation (μg/cm²) 1830–1981

<table>
<thead>
<tr>
<th>E–30</th>
<th>G–32</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass (g/cm²)</td>
<td>5.4</td>
<td>9.3</td>
</tr>
<tr>
<td>Focusing factor</td>
<td>1.17</td>
<td>1.74</td>
</tr>
<tr>
<td>Organic carbon (mg C/cm²)</td>
<td>138.0</td>
<td>273.0</td>
</tr>
<tr>
<td>Phenanthrene (μg/cm²)</td>
<td>1.9</td>
<td>2.7</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>3.5</td>
<td>4.6</td>
</tr>
<tr>
<td>Pyrene</td>
<td>2.5</td>
<td>3.3</td>
</tr>
<tr>
<td>Benzo(a)pyrene</td>
<td>2.5</td>
<td>3.3</td>
</tr>
</tbody>
</table>
higher mass accumulation rate in the Lake Erie sediment resulting in more dilution by inert materials. Considering the errors involved in these analyses, the peak concentrations of PAH at the two Ontario sites are approximately equal, except for BAP, which was generally higher in concentration at station E-30. Since these sites are in the same depositional basin of Lake Ontario and are only separated by about 30 km, it is difficult to understand this difference in BAP. For all four PAH, peak concentrations in the mid-1950s were approximately two to three times present values. The total accumulation of the four PAH, from background levels around 1860, was greater in core G-32. The ratio of PAH accumulation in the two cores was substantially lower than the ratio of mass or organic carbon accumulation and more closely approximated the accumulation of $^{137}$Cs and $^{210}$Pb from which the focusing factors are derived.

**Pore Waters**

Understanding the distribution of HOC within the sediment matrix is important for understanding the exposure of organisms to these contaminants. Organisms that live and feed in the surface sediments suffer elevated exposure to HOCs from both the inventory attached to particles in the sediments and that in the interstitial water.\(^{13,25-27}\) Models applied to measured PAH concentrations, assumed to be in equilibrium among Great Lakes sediments, pore waters, overlying waters, and benthos, implied that a large fraction of the combustion PAH in oligochaetes and the amphipod *Diporeia* resulted from exposure to pore water and sediments.\(^{13,25}\)

Pore-water samples were extracted from this core in an attempt to measure the PAH concentrations. Ambient measurements of trace organics in pore waters are rare since samples are relatively small, and low concentrations generally force analyses to near the detection limit. In this case, this was most apparent for BAP. Based on separate analyses of a large pore-water sample, split to approximately this size, we estimate our coefficient of variation to be 100% for these four PAH.

Overlying water concentration of BAP in Lake Erie is estimated as 0.3 ng/L, and average pore-water concentration (Table 9.2) is 17 ± 14 ng/L.\(^{23,28}\) In laboratory toxicokinetic studies, the pore-water contribution to bioaccumulation was modified by the presence of DOC, which reduced the bioavailability of HOC.\(^{29,30}\) The uptake of the unassociated fraction of PAH in pore waters by
Diporeia was similar to the uptake from overlying water. Estimates of the fraction bound to DOC in these sediments can be made from laboratory measurements of the mean equilibrium distribution coefficient of BAP to DOC \((K_d)\) of 32,000 and the average DOC in this core (12.3 mg C/L).\(^{31,32}\) The result is that approximately 70% of the BAP in pore water is not associated with DOC and is thus potentially available to benthos. The balance of the two sediment source terms, ingested particles and respired interstitial water, remains in question, but the contribution of the interstitial water pathway is apparently large for compounds such as phenanthrene and pyrene and smaller, but still significant, for compounds such as 2,4,5,2',4',5'-hexachlorobiphenyl.\(^{33}\)

Pyrene concentrations in Lake Erie pore waters are shown in Figure 9.5 along with the sediment values for the same intervals. The structure in the pore-water concentration profile is not different from a constant concentration with this measurement error. Calculated mean equilibrium distribution coefficients (Table 9.2) are significantly (> 20 times) lower than values reported for ambient Great Lakes water samples,\(^ {32}\) possibly a consequence of the mysterious particle concentration effect on \(K_d\) observed in laboratory studies.\(^ {34}\) These smaller distribution coefficients imply an elevated bioavailability of these compounds to benthic organisms.

**PAH Inventories/PAH Fluxes**

If we assume that there is little degradation of the combustion-based PAH within aquatic systems, we can compute and compare fluxes estimated from concentration profiles in radiometrically dated cores. In order to compare regional fluxes from these sediment calculations, we would need to correct for within-system sediment-focusing effects. Sediment focusing results in the lateral inhomogeneous distribution of sediment and constituent accumulation.\(^ {6,10}\) Maximum sediment accumulation is usually, but not always, coincident with maximum lake depths. Focusing factors are calculated as the inventory of a constituent in a core to its total areal load to the system. Radionuclides are excellent for this purpose since the inputs of \(^{137}\)Cs and \(^{210}\)Pb are reasonably well known. The average values for Lake Ontario cores E-30 and G-32 are reported in Eisenreich et al.\(^ {10}\) The sampling range for the Lake Erie box core does not cover a sufficient length of time to reach preindustrial background; thus, we cannot calculate an inventory of PAH. Lacking focusing factors, it is not possible to estimate whether the core-derived fluxes are representative of the entire lake system or region.

In their analysis of PAH in cores from nine lakes, summarized into four regions, Furlong et al. report the post-1890 inventory of the sum of the four combustion PAH that we examined for Lake Ontario plus chrysene, triphenylene, benzo(e)pyrene, and benzo(ghi)perylene.\(^ {19}\) These combustion PAH are well correlated with each other, a property of a common source. In our experience, these four extra compounds generally account for approximately 30% of
the sum; we will use this approximation to reduce their calculated fluxes in order to compare the different cores. Tan and Heit report the postindustrial accumulation of the four PAH in the Adirondack sediments of Lakes Sagamore and Woods. We compare the postindustrial inventories with those that we measured for Lake Ontario in Table 9.3.

This comparison shows that the highly populated and industrialized Great Lakes has received more combustion PAH than has been measured in cores from areas with less local PAH production. As is evident from the inventories of the two Lake Ontario cores, the focusing correction is very important in estimating regional accumulations, and therefore the comparison among regions. Estimates of recent PAH fluxes are in the range reported by Gschwend and Hites, with Lake Ontario in the range of their high values.

**Deriving a Lower Great Lakes BAP Source Function**

In the following section, we use the measured down-core concentrations of BAP in the Lake Ontario sediments along with the radionuclide-determined mixing and accumulation values to reconstruct the load of BAP to the lakes. We then test this source function against the measured down-core concentration of BAP in Lake Erie and some published atmospheric measurements.

The sedimentary profiles of BAP for Lake Ontario E-30 and G-32 are redrawn in Figure 9.6a, after normalizing the concentrations in core G-32 by multiplying the measured concentration by the ratio of the inventories of BAP.
Table 9.3. PAH Fluxes (ng/cm² year) and Postindustrial Inventories (ng/cm²)

<table>
<thead>
<tr>
<th>Location</th>
<th>Recent Flux</th>
<th>Inventory</th>
<th>Focus-Corrected Inventory</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lake Ontario E-30</td>
<td>119</td>
<td>10450</td>
<td>8932</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>26</td>
<td>1930</td>
<td></td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>31</td>
<td>3500</td>
<td></td>
</tr>
<tr>
<td>Pyrene</td>
<td>24</td>
<td>2509</td>
<td></td>
</tr>
<tr>
<td>BAP</td>
<td>38</td>
<td>2511</td>
<td></td>
</tr>
<tr>
<td>Lake Ontario G-32</td>
<td>156</td>
<td>13978</td>
<td>8033</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>28</td>
<td>2735</td>
<td></td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>50</td>
<td>4559</td>
<td></td>
</tr>
<tr>
<td>Pyrene</td>
<td>41</td>
<td>3331</td>
<td></td>
</tr>
<tr>
<td>BAP</td>
<td>37</td>
<td>3353</td>
<td></td>
</tr>
<tr>
<td>Ontario average</td>
<td>96a</td>
<td>12214</td>
<td>8483</td>
</tr>
<tr>
<td>Sagamore Lake</td>
<td></td>
<td>1150</td>
<td></td>
</tr>
<tr>
<td>Woods Lake</td>
<td></td>
<td>1400</td>
<td></td>
</tr>
<tr>
<td>Adirondacks</td>
<td>91</td>
<td>5040</td>
<td></td>
</tr>
<tr>
<td>North of Great Lakes</td>
<td>12</td>
<td>546</td>
<td></td>
</tr>
<tr>
<td>No. Florida Lakes</td>
<td>27</td>
<td>525</td>
<td></td>
</tr>
<tr>
<td>No. New England Lakes</td>
<td>26</td>
<td>1190</td>
<td></td>
</tr>
</tbody>
</table>

*aRecent flux average for Lake Ontario is focus corrected.*

in the two cores (1.34). The smoothed line, a least-squares Gaussian fit to the data (after a background BAP concentration of 36 ng/g was subtracted), was then used as the uncorrected source function for a simulation of BAP in a coupled lakes model optimized for 137Cs.35,36 Since measured distribution coefficients for BAP and 137Cs are similar (500,000 mL/g), the transport parameters used for 137Cs were not changed for this simulation. The inventory of sedimentary BAP calculated by the model was then divided into the focus-factor-corrected inventory of BAP (2100 ng/cm²) measured in cores G-32 and E-30. This ratio was then used to correct the Gaussian source function, resulting in our estimate of the total BAP source function for Lake Ontario (Figure 9.6b). The calculation shows a peak input of approximately 2 ng/cm² month in 1947, declining to an input of 1.45 ng/cm² month in 1981. The modeled cumulative inventory of BAP in Lake Ontario (Figure 9.6c) shows that over the period 1830–1981, approximately 2100 ng/cm² were stored in the sediments, the equivalent of 400 ng/cm² have flowed out of the lake through the St. Lawrence River, and a small amount, approximately 30 ng/cm², is in the water column. This converts to a total concentration of approximately 4 ng/L in the water.

We attempt to evaluate the validity of the Lake Ontario sediment-derived BAP source function by examining independent data from Lake Erie. There are two separate data sets that are available: (1) the BAP that we measured in the core from the eastern basin (Figure 9.4) and (2) BAP concentrations measured locally in the atmosphere by the EPA from 1966 through 1979.37,38 We convert the measured sediment concentrations in a similar manner to that used
Figure 9.6. (a) The depth profile of BAP in the Lake Ontario cores (filled-in circles), with the G-32 concentrations multiplied by 1.34, the ratio of the BAP inventories from 1830 to 1981. The line is a least-squares fitted Gaussian used as input to the coupled lakes model. (b) The reconstructed BAP source function for the lower Great Lakes (see text for value). (c) The coupled lakes modeled cumulative distribution of BAP in Lake Ontario. The small region between the lines is the inventory in the water column.
for the Lake Ontario calculations. The mass accumulated in each 2-cm section of the Lake Erie core was multiplied by the BAP concentration to yield the uncorrected BAP flux. In order to compare this to the regional flux, it must be corrected for focusing. The $^{137}$Cs focusing factor for this core is 6.3, meaning that 6.3 times as much $^{137}$Cs is stored at this site than in the average lake sediment. Dividing the calculated BAP fluxes by this correction results in the flux values (filled-in rectangles) illustrated in Figure 9.7. The agreement with the solid line, which is the Lake Ontario sediment-derived source function, supports the idea of a generalized regional source for the lower lakes, without significant local sources to either lake.

A second independent confirmation for this source function from the atmospheric measurements at Toledo, Ohio (on the western shore of Lake Erie) is also illustrated in Figure 9.7. The measured concentrations were converted to fluxes using the Pelletier-Whipple-Wedlick (PWW) model, which relates monthly deposition rates to atmospheric concentrations. The model has been calibrated with measured atmospheric concentrations and deposition of radionuclides in the Great Lakes region.35

\[ \text{deposition (ng/cm}^2/\text{month)} = 1.7 \times \text{atmos. conc. (ng/m}^3) \]

The atmospheric BAP concentration at Toledo declined from a maximum of 2 ng/m$^3$ in 1967 to values around 1 by the early 1970s. Atmospheric BAP con-

![Figure 9.7](image)

**Figure 9.7.** Validating the lower Great Lakes BAP source function: the portion of our calculated source function for the time period covered by the independent Lake Erie sediment and atmospheric data (solid line), the BAP fluxes calculated from the 1983 Lake Erie box core concentration measurements (filled-in rectangles), and the fluxes calculated from the measured atmospheric concentrations of BAP in Toledo, Ohio (asterisks).
centrations of approximately 1 ng/m³ are also reported by several investigators for the lower Great Lakes region for the 1970s. After 1972, the fluxes calculated from these data are in excellent agreement with the sediment-derived source function, supporting the magnitude of the source function and the underlying assumptions of rapid transfer from atmosphere to sediments with little decomposition.

These relatively successful independent tests of the source function give us confidence that our approach has been valid. Our estimate of the BAP source function for the lower Great Lakes, as illustrated in Figure 9.6b, is

\[
\text{BAP (ng/cm}^2\text{ month)} = \text{BAP}_b + \text{BAP}_{\text{max}} \exp \left(-\frac{(t - t_m)^2}{2\sigma^2}\right)
\]

where \( \text{BAP}_b = 0.12\)
\( \text{BAP}_{\text{max}} = 1.88\)
\( t_m = 1946\)
\( \sigma = 41.7\)

Since there are many major cities and industrial complexes on Lakes Erie and western Ontario, and the prevailing wind is from the southwest, the source for the upper (and upwind) Great Lakes may be somewhat different—presumably smaller.

It is clear from the sedimentary profiles presented that the fluxes and resultant concentrations of combustion PAH are lower than peak values reached in the 1950s. However, this reduction of approximately 25% from the peak is much smaller than the three-to five-times reductions in chlorinated hydrocarbons (CHC) in these same cores and reductions of PCB in fish, which have dropped by more than a factor of five since the early 1970s. The lakes have responded rapidly and efficiently to the regulatory controls applied to the CHC; less stringent controls have been applied to combustion emissions, and the fluxes may again begin to increase with increased fossil energy usage.

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REFERENCES


