Hydrocarbons in Lake Washington Sediments. A 25-Year Retrospective in an Urban Lake

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Aliphatic and polycyclic aromatic hydrocarbon and stable and radiocarbon isotope distributions are compared for dated cores from the 1970s and 2000 for a 25-year retrospective in Lake Washington, Seattle, WA (USA). Contamination of Lake Washington sediments by petrogenic aliphatic hydrocarbons and pyrolytic polycyclic aromatic hydrocarbons via atmospheric deposition and stormwater runoff peaked between the 1950s and 1970s and has since decreased as stormwater inputs have been reduced. Radiocarbon signatures (Δ14C, %) of total organic carbon decrease (increased “age”) in the depth interval of highest hydrocarbon concentration. Graphitic black carbon in the year 2000 core showed a historical profile similar to that of the PAH; however high background sediments deposited before the founding of Seattle indicates a considerable nonindustrial component derived from weathering in the watershed. Unlike hydrocarbon contamination, input of terrestrial organic matter (tracked by long-chain fatty alcohols) has increased throughout the late 20th century, documenting a shift in pollutant sources away from hydrocarbons and toward anthropogenic erosion of the region’s soils.

Introduction

Aliphatic hydrocarbons (AHCs) and polycyclic aromatic hydrocarbons (PAHs) are widely studied sedimentary contaminants that are often used to track degradation of water bodies. The varied molecular compositions of AHCs and PAHs provide a means of distinguishing inputs from biogenic vs anthropogenic sources, and analyses of sediment cores often show historical trends of hydrocarbon distributions and concentrations shifting from natural levels of biogenic compounds in sediments deposited before the mid-19th century to elevated levels of compounds derived from anthropogenic activities. In the mid-1970s, a study (1–5) was undertaken to determine the sources and historical record of AHCs and PAHs in Lake Washington, an urban lake surrounded by metropolitan Seattle in western Washington state, USA. Surface sediments contained 50-fold and 10-fold higher AHC and PAH concentrations, respectively, than background levels in sediments deposited prior to about 1850. AHCs in surface sediments were largely petrogenic, being dominated by an unresolved complex mixture (UCM) while PAHs were pyrogenic, and both were associated with increased hydrocarbon pollution of the lake’s watershed as a consequence of urban expansion. A budget of hydrocarbon sources and sinks for Lake Washington (2) showed that greater than 85% of the AHC burden to the lake derived from stormwater runoff containing the petrogenic UCM from used motor oils (3) and pyrogenic PAHs from street dust (4); roughly 75% of the AHCs entering the lake were deposited in the sediments.

Environmental pollution abatement programs over the past decades, notably shifts in fossil fuel usage and diversion of wastewaters away from aquatic systems, may have had positive impacts on contamination of sediments, although studies on PAHs over the past 5 years show mixed results. In some instances, PAH concentrations in lake sediments have decreased since maxima in the 1960–1970s (6, 7) or have increased (6, 8). A high-resolution PAH record in the Pettaquamscutt River (10) shows a complex pattern of increasing concentrations above background since 1900 rising to peak concentrations in the 1960s, followed by decreasing concentrations until the mid-1980s, constant concentrations until about 1996, and increasing concentrations since 1996. Clearly there are sources and inputs of PAHs to aquatic sediments are complex and highly variable.

Has the hydrocarbon burden in Lake Washington been reduced by recent stricter environmental standards? We report here results of a 25-year retrospective study on AHCs and PAHs in Lake Washington that compares sedimentary distributions in the 1970s and in 2000. Chronologies for sediment cores were determined by210Pb, 137Cs, and 241Am analyses. Stable and radiocarbon isotopes were measured on total organic carbon and AHCs. Graphitic black carbon (GBC) was measured in the year 2000 core to evaluate its association with PAH. We found dramatic declines in the concentrations of both AHCs and PAHs in the most recently deposited sediments. Carbon isotope data point to a shift in pollutant sources away from fossil fuel and toward erosion.

Materials and Methods

Study Site. Lake Washington, 50 km long, 4 km wide, and up to 65 m deep, lies between the Cascade Mountains and Puget Sound in western Washington state. The lake is now heavily influenced by metropolitan Seattle that was first settled in the mid-19th century and has grown to a million inhabitants. The watershed of Lake Washington has been heavily logged and is now heavily urbanized. During the first half of the 20th century, Lake Washington received untreated, and later partially treated, sewage that led to substantial eutrophication and subsequent concern by the local population. By 1968, sewage had been diverted away from the lake, significantly improving the health of the lake and returning it to its present mesotrophic state (11, 12). Urban
stormwater runoff, the major source of hydrocarbon contamination in the 1960–1970s, has now also been diverted away from the lake, except for combined storm sewer overflow during periods of heavy precipitation.

**Hydrocarbon Analyses.** Sediments were sampled off Madrona Park in central Lake Washington (see Figure 1 of ref 1). Cores were collected in 1972 and 1977 using a multicorer and again in 2000 by box coring. Sediments deeper than about 50 cm were obtained from gravity cores. Cores were sectioned soon after collection and subsections were stored frozen until analysis. Plankton was collected in the lake with a 26-μm plankton net. In 1972, stormwater runoff was collected from storm sewers that routinely drained into the lake; in 2000 stormwater was collected during an overflow period.

We took special care to try ensure that our year 2000 data would be as internally consistent as possible with our 1970s data, recognizing that procedural changes can significantly affect concentration data obtained. Major changes in analytical procedure were instituted between analysis of the 1972 and 1977 cores (cf. refs 1 and 4), and we believe that AHC concentrations for the 1972 and 1977 cores are in fact not readily comparable. AHC concentrations for the 1972 cores are not discussed further here, although stable carbon and radiocarbon analysis results are. Analysis of the 1977 and 2000 cores followed similar (although not identical) procedures that we feel yielded comparable results.

**1977 Analysis.** AHCs and PAHs in the 1977 core were determined according to Giger and Schafner (13). Briefly, freeze-dried sediments were extracted with methylene chloride in a Soxhlet extractor and AHC and PAH fractions were obtained by sequential Sephadex LH-20 and silica gel chromatographies. Elemental sulfur was removed using activated copper and weights of AHCs were estimated using a Cahn electrobalance. AHCs and PAHs were analyzed further by glass capillary gas chromatography (GC) and gas chromatography–mass spectrometry (GC-MS) (13). AHC and PAH blanks were routinely run with batches of sediments and if necessary were subtracted from the sediment concentrations.

PAH concentrations were calculated from GC runs against an internal standard added immediately prior to GC analysis. Unfiltered stormwater samples were extracted with hexane and subjected to the same cleanup as were sediment extracts.

**2000 Analysis.** Sediments from the 2000 core were analyzed by a slightly modified procedure. Freeze-dried sediments were spiked with perdeuterated surrogates (fluorene-d12, phenanthrene-d10, chrysene-d12, and perylene-d12) and Soxhlet extracted with methylene chloride. After elemental sulfur was removed, the extracts were dissolved in hexane and charged to a column of 20 g of activated silica packed on top of 10 g of activated alumina (14). Aliphatic hydrocarbons were eluted with hexane, and polar material was eluted with hexane—methylene chloride (1:1). Hexane–DCM fractions were evaporated until only hexane remained, and this was charged to a 50 g Sephadex column. Sixty milliliters of hexane—methylene chloride—methanol (6:4:3) was discarded, and the following 100 mL containing the PAHs was collected. Estimates of weights of AHCs were again obtained on a Cahn electrobalance to facilitate comparison with the 1977 core.

Fatty alcohols were isolated from the year 2000 extracts by fractionation on silica gel and elution with 15% ethyl acetate in hexane; sterols were eluted with 20% ethyl acetate but were not analyzed. The alcohols provide an independent assessment of vascular plant inputs to the lake sediments and allow us to evaluate the history of erosion in the watershed.

AHCs and fatty alcohols (as trimethylsilyl ethers) were analyzed by GC and GC-MS. PAHs were quantified by selected-ion monitoring GC-MS using a Finnigan Incos 50 mass spectrometer and relative to the perdeuterated surrogates and a five-point calibration curve generated from standard solutions of the surrogates. AHC and PAH blanks were run with each batch of 10 samples, and AHC and PAH concentrations were corrected if necessary, although usually blanks contained negligible or undetectable hydrocarbons or individual PAH. Precision and accuracy of PAH analyses in 2000 were assessed by replicate analyses of the National Research Council/Canada marine sediment reference material HS-6. Replicate analyses were generally within ±15% of certified values, and precision was around 5%. Thus year 2000 PAHs have been internally corrected for recovery whereas the 1977 PAHs were not; this fact should be kept in mind during the following discussion of PAH concentrations as actual 1977 sediment concentrations may be higher than the reported concentrations.

**Organic Carbon.** Organic carbon content of the 1977 core was determined with an F&G model 185 CHN analyzer after removal of inorganic carbon with 0.1N HCl followed by oven drying. Sediments from the 2000 core were analyzed using a Carlo Erba CNS 1500 elemental analyzer after vapor-phase acid treatment (15).

**Stable Carbon Isotope Compositions.** The δ13C signatures of bulk (dried and acidified) sedimentary organic matter and isolated AHCs were determined on selected sediments from the 1972 core by combustion (see radiocarbon section below) and using a Consolidated Engineering Corp. model 21–210 dual beam isotope ratio mass spectrometer.

Sediment TOC from the year 2000 core was analyzed for δ13C with a Thermoquest continuous flow Finnigan-MAT isotope ratio mass spectrometer. AHC and alcohol (ALC) fractions were analyzed using a Finnigan elemental analyzer interfaced to a Finnigan 252 isotope ratio mass spectrometer.

**Radiocarbon.** Sediment TOC (acidified with HCl) and isolated AHCs from the 1972 core were combusted in a stream of oxygen at 900 °C in a quartz tube with CuO, and the CO2 produced was trapped with liquid D2. The CO2 was catalytically converted to methane, and radiocarbon was determined by counting with gas proportional counters in the radiocarbon laboratory at the University of Washington. Radiocarbon activities were determined relative to 95% NBS oxalic acid.

Radiocarbon in the year 2000 samples was determined by accelerator mass spectrometry (AMS) on sedimentary TOC and hydrocarbon and fatty alcohol fractions of sediment extracts. Acidified sediments and hydrocarbons and fatty alcohol fractions were combusted at 900 °C in quartz tubes in the presence of CuO and Ag. and CO2 produced was condensed to graphite through reaction with H2 over an iron catalyst (16). Radiocarbon was measured at the Center for AMS at Lawrence Livermore National Laboratory. Corrections were made for the δ13C content as determined on an aliquot of the CO2 using an isotope ratio mass spectrometer. Radiocarbon ages are calculated using the Libby half-life of 5568 years.

**Graphitic Black Carbon (GBC).** GBC (here defined as soot + graphitic black carbon) was determined on the year 2000 core as described by Gélinas et al. (17). Sediment samples were freeze-dried, ground, and demineralized with HCl and HF. Subsamples of demineralized sediment were treated sequentially with trifluoroacetic acid and then 6 N HCl to remove hydrolyzable organic matter (HOM). Demineralized and HOM-free samples were thermally oxidized in a calibrated muffle furnace at 375 °C for 4 h, and oxidized samples were then analyzed for carbon using a Carlo Erba elemental analyzer (model 1105). A comparison of several methods for analyzing GBC, including that used here, is given by Schmidt et al. (18).
TABLE 1. Elemental and Hydrocarbon Concentrations in Lake Washington Sediments in 1977 and 2000

<table>
<thead>
<tr>
<th>depth (cm)</th>
<th>1977 core</th>
<th>2000 core</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AHC (µg g⁻¹)</td>
<td>AHC/OC (µg g⁻¹)</td>
</tr>
<tr>
<td>0–1</td>
<td>4.90 0.49 10.0</td>
<td>770 15.7 6.5</td>
</tr>
<tr>
<td>1–2</td>
<td>4.38 0.52 9.9</td>
<td>480 10.9 3.1</td>
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<td>470 10.6 2.8</td>
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<td>430 9.9 4.9</td>
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<td>4.00 0.46 10.2</td>
<td>260 6.5 4.5</td>
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<td>14.36 9.2</td>
</tr>
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<td>4.35 0.45 11.3</td>
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<td>150.0 17.0 6.5</td>
</tr>
<tr>
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<td>80 1.4 1.2</td>
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<td>11 0.41 0.02</td>
</tr>
<tr>
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</tr>
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<td>30 0.66 0.70</td>
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<tr>
<td>37–38</td>
<td>4.55 0.46 11.3</td>
<td>27 0.47 0.47</td>
</tr>
</tbody>
</table>

* No data.

Sediment Chronology. Sediment chronologies of the 1970s cores were determined using the 210Pb/210Po technique (19). Dried sediments were dissolved in acid, and radionuclides were plated onto silver disks, and isotope activities were determined using γ spectrometry. Cesium-137 (137Cs) was determined using intrinsic germanium spectrometers. Ages of pre-1900 sediments were obtained by radiocarbon analysis.

Radiochronology of the year 2000 core was determined with the method of Alexander and Simoneau (20). Sediments were dried at 60 °C, ground, and sealed in 30-mL polypropylene jars. After being allowed to stand 20 days to allow ingrowth of intermediate daughter products of the 210Pb decay chain, samples were counted for 24 h. The radionuclides 210Pb (at 46.5 keV), 241Am (at 59.5 keV), 226Ra (from 214Pb and 214Bi at 295, 352 and 609 keV), and 137Cs (at 661 keV) were measured simultaneously using intrinsic germanium detectors. Detector efficiencies were determined using NBS and EPA standards, and self-absorption corrections were made (21). Ages of deep sediments were obtained by radiocarbon analysis of TOC.

Results and Discussion

Geochemical Background. Radionuclides chronologies for cores collected in the 1970s and in 2000 indicate a vertical offset of about 4–5 cm, based on peaks in 137Cs activity (about 1964) at about 7–8 cm in the 1970s cores vs peaks in 137Cs and 241Am at 10–12 cm in 2000. 210Pb profiles for both the 1970s and 2000 cores further suggest three sedimentation rates over the past 100+ years. A sedimentation rate of ~0.25 cm year⁻¹ corresponds to a mesotrophic lake during the mid-twentieth century when sewage inputs and erosion in the watershed were high, resulting in a sedimentation rate of ~0.5 cm year⁻¹. Oligotrophic Lake Washington prior to introduction of sewage effluents in the early twentieth century had a sedimentation rate of ~0.1 cm year⁻¹. Ages of the bottoms of the cores were about 4000 years BP for 380–395 cm depth horizon in the 1972 sediments and 3400 years BP for the 300–305 cm interval of the year 2000 sediments by radiocarbon dating of organic carbon.

Organic carbon (OC) contents of both 1977 and year 2000 sediments ranged between 3 and 7% (by weight; Table 1). General trends in both cores were similar: OC concentrations of 4–6% in upper sediment layers, reduced concentrations (3–4%) at mid-core, and increased concentrations toward the bottom of the core (5–7%). Atomic C/N ratios (C/N(a); Table 1) ranged from 10 to 13, again with the highest ratio (C/N(a) = 13) at mid-century when urban development and logging in the lake’s watershed may have increased inputs of carbon-rich soil material. Stable carbon isotopes were measured to evaluate OC and, by extension, hydrocarbon sources to the lake. δ13C values for TOC (δ13CTOC) in the three sediment intervals from the 1972 core that were analyzed (Table 2) ranged from ~30.5 to ~26.1‰. The more detailed δ13C profile for TOC obtained on the year 2000 core (Table 2) provides better insight into the ecological condition of Lake Washington over the history covered by the core. The δ13C enrichment of 3–4‰ for the 50–10 cm depth interval, or from between the 1850s and 1970s, can be interpreted as showing the shift from an oligotrophic lake to an eutrophic lake up until the early 1970s followed by a return to mesotrophy in the past 3 decades following diversion of sewage effluents. Overall δ13CTOC values
were not particularly useful as source indicators for TOC in Lake Washington, however, since representative organic carbon sources—stormwater hydrocarbons (−27.8% in 2000), soil (−25.5% in 1977), and plankton (−24.0% in 1977)—taken from the Lake Washington area had similar δ13C values (Table 2).

Hydrocarbon Record in Lake Washington. Gas chromatographic analysis showed similar compositional patterns in both the 1970s and 2000 cores (Table 3). Chromatograms from the year 2000 core see also refs. 1 and 4. Near-surface sediments contained AHCs consisting largely of a petroleum-derived unresolved complex mixture (UCM) with a lesser contribution from odd-carbon number predominant C17–C35 n-alkanes of algal and vascular plant origins (CPI20−24 ~ 4). PAH distributions in upper sediments were dominated by nonylalkylated compounds ranging from acenaphthene to coronene, indicative of high-temperature pyrolysis/combustion sources. Sediments deposited prior to about 1850 contained AHC with a strong vascular plant signal and no UCM, and very low levels combustion PAH but abundant perylene, a common product of diagenesis (5).

Concentration profiles, on the other hand, differed markedly between 1977 and 2000. Whereas differences in methodology may complicate comparing absolute PAH concentrations between 1977 and 2000, shapes of depth profiles should be unaffected. The 1977 core was characterized by maximum concentrations in surface sediments (770 μg of AHC g−1 of dry weight sediment and 6.5 μg g−1 PAH; Table 1 and Figure 2); the UCM constituted >98% of the AHC loading. Concentrations decreased downslope, reaching stable background values (~20 μg g−1 AHC with negligible UCM and <1 μg g−1 PAH) below the 34–39 cm interval deposited ca. 1880. In contrast, the year 2000 core had strong subsurface maxima in AHC and PAH concentrations, at ~900 μg g−1 for AHC at 10–12 cm and 10.6 μg g−1 for “combustion-derived” PAH at 14–16 cm. Combustion-derived PAHs are the summed concentrations of anthracene, benz[a]anthracene, chrysene, triphenylene, benz[a]fluoranthene + benz[k]fluoranthene, benz[a]pyrene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, benzo[ghi]perylene, and coronene. Hydrocarbon concentrations near-surface (<5 cm depth) sediments were lower (300–400 μg g−1 AHC and 1–5 μg g−1 PAH). Background sediments (50 cm depth) contained 20–30 μg g−1 AHC and <1 μg g−1 combustion PAH.

The shapes of the depth profiles suggest that inputs of petrogenic aliphatic hydrocarbons and pyrogenic PAH to Lake Washington have decreased during the past 25 years. Using 210Pb chronology of the year-2000 core, we can estimate AHC and combustion PAH fluxes to the lake’s sediments in the past. For sediments shallower than 20 cm, a sediment accumulation rate of 0.07 g cm−2 year−1 is estimated, while for sediments deeper than 20 cm the accumulation rate would be 0.02 g cm−2 year−1. Applying AHC and combustion PAH concentrations, we calculate accumulations of 28 μg of AHC cm−2 year−1 for 0–5 cm, 63 μg of AHC cm−2 year−1 for 10–12 cm, and 0.5 μg of AHC cm−2 year−1 for >50 cm. Thus AHC fluxes have decreased by ~50% since a maximum some 25 years ago but remain nearly 50-fold greater than the preindustrial background. As noted above, the UCM comprised the bulk of the AHC in sediments deposited over the past 50 years. Corresponding PAH accumulation rates are 0.21 μg of PAH cm−2 year−1 for 0–5 cm, 1.4 μg of PAH cm−2 year−1 for 14–16 cm, and 0.004 μg of PAH cm−2 year−1 for

### Table 2. Stable Carbon and Radiocarbon Isotope Compositions for TOC, AHC, and Fatty Alcohols (ALC) for Lake Washington Sediments

<table>
<thead>
<tr>
<th>approx.</th>
<th>1972 core</th>
<th>2000 core</th>
<th>plankton</th>
<th>stormwater</th>
</tr>
</thead>
<tbody>
<tr>
<td>age</td>
<td>δ13C TOC (‰)</td>
<td>Δ13C TOC (‰)</td>
<td>δ14C TOC (‰)</td>
<td>δ13C AHC (‰)</td>
</tr>
<tr>
<td>0–5</td>
<td>−26.1</td>
<td>−225</td>
<td>0.77</td>
<td>−34.9</td>
</tr>
<tr>
<td>10–15</td>
<td>−28.1</td>
<td>a</td>
<td>a</td>
<td>−35.1</td>
</tr>
<tr>
<td>35–55</td>
<td>−30.5</td>
<td>−86</td>
<td>0.92</td>
<td>−35.3</td>
</tr>
<tr>
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<td>a</td>
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<td>plankton</td>
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<td>a</td>
<td>a</td>
<td>−26.9</td>
</tr>
<tr>
<td>stormwater</td>
<td>a</td>
<td>a</td>
<td>a</td>
<td>−27.5</td>
</tr>
</tbody>
</table>

* No data.
considerably higher than values reported for Lake Michigan and Europe (6) fit historical patterns observed in lakes in the U.S. (10) deposited since the 1950s also still some 50-fold above background.

**FIGURE 1.** Gas chromatograms of aliphatic hydrocarbons (AHCs) and PAHs in Lake Washington from the year 2000 core: a and b, AHCs from 10–12 and 50–52 cm sections, numbers correspond to carbon numbers for n-alkanes; c and d, PAHs from the 10–12 and 50–52 cm sections. Abbreviations: Phe = phenanthrene; Flu = fluoranthene; Pyr = pyrene; Ret = retene; Chry = chrysene/triphenylen; BF = benzo[b]fluoranthene + benzo[k]fluoranthene; BeP = benzo[e]pyrene; BaP = benzo[a]pyrene; Per = perylene; IPyr = indeno[1,2,3-cd]pyrene; BPer = benzo[g,h,i]perylen.

> 50 cm, or a decrease of nearly 85% in the past 25 years, but also still some 50-fold above background.

Decreasing concentrations of hydrocarbons in sediments deposited since the 1950s–1970s Lake Washington sediments fit historical patterns observed in lakes in the U.S. (10, 22) and Europe (6, 7). Fluxes for AHC to Lake Washington are considerably higher than values reported for Lake Michigan (0.006 µg of AHC cm⁻² year⁻¹ prior to 1880 and 0.1 µg of AHC cm⁻² year⁻¹ in 1980; ref 23). PAH fluxes, however, are similar to values in the Pettasquamsett River in the northeastern USA (0.002 µg of PAH cm⁻² year⁻¹ during preindustrial times to a maximum of ~0.5 µg of PAH cm⁻² year⁻¹ around 1960, 0.2 µg of PAH cm⁻² year⁻¹ from 1978 to 1996, and ~0.3 µg of PAH cm⁻² year⁻¹ in 1999; ref 10) but considerably higher than values obtained in remote lakes (6, 7, 22). It is also noteworthy that although both classes of hydrocarbons apparently have been delivered to Lake Washington largely via stormwater runoff, their origins may be different. AHCs are characteristic of petroleum residues, such as used motor oil deposited directly onto urban streets (3) and carried to the lake by urban stormwater runoff. PAHs, on the other hand, are high-temperature pyrolysis products that once emitted into the atmosphere may be reach the lake either directly by deposition of atmospheric aerosols on to the lake's surface or indirectly by deposition onto urban areas and subsequent incorporation into street dust and urban runoff (4). The importance of runoff from streets and highways in urbanized areas as the dominant source of hydrocarbons to adjacent sediments has been confirmed by the AHC budget for Lake Washington in which 85% of AHC delivered to the lake entered via stormwater (2) and by a study by Hoffman et al. (24) estimating that urban runoff accounted for 71% of the PAHs entering Narragansett Bay. Interestingly, there is an offset of ~4 cm between the depth of the peak concentration of AHC (10–11 cm) and that of PAH (14–16 cm). This offset could arise if the PAH profile reflects maximum inputs of coal-derived pyrolytic PAHs during the 1940s–1950s, after which a shift toward petroleum-based fuel use and increased automotive traffic led to maximum inputs of petrogenic AHCs during the 1960s–1970s.

**Stable Carbon Isotopes of Hydrocarbons and Alcohols.** Stable carbon δ¹³C values for the AHC fraction of the 1972 core were about −35‰ (Table 2). The 7% depletion in δ¹³C for hydrocarbons relative to TOC could result from the biosynthetic isotope fractionation of lipids compared to the protein and carbohydrate fractions (25) that constitute a larger proportion of organic carbon in organisms and sediments. AHCs from stormwater runoff were enriched in δ¹³C (−27.5‰) considerably higher than δ¹³C isotope values for the AHC fraction of the sediments.

Stable carbon δ¹³C values for hydrocarbons in sediment from the year 2000 core ranged between −29.1‰ in 3400 year old sediments at the bottom of the core and −27.8‰ in highly contaminated sediments near the top of the core (Table 2). We have no explanation as to why the δ¹³C values in the year 2000 sediments were depleted by 5–7‰ compared to the 1972 values, although making the isotopic measurements on AHC fractions in the 1970s was pushing the capabilities of the analytical techniques at the time. Vascular plant derived fatty alcohols, characterized by a distinct long-chain (C₂₀–C₃₀), even-carbon predominant character of their gas chromatograms throughout the year 2000 core (data not shown), had δ¹³C values of ~31.3‰ to ~29.6‰. If we assume that the δ¹³C values for the alcohols are typical for vascular plant lipids in the Lake Washington watershed, then vascular plant derived AHCs should have similar isotopic compositions (about −30‰), and in fact δ¹³C values for both AHCs and alcohols are similar (~29.1‰ and ~29.6‰, respectively) at the bottom of the core. However, there is a 2–4‰ offset between δ¹³C values of AHCs and alcohols in the upper sections of the core that are heavily oiled. This offset reflects the high proportion of AHC in upper sediments that are derived from
the petroleum UCM. A δ¹³C value of −27.8‰ was measured for stormwater AHC in 2000, similar to the year 2000 sediment AHC and the 1972 stormwater AHC fraction.

**Radiocarbon for Evaluating Carbon Sources.** Radiocarbon measurements were made on TOC from two depth intervals (0–5 cm and 35–55 cm) of the 1972 core and on AHCs from one interval (0–5 cm; Table 2). Δ¹³C of −225‰ (see ref 26 for the Δ¹³C notation) for TOC of 0–5 cm sediment was depleted in ¹³C relative to 35–55 cm sediments (Δ¹³C = −86‰), confirming the fossil component seen in the gas chromatograms. Stormwater AHCs in 1972 had Δ¹³C −988‰. These ¹³C activities allow estimation of the fraction of “modern” carbon (fₘ; Table 2) in a sample. Thus 77% of the carbon in the 0–5 cm sediment TOC was modern, compared to 92% at 35–55 cm. A minimum estimate of about 15% of the OC in the AHC fraction of the 0–5 cm sediment was modern.

Application of AMS measurement of radiocarbon isotopes has led to a significant decrease in sample size (100's of mg of organic carbon for gas proportional counting vs 10's of µg for AMS). Thus for the year 2000 core, a higher resolution ¹⁴C database is available (Table 2 and Figure 3). TOC in the year 2000 core had Δ¹⁴C values ranging from −48.3‰ (fₘ = 0.96) in uncontaminated 40–42 cm sediment to −333.0‰ (fₘ = 0.67) at 300 cm, with a marked ¹⁴C depletion (Δ¹⁴C = −254.6 to −278.9‰; fₘ 0.75 and 0.74, respectively) centered over the 14–18 cm depth intervals. Using the radiocarbon content of the 300-cm interval (−333.0‰) gives a Libby age of about 3400 years BP, which in turn yields a preindustrial sedimentation rate of 0.09 cm/year that is remarkably close to the 0.1 cm/year extrapolated from ²¹⁰Pb chronology. The Δ¹⁴C values for 14–18 cm sediments in 2000 (−254.6 to −278.9‰) are similar to the Δ¹³C of −225‰ measured in 0–5 cm sediments in the 1970s. Plankton collected in Lake Washington in 2000 had a Δ¹³C of −35‰ (fₘ = 0.97); stormwater runoff in 1972 and 2000 had Δ¹³C of −988‰ (fₘ = 0.01) and −998‰ (fₘ = 0.002), respectively.
Radiocarbon content of isolated AHC fractions ($\Delta^{14}C_{\text{AHC}}$), along with the chromatographic nature of the hydrocarbons, helps explain the depletion in $^{14}C$ of TOC in the 14–18 cm sediments. AHC isolated from sediments at 50 and 300 cm that are dominated by long-chain saturated, vascular plant-derived compounds had $\Delta^{14}C_{\text{AHC}}$ values that tracked $\Delta^{14}C_{\text{TOC}}$ remarkably well. $\Delta^{14}C_{\text{AHC}}$ values from sediments shallower than 50 cm that contained the UCM were depleted in $^{14}C$, decreasing to $\Delta^{14}C = -965\pm0.04$ at 0–1 cm. The AHC fraction of the 10–12 cm sediment was further partitioned into saturated (urea adductable) and branched/cyclic (urea nonadductable) fractions. The saturates that include a mix of contemporary vascular plant and fossil n-alkanes are enriched in $^{14}C$ ($\Delta^{14}C = -716\pm0.29$) relative to the predominately fossil UCM-dominated branched/cyclic fraction ($\Delta^{14}C = -958\pm0.04$). Clearly, the minimum in $\Delta^{14}C_{\text{TOC}}$ corresponds to the depth of maximum accumulation of petroleum-derived material devoid of $^{14}C$. Petroleum hydrocarbons continue to dominate the AHC fraction in the shallowest sediments as evidenced by the abundant UCM and the highly depleted $^{14}C$ content. However, the enrichment in $^{14}C$ of TOC in the shallowest sediments indicates some younger non-AHC organic matter enriched in $^{14}C$ since concentrations of petroleum-derived AHC decrease at the top of the core.

Deviations in radiocarbon ages for sedimentary TOC from “true” geological ages result from inputs of “preaged” carbon (27). Preaged carbon can arise from remobilization of soil carbon or from fossil kerogen-derived carbon of eroded rocks. In the case of preindustrial sediments in Lake Washington, for example, a radiocarbon content of $-129.6\%$ for 50–52 cm TOC would correspond to a $^{14}C$ age of ~1000 years BP for sediment that was actually deposited about 1850 based on $^{210}Pb$-derived sedimentation rates, or 150 years BP, reflecting incorporation of preaged and $^{14}C$-deficient organic carbon of nonanthropogenic origin. Incorporation of proportionally more preaged carbon to surface sediments may help explain the observation that TOC at 0–1 cm ($-93.3\%$) is more depleted in radiocarbon than at 4–5 cm ($-54.4\%$).

It is probable that a major natural source of OC in Lake Washington is soil carbon that is eroded from the watershed and redeposited in Lake Washington. Riverborne particulate OC contains a mix of carbon of different ages, from modern plant debris to fossil rock-derived carbon (27–29). To minimize problems with such a mix of $^{14}C$ contents in soil OC, the aliphatic hydrocarbon fraction has been used (30) to obtain ages of soil horizons that are thought to be more reliable than ages determined from TOC. By extrapolation, this approach could provide insight into the “preaging” of organic material on land prior to transfer to aquatic sediments. However, such an approach is not feasible for Lake Washington sediments due to contamination of the hydrocarbon fraction by petroleum residues.

On the other hand, long-chain alcohols are also derived from epicuticular coatings on vascular plants and are common in soils. If the alcohol fraction is free of a fossil component, it might provide an alternate approach for estimating the preaging of TOC in Lake Washington. Fatty alcohols in the Lake Washington core were analyzed by gas chromatography (data not shown) and were long-chain (e.g., C$_{24}$–C$_{30}$), even-carbon predominant and of vascular plant origin. $\Delta^{14}C$ of the alcohol fraction ($\Delta^{14}C_{\text{Alc}}$) in five depth intervals were determined by AMS (Table 2 and Figure 3). For 30–32 cm, 50–52 cm, and 300–305 cm sediments, $\Delta^{14}C_{\text{Alc}}$ values were essentially the same as $\Delta^{14}C_{\text{TOC}}$ values, and furthermore, $\Delta^{14}C_{\text{Alc}}$ values at 50–52 cm and 300–305 cm were the same as values $\Delta^{14}C_{\text{AHC}}$. Thus, for sediments deeper than about 30 cm, the radiocarbon content of TOC is equivalent to that of fatty alcohols, and below 50 cm, $\Delta^{14}C$ values of all three fractions (TOC, alcohols, and hydrocarbons) correspond remarkably well. This is consistent with all three fractions having the same source prior to about 1850.

However, in the 0–1 and 10–12 cm sediments, $\Delta^{14}C_{\text{Alc}}$ is also depleted relative to $\Delta^{14}C_{\text{TOC}}$. While we cannot rule out that the alcohol fraction contained “old” carbon that was “invisible” to gas chromatography, this deviation could also...
be explained if the alcohol fraction derived from soil organic matter has a $\Delta^{13}C$ of about $-460\pm 0.55$. Soil eroded from unregulated construction releases highly $14$C-depleted carbon into watersheds (31, 32). Mobilization of subsurface soil undoubtedly occurs in the Lake Washington watershed since it is highly impacted by urban sprawl and logging in the foothills of the Cascade Mountains, although we do not know the $14$C age of soil TOC being delivered to the lake. These results suggest increased effects of erosion on Lake Washington. It is also apparent that with a $\Delta^{14}C = -93\pm 0.91$ of contemporary $14$C-enriched organic matter, such as algal carbon. However, even the plankton sample apparently contains preaged carbon, as indicated by a $\Delta^{14}C$ of $-34\pm 3$, and although we do not know the $\Delta^{14}C$ of inorganic carbon in Lake Washington, it may be depleted in $14$C if its source is weathered rocks in the watershed or remineralization of soil organic matter in the lake.

**Graphitic Black Carbon as a Carrier of PAH.** Black carbon (BC) has been found widely distributed in soils and sediments (33) consistent with its widespread production in fossil fuel and biomass combustion processes and its recalcitrant nature. BC is a continuum from partly charred plant material through char and charcoal to graphite and soot particles that have recondensed from the gas phase. Soot and graphitic black carbon, collectively referred to as GBC, are formed exclusively in the vapor phase and thus, as fine particles, can be rapidly dispersed through aerosol formation and atmospheric transport and deposition (34, 35). However, the heterogeneous nature of BC means that both its definition and methods for measurement are highly operational and rather diverse (17, 18, 36–37).

GBC has been shown to be an important carrier phase that influences the environmental behavior of PAH (38). PAHs isolated from a near-surface soil have low $\Delta^{14}C$ values suggesting that their origin is mainly from fossil fuel combustion (39), and similar $\Delta^{14}C$ values for GBC and PAH in an urban aerosol (40) show that both GBC and PAH condense out of the same hot combustion gases. It is therefore not surprising that PAH and GBC show similar temporal profiles in the year 2000 Lake Washington sediments (Table 1 and Figure 4), although a linear regression of PAH concentrations vs GBC concentration over the upper 30 cm yielded $r^2 = 0.56$. A subsurface maximum in GBC concentration at $\sim 0.06$ wt % at 14–16 cm corresponds with the PAH concentration maximum in the same sediment interval. Like PAH, GBC concentration decreases toward the sediment surface, but unlike PAH, GBC concentrations remain relatively high in pre-1850 sediments, at $\sim 0.03$ wt %. Such high presettlement concentrations are most likely due to the presence of naturally occurring, petrogenic or graphitic carbon weathered from the watershed bedrock (41).

These results suggest that only about half of the GBC measured at 14–16 cm originates from anthropogenic fossil fuel combustion. However, although the 30–300 cm concentrations of petrogenic graphite are constant ($0.027 \pm 0.002$ dry wt %), the graphitic carbon contribution cannot be subtracted from the total GBC concentrations measured between 0 and 30 cm (to get an estimate of the soot-only inputs) because watershed characteristics, and thus weathering products inflow, have been profoundly modified during the last century. The lower GBC concentrations found at the surface ($0.023$ wt %), where an appreciable soot contribution is very likely based on the PAH results, agrees with the hypothesis of variations in petrogenic graphite accumulation rates during the last 100 years. Because the $\Delta^{13}C$ and $\Delta^{14}C$ signatures of soot and graphitic carbon are very similar (41), it is impossible to apportion the GBC inputs into natural and...
anthropogenic sources, and thus the percentage decrease in soot inputs in the last 25 years unfortunately cannot be estimated.

**Overview.** It is the recalcitrance of hydrocarbons in sediments that makes them robust indicators of contamination history. The record of long-term contamination of Lake Washington sediments over the past century complements a similar record of acute hydrocarbon contamination of marsh sediments in Buzzards Bay, MA (42). In 1969, some 650,000 L of No. 2 fuel oil was spilled into Buzzards Bay, and the environmental impact and fate of the resulting West Falmouth oil spill also has been studied for some 30 years. Both case studies show down-core concentration peaks unambiguously associated with the period of maximum hydrocarbon input, whether by dispersed and chronic discharge of hydrocarbon-containing stormwater runoff to Lake Washington over several decades during the early second-half of the 20th century or by the one-time spill of fuel oil into Buzzards Bay. Residual oil, primarily a highly degraded UCM, in West Falmouth sediments is restricted, with some smearing of the concentration peak due to sediment mixing, to the depth interval deposited at the time of the spill; petroleum residues were not detected in sediments deposited prior to and after the spill. Surface sediments in West Falmouth contain low concentrations of hydrocarbons because uncontaminated sediments have been deposited on top of oiled sediment. Surface sediments of Lake Washington record high concentrations of hydrocarbons during a period of high stormwater discharge to the lake and subsequent reduced concentrations in response to a reduction in stormwater inflow. Significantly, the two historical records conclusively demonstrate that although degradation of low molecular weight and normal alkanes may occur in sediments, the complex mixture of branched and cyclic hydrocarbons that comprise the UCM can persist for long periods in the sedimentary record, long after the source of contamination has been eliminated.

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