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SOURCE APPORTIONMENT OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) INTO CENTRAL PARK LAKE, NEW YORK CITY, OVER A CENTURY OF DEPOSITION

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Abstract

Relative contributions of polycyclic aromatic hydrocarbons (PAHs) from combustion sources of wood, petroleum, and coal were computed in sediments from Central Park Lake in New York City (NY, USA) by chemical mass balance based on several reliable source indicators. These indicators are the ratio of retene to the sum of retene and chrysene, the ratio of 1,7-dimethylphenanthrene (DMP) to 1,7-DMP and 2,6-DMP, and the ratio of fluoroanthene to fluoroanthene and pyrene. The authors found that petroleum combustion-derived PAH fluxes generally followed the historical consumption data of New York State. Coal combustion-derived PAH flux peaked approximately in the late 1910s, remained at a relatively high level over the next 3 decades, then rapidly declined from the 1950s to the 1960s; according to historical New York State coal consumption data, however, there was a 2-peak trend, with peaks around the early 1920s and the mid-1940s. The 1940s peak was not observed in Central Park Lake, most likely because of the well-documented shift from coal to oil as the major residential heating fuel in New York City during the late 1930s. It was widely believed that the decreased PAH concentrations and fluxes in global sediments during the last century resulted from a major energy shift from coal to petroleum. The data, however, show that this shift occurred from 1945 through the 1960s and did not result in an obvious decline. The sharpest decrease, which occurred in the 1970s was not predominantly related to coal usage but rather was the result of multiple factors, including a decline in petroleum

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SUPPLEMENTAL DATA

Parts S1–S3

Table S1.

Figures S1–S8. (1.8 MB DOCX).

The authors have no conflicting interests.

All Supplemental Data may be found in the online version of this article.

usage largely, the introduction of low sulfur-content fuel in New York City, and the introduction of emission-control technologies.

Keywords

Polycyclic aromatic hydrocarbon (PAH); Urban lake; Sediment; Contamination history

INTRODUCTION

In urban waters, polycyclic aromatic hydrocarbons (PAHs), which contain suspected carcinogens and mutagens, can be from both pyrogenic (combustion-related) and petrogenic sources derived from crude oil and other fossil fuels [1,2]. Except at sites that have been heavily impacted by oil spills (e.g., Arthur Kill), pyrogenic sources such as residential heating and motor vehicle exhaust usually dominate PAH fluxes to urban lakes, especially to those receiving primarily atmospheric contaminant inputs [3,4]. Previous studies from our group have demonstrated that Central Park Lake in New York City (NY, USA) is such a lake [4-7]. Chillrud et al. [5] found that historical accumulation of Pb, Zn, and Sn in Central Park Lake sediments was mainly tied to the history of local municipal solid waste incineration, specifically for Pb, and combustion of gasoline was a less important source to the New York City atmosphere. Historical polychlorinated dibenzo-*p*-dioxin and polychlorinated dibenzofuran (PCDD/F) trends in Central Park Lake also suggest that the sediments can be used to interpret the record of combustion-derived organics to the New York urban area [7], and Louchouart et al. [6] demonstrated that the chronology of black carbon in the lake sediments primarily reflects local municipal waste incineration and liquid fuel combustion.

Most historical studies agreed that fluxes of Σ PAH (the sum of principal parental PAH compounds) to sediments worldwide increased significantly from the 1860s to the 1920s as coal became the dominant global energy source [8-10]. Post-1930 trends of Σ PAH vary substantially, mainly reflecting local and regional industrialization and urbanization. In developed countries, a decreasing trend following a peak around the 1960s is typically observed. Wakeham et al. [10] found that Σ PAH fluxes into Lake Washington (Seattle, WA, USA) peaked at that time and exhibited a continuous decline to the end of the last century, reaching a level similar to the preindustrial era. A steady decline from the 1960s peak to the present was also observed in a moat sediment core from Tokyo, Japan [11], and a core from Halifax Harbor, Canada [12]. In contrast, PAHs were reported to increase continuously in sediments of some areas in developed countries where urbanization is ongoing. For example, based on dated sediment cores from 10 lakes and reservoirs in 6 US metropolitan areas, Van Metre et al. [13] demonstrated that PAH levels have increased substantially over the past several decades. The authors linked the continuing rise to urban sprawl and heavier traffic in urban and suburban areas.

In developing countries with relatively lax environmental regulation, PAH levels have generally increased in the past 40 yr as a result of increasing energy demand and usage. Liu et al. [14] observed a tripling in PAH levels over the last 15 yr of the 20th century in a

sediment core collected from south China, a period characterized by a rapid increase in power generation and the number of motor vehicles in response to China's economic reforms and open-door policy initiated in the early 1980s. Substantial increases in PAH levels over the past 40 yr were also observed in the upper Gulf of Thailand [15] and the Santos Estuary, Brazil [16].

Most PAH studies report total PAH concentrations or fluxes without further apportionment analysis. O'Malley et al. [17] applied compound-specific stable isotope analysis to distinguish petrogenic (e.g., fuel spills) and pyrogenic sources, such as the incomplete combustion of fossil fuels (petroleum and coal) or biofuels. Studies to date have shown that pyrogenic sources are quantitatively the largest sources of PAHs in most lake sediments. Some efforts have been made to estimate various pyrogenic PAH fluxes using chemical mass balance models [18-20] and statistical analysis [21,22]; however, those studies are based on relative abundances of principal parental and alkylated PAHs, which can be similar in multiple sources and can vary substantially within a single combustion source [23,24]. This leads to high uncertainty in source estimation. The Unmix model has also been used for apportioning aerosol sources in large cities [25], but it is not particularly applicable to the 150-yr history recorded in Central Park Lake sediments, where changing combustion techniques play a significant role in determining the composition of the PAH signal.

In the present study, we utilized several previously suggested, reliable source indicators to estimate the relative contributions from various pyrogenic sources into Central Park Lake. Calculated PAH fluxes representing different energy sources were then compared with New York State consumption data. The overall goal of this comparison was to identify robust source-sensitive indicators for combustion-derived PAH sources. Such tracers would be most useful in efforts to elucidate major sources responsible for the increasing PAH levels in some urban areas in developed countries [13] and areas in developing countries with ongoing urbanization and industrialization [14-16].

METHODS

Sample collection, organic extraction and purification, and analysis methods have been described previously [4,5]. Briefly, 4 sediment cores were collected through the ice from Central Park Lake in January 1996 (Supplemental Data, Figure S1). After collection, each core was sectioned at 2-cm intervals. The sections were dried at 35 °C under a flow of air filtered through a column of Florisil® and ground into a uniform powder with mortar and pestle. Several grams of dried sample were used to determine radionuclide activities of ⁷Be, ¹³⁷Cs, and total and supported ²¹⁰Pb for sediment dating. All 4 cores showed consistent radionuclide profiles, indicating continuous particle accumulation since the late 1860s [5]. Central Park core F (CPF) was used for PAH, saturated hydrocarbon, and black carbon studies [4,6]. We found that PAHs in the dry sediments archived in prefired (450 °C overnight) glass vials with Teflon-lined screw caps at room temperature are quite stable and show no detectable compositional differences when compared with those in fresh sediments. In 2002, approximately 4 g of sediment from each core section were Soxhlet-extracted overnight using dichloromethane as the solvent. Extracts were concentrated under a gentle flow of N₂ in a Turbovap® programmable concentrator. Extract cleanup and fractionation

were performed using alumina and silica chromatographic columns, respectively. Activated copper was added to remove elemental sulfur. Gas chromatography (GC) and mass spectrometry (MS) were used for quantification.

In the present study, calculated PAH fluxes were compared with the historical consumption data of individual energy sources (e.g., usage of wood, petroleum, and coal) of New York State. These historical consumption data were retrieved from several data sets. New York State data for 1960 through 2005 were compiled by the Energy Information Agency of the US Department of Energy. Because of the lack of state-specific energy-consumption data before 1960 in the Department of Energy data set, energy usage data from 1900 through 1960 were recovered from Gschwandtner et al. [26] (see Supplemental Data for more details).

RESULTS

To evaluate environmental impacts of contaminants in natural waters, concentration units (e.g., ng/g of sediments or waters) are normally reported and discussed because of the assumed direct relationship to toxicity. Fluxes, however (e.g., ng/cm²/yr), are far more useful in the interpretation of source strengths. Concentrations of contaminants within the core are influenced not only by strength of the source input but also by particle accumulation rate, which can vary in lakes by at least 1 order of magnitude [27,28].

The center of a lake often has higher sediment accumulation rates because of advective transport from the basin periphery, a natural event called “sediment focusing” [29]. It is reasonable to expect that cores from areas of rapid fine-particle accumulation will receive a greater total amount of particle-associated radionuclides ¹³⁷Cs or ²¹⁰Pb [7]. This focusing factor can be estimated by comparing the integrated inventory of ¹³⁷Cs or unsupported ²¹⁰Pb in the core, decay corrected to the date of core collection, with their expected delivery from the atmosphere [5,8,30]. For a core collected in January 1996 from Central Park Lake (~40°N latitude), the expected total delivery of ¹³⁷Cs from fallout would be approximately 72 mCi/km² [7]. Similarly, a value of 29.25 dpm/cm² would be expected for ²¹⁰Pb, based on the average of values reported for Adirondack soil cores [31] and lowland New England soils [32]. In the Central Park Lake cores, the focusing factors range from 1.1 to 1.2 (based on ¹³⁷Cs) and from 1.2 to 1.4 (from ²¹⁰Pb) [7]. In the present study, reported flux values are all corrected for sediment focusing by a factor of 1.2.

Profiles of PAH fluxes

The “total PAH” concentration often used in environmental studies generally refers to the sum of principal 2-ring to 6-ring parental compounds. This convention underestimates the PAH flux from petroleum combustion, which contains abundant alkylated compounds [33]. To better compare our results with those of other studies, we quantify the Σ_{16} PAH concentration as the sum of 16 US Environmental Protection Agency parental PAHs but also present total PAH as the sum of all measured parental and alkyl-substituted PAHs (see Supplemental Data for a list of PAH compounds quantified).

The $\Sigma_{16}\text{PAH}$ flux remained relatively low until the onset of the 20th century (Figure 1), followed by an abrupt increase which predated the rapid increase in total saturated hydrocarbons by approximately 20 yr (data not shown) [4]. The $\Sigma_{16}\text{PAH}$ flux reached the first maximum as well as the highest level ($\sim 4000 \text{ ng/cm}^2/\text{yr}$) in the mid-1910s, enhancing the flux by more than 30 times in approximately 15 yr. This continuous and extremely rapid rise is attributed to a shift of residential heating fuels from wood to coal in New York City [4]. A first-order decline rate of approximately $120 \text{ ng/cm}^2/\text{yr}^2$ during the next 2 decades led to the $\Sigma_{16}\text{PAH}$ flux being cut roughly in half. Following this decline, the flux increased at a relatively slow, first-order rate to a broad peak in the late 1940s to early-1950s. Fluxes were relatively constant in the 1960s, followed by a rapid decline during the 1970s, and have remained at similar levels since 1980. It is noteworthy that the 2 peaks in black carbon fluxes attributed to emissions from municipal waste incinerators [4] were not seen in the profile of $\Sigma_{16}\text{PAH}$ fluxes and various PAH indicators. By a rough calculation, incineration would be a less important PAH source (Supplemental Data). In the surface sample, the $\Sigma_{16}\text{PAH}$ flux of approximately $800 \text{ ng/cm}^2/\text{yr}$ (uncorrected for sediment mixing or basin drainage holdup) was approximately 20% of the peak level in the 1910s but 15 times higher than that from a century ago. The Central Park Lake surface flux was 2 to 3 times that found in the Pattaquamscutt River [8], about 4 and 11 times greater than those in Greater Traverse Bay and Lake Washington (estimated from concentration) [10], and approximately twice that in the surface sediment of Chidorigafuchi Moat, Japan (estimated from PAH concentrations and sedimentation rates) [11].

Although the temporal profile of total PAH flux is similar to that of $\Sigma_{16}\text{PAH}$ prior to 1920, total PAH and $\Sigma_{16}\text{PAH}$ fluxes have decoupled since then (Figure 1). We associate this offset with the beginning of significant petroleum use in the United States in the early part of the 20th century. The ratio of $\Sigma_{16}\text{PAH}$ to total PAH drops from an average of just over 0.6 in samples that date prior to about 1920 to approximately 0.4 in more recent deposition.

The chronologies of PAH fluxes reported in the present study can differ somewhat from the history of PAH fluxes to the core site as a result of postdepositional mixing. Models of contaminant profiles indicate that this effect is minor but not insignificant [7], with complete mixing limited to no more than the upper 2 cm of the sediment column representing no more than 4 yr of net deposition. This conclusion was supported by data on the activity of the short-lived natural radionuclide Be-7 in the upper few centimeters of more recent cores collected from Central Park Lake in 2002 (data not shown). The chronology of PAH fluxes to sediments at the core site can differ significantly from the history of atmospheric fluxes of PAHs to the drainage basin as a result of drainage basin or lake holdup. Depth profiles of radionuclide activities in the Central Park Lake cores have been reproduced with a model that included complete mixing of 2 yr of net deposition and an 8-yr drainage basin and/or in lake half-holdup time [7]. An important effect of both processes is the broadening of inputs within the sediment record. The most significant result for many contaminants, including PAHs, is that fluxes computed from measured concentrations and net sediment accumulation rates will overestimate atmospheric fluxes over the past few decades as direct inputs have declined [7].

Diagnostic ratios

Generally, a ratio of fluorene to fluorene and pyrene ($Fl/[Fl + Py]$) lower than 0.4 indicates a petrogenic source, a ratio between 0.4 and 0.5 indicates liquid-fossil combustion or mixed sources from petrogenic and combustion, and a ratio greater than 0.5 suggests a dominant wood or coal combustion source [24]. Although this ratio is not a sensitive, quantitative indicator, it is quite reliable for general source characterization [34] ($Fl/[Fl + Py]$ results reported in Supplemental Data).

Benner et al. [35] originally proposed the ratio of 1,7-dimethylphenanthrene [DMP]/(1,7-DMP + 2,6-DMP) for source characterization. These 2 isomers, 1,7-DMP and 2,6-DMP, have a similar molecular structure and are presumed to have similar environmental behaviors. A value of approximately 0.9 was found for softwood combustion emissions, approximately 0.43 was found for products of petroleum combustion [35], and approximately 0.67 was found for emissions from brown coal-fired residential stoves [36] and bituminous coal (B.R.T. Simoneit, Oregon State University, Corvallis, OR, personal correspondence). Both bituminous coal and anthracite were used in New York (see Supplemental Data), with decreased usage of anthracite from approximately 30% in 1900 to 2% around 1970. There has been no report of this ratio for anthracite combustion; however, total PAH produced by burning bituminous is about 2 orders of magnitude higher than that by anthracite [37]. Even if it is assumed that all anthracite use in New York State was for space heating in New York City, PAHs from coal combustion in the city would mainly reflect the burning of bituminous coal.

The ratio of retene to retene plus chrysene ($Ret/[Ret + Chy]$) was higher (0.60–0.96) for emissions from softwood burning compared with that for emissions from diesel combustion (0.23 ± 0.05) [38]. Smoke particles produced by sub-bituminous coal have a high $Ret/(Ret + Chy)$ ratio (0.73), but in emissions of low-volatile bituminous coal and semianthracite—which were widely used in New York City in the first half of the 20th century—the ratio $Ret/(Ret + Chy)$ is approximately 0.23 [38]. Both retene, a C₄-methylphenanthrene (3-ring PAH) compound, and chrysene (a 5-ring PAH) are weathering-resistant [39]. Retene has been found to be abundant in ancient rocks, further demonstrating its refractory nature. In addition, the $Ret/(Ret + Chy)$ ratio in the present study is used to identify softwood combustion, which normally produces large soot particles in which PAH can be encapsulated and protected from degradation [34].

Retene can also be derived from a diagenetic process rather than from wood combustion [40]; however, in this sediment core, diagenesis does not appear to play a major role. The concentrations of other common diagenetic PAHs, such as perylene and the alkylated hydrochrysene series [41], are relatively low; and 1,7-DMP, which is produced in softwood combustion but not from the diagenetic process, is abundant in the bottom sections. Both observations support our inference that softwood-combustion sources were dominant 100 yr ago in New York City.

The 3 sections of the core most dominated with single sources were used to verify the assumptions of this mass balance method. The penultimate section of the core (~1890s, 46–48 cm) has similar ratios to those from softwood combustion (Table 1). This section is

characterized by elevated ratios of 1,7/(1,7 + 2,6)-DMP and Ret/(Ret + Chy) (0.89 and 0.82, respectively). The 38-cm to 40-cm section (~1910) has ratios similar to coal combustion. The U/R (the area ratio of unresolved complex mixtures [UCM] to resolved peaks [R] in GC chromatogram) ratio of this section is lower than 4.0, indicating a little or low petroleum input, and the Ret/(Ret + Chy) ratio is around 0.25, which suggests little contribution from softwood combustion. Indicator ratios calculated from the 6-cm to 8-cm (mid-1980s) interval show low Ret/(Ret + Chy) and 1,7/(1,7 + 2,6)-DMP ratios, suggesting that petroleum combustion was the dominant input during this period. These observations are entirely consistent with the known history of energy use and combustion in New York City.

Mass balance equations

The molecular indicators suggest no obvious “petrogenic” raw petroleum source inputs to Central Park lake sediments, consistent with radionuclide and trace metal results, which indicate that atmospheric deposition dominated contaminant inputs to the lake with little impact from road runoff from park roads. Thus, “pyrogenic” sources are assumed to dominate the PAH record in the core. The contribution from municipal solid waste incineration was not calculated because we are not aware of any diagnostic ratios for this source. Furthermore, as noted above, black carbon results suggest a limited influence of this source on PAH levels in this core [4]. In the present study, 3 pyrogenic sources—combustion of wood, coal, and petroleum—are considered.

As 1,7-DMP can originate from 3 combustion sources, the mass balance equation of this compound is

$$1,7_{wood} + 1,7_{coal} + 1,7_{petro} = 1,7_{sample} \quad (1)$$

Each side is divided by the sum of 1,7-DMP and 2,6-DMP in the sample, changing Equation 1 to

$$\frac{1,7_{wood}}{(1,7+2,6)_{sample}} + \frac{1,7_{coal}}{(1,7+2,6)_{sample}} + \frac{1,7_{petro}}{(1,7+2,6)_{sample}} = \frac{1,7_{sample}}{(1,7+2,6)_{sample}} \quad (2)$$

This is equivalent to

$$\begin{aligned} & \left(\frac{1,7_{wood}}{(1,7+2,6)_{wood}} \times \frac{(1,7+2,6)_{wood}}{(1,7+2,6)_{sample}} \right) \\ & + \left(\frac{1,7_{coal}}{(1,7+2,6)_{coal}} \times \frac{(1,7+2,6)_{coal}}{(1,7+2,6)_{sample}} \right) \\ & + \left(\frac{1,7_{petro}}{(1,7+2,6)_{petro}} \times \frac{(1,7+2,6)_{petro}}{(1,7+2,6)_{sample}} \right) \\ & = \left(\frac{1,7_{sample}}{(1,7+2,6)_{sample}} \times \frac{(1,7+2,6)_{sample}}{(1,7+2,6)_{sample}} \right) \end{aligned} \quad (3)$$

In Equation 3, $1,7_{wood}/(1,7+2,6)_{wood}$, $(1,7+2,6)_{wood}/(1,7+2,6)_{sample}$ are diagnostic ratios of 1,7/(1,7 + 2,6)-DMP and the proportion of 1,7 + 2,6-DMP from softwood combustion to sample, respectively. Diagnostic ratios of 1,7/(1,7 + 2,6)-DMP_{sample} of softwood, coal, and

petroleum are known from the references listed in Table 1; $1,7/(1,7 + 2,6)\text{-DMP}_{\text{sample}}$ is the ratio measured in the core samples; and $f_{\text{wood,DMP}}$ (i.e., the proportion of 1,7 + 2,6-DMP from softwood combustion), $f_{\text{coal,DMP}}$, and $f_{\text{petro,DMP}}$ are unknown.

As noted above, only 3 major PAH sources are considered, so

$$f_{\text{wood,DMP}} + f_{\text{coal,DMP}} + f_{\text{petro,DMP}} = 1 \quad (4)$$

This analysis did not consider other potential sources (e.g., coke production). Losses resulting from microbial decomposition after deposition were also ignored. It is expected that such loss would be minor because most high-molecular weight PAHs are resistant to biodegradation [42]. It is also noteworthy that the fractions calculated in the chemical mass balance equations are mass fractions of the 2 compounds from 3 sources rather than the mass fraction of total PAH; however, the sum of 2 compounds (1,7 + 2,6-DMP) is strongly correlated with total PAH ($R^2 = 0.94$; Figure 2). Therefore, it is a reasonable conclusion that the calculated fractions reflect the proportion of total PAH from different sources.

Mass balance equations similar to Equation 4 can also be established for the Ret/(Ret + Chy) ratio. In addition, other ratios can provide some constraints for PAH sources. Based on the U/R ratio, there was little or no petroleum use prior to the 1910s [4], so for deposition predating this time, f_{petro} is assumed to be 0 and only fractions from wood and coal (f_{wood} and f_{coal}) need to be determined.

After the mid-1910s, 3 sources (wood, petroleum, and coal) coexist in the New York State historical energy-use records [4]. As described in the text and shown in Table 1 and Supplemental Data, Figure S2, ratios of Ret/(Ret + Chy) from combustion of both petroleum and coal are similar at approximately 0.22. Consequently, using the mass balance equation of Ret/(Ret + Chy), the fraction of wood was computed (Supplemental Data, Figure S2) and then the $1,7/(1,7 + 2,6)\text{-DMP}$ ratio was used to estimate fractions of coal and petroleum (f_{coal} and f_{petro}). Contributions of coal and petroleum were also calculated by the FI/(FI + Py) ratio (Supplemental Data, Figure S3), and the results were similar to those derived from DMP.

DISCUSSION

As expected, PAH sources were dominated by wood combustion in the 19th century, then shifted to dominantly coal combustion from approximately the early 1900s to the 1960s (Figure 3A). There was a mixture of coal and petroleum from the 1930s to the 1950s, and petroleum combustion has dominated thereafter. The 3 aforementioned depth sections (46–48 cm, 38–40 cm, and 6–8 cm) show PAHs dominated by softwood, coal, and petroleum combustions, respectively (Table 1).

Detailed information on New York City energy use was revealed by this source apportionment method. There is no identifiable wood combustion contribution in the Central Park Lake record from approximately 1920 to approximately 1960 (Figure 3A and B), which is probably an accurate reflection of the dominance of fossil fuel energy usage in New York City during this time. In general, the local New York City wood-derived PAH fluxes

calculated from this core (Figure 3B) vary substantially from the nationwide trends reported in the historical New York State data. The difference is expected because wood combustion has been only a minor energy source in modern cities since 1910. The more recent increase (1960s–1970s) suggested by the indicator ratios in the CPF core may just be an artifact given the low use of wood burning in cities and the possibility that the indicators used in the present study may be not sensitive enough to determine softwood combustion when PAHs from petroleum and/or coal are so much higher.

The coal combustion–derived PAH flux in core CPF roughly follows the New York State coal usage trend (Figure 3D). Both the CPF accumulation rate data and the New York State historical consumption data indicate a peak in coal-derived flux around 1920. However, the state data show an obvious second peak in coal consumption around the mid-1940s, while accumulation rates for coal-derived emissions in core CPF have only a “shoulder”—not a peak—during this period. The absence of a more prominent peak in this period is most likely the result of a local shift from coal to petroleum as the dominant energy source in residential space heating during the 1930s and 1940s, which is consistent with available records of residential coal ash generated in New York City [43]. The Central Park Lake core also suggests that coal consumption in the city decreased dramatically in the 1950s and 1960s with near no coal-derived PAH emissions after 1970, consistent with the timing and amount of residential coal usage in New York City [43]. The New York State data for coal usage do show large decreases in coal combustion during the 1950s and 1960s but still suggest significant use at a level about 30% of peak usage (~1945) and relatively constant until 2000. We are aware that coal-burning boilers were used in some New York City schools until 2001, but this was still rather minor use. Overall, the history of coal consumption reconstructed by the CPF core appears more consistent with residential New York City coal usage than with New York State coal consumption. Whether the record in Central Park Lake sediments reflects reduced coal combustion in nearby apartment buildings or in New York City as a whole (i.e., also influenced by local power plants) is not currently known. If the latter, then New York City would have been exemplary in reducing coal usage decades earlier than the rest of New York State and the country.

Before 1970, calculated petroleum-combustion flux follows the trend of petroleum-consumption data (Figure 3D) and that of excess vanadium (Figure 3E) reported previously [5]. Excess vanadium is a tracer of high-sulfur Venezuelan fuel oil use, which comprised approximately 35% of the residual fuel oil used in New York City in 1966 but declined after 1966 because of restrictions on the sulfur content of fuel oil by New York City Local Law 1. After 1970, historical petroleum-consumption data show a decline corresponding to the worldwide “energy crisis” in the 1970s; however, estimated petroleum emissions as derived directly from accumulation rates in core CPF declined faster (Figure 3D) than the historical data for New York State but slower than excess vanadium (Figure 3E).

Sediment-derived accumulation histories reflect not only the history of atmospheric inputs but also processes of basin drainage holdup, in basin transport processes and postdepositional mixing. Radionuclide normalization does correct for the integrated amount of particle focusing over the last 50 yr to 100 yr but does not correct for mixing and holdup. To derive better estimates of atmospheric deposition, one would have to correct fluxes

calculated and reported in the present study for these additional processes. It is beyond the scope of the present study to make even semiquantitative corrections; however, we can clearly say that these corrections would result in sharper peaks in the profiles and reduce the contaminant fluxes progressively from periods of maximum contaminant inputs (e.g., the 1970s for petroleum-derived PAHs).

When the impacts of basin drainage holdup and sediment mixing are considered, it becomes obvious that petroleum-derived PAH accumulation is decreasing at a much faster rate than petroleum consumption. The excess vanadium accumulation rates are decreasing even faster than the petroleum-derived PAH rates, as would be expected since vanadium is primarily a tracer of high-sulfur residual oils, which only comprised 35% of the total in 1966 and quickly declined thereafter as a result of local regulations [5]. In the present study, it is difficult to estimate the relative contributions of emission control and fuel switch to the decreased PAH fluxes without modeling the sediment processes mentioned above and quantitative determination of the decrease in PAH emissions from different petroleum fuel types. The introduction of lower-sulfur fuel can produce PAHs at a lower emission rate [44], but there is no reliable study measuring the PAH emission rate from the combustion of Venezuelan high-sulfur residual oils. The post-1970 PAH accumulation rate decrease likely reflects some combination of the following 3 factors: 1) the decrease in petroleum consumption, 2) the adoption of more effective emission-control techniques, and 3) the switch from high-sulfur Venezuelan oil to low-sulfur oils as the primary residual fuels used in New York City.

Other authors have reported a decline in total PAH as a result of a changeover from older, “dirtier” coal usage to cleaner petroleum sources during the first half of the 20th century [45]. The data from the CPF core indicate a local shift from coal to petroleum occurring between the 1930s and 1950s, but total PAH flux does not decrease much during this period (Figure 1). This is most likely the result of a substantial net increase in combustion—particularly vehicular combustion—in New York City.

We acknowledge additional limitations in our approach. The standard deviation of calculated fluxes cannot be provided because of the limited reports of these 2 indicator ratios, especially Ret/(Ret + Chy) from different sources. We only report on softwood combustion with the present approach and assume it is a good indicator of the trends for hardwood combustion. The direct contribution from hardwood combustion cannot be determined since it produces indicator ratios similar to those from coal and petroleum combustion. In addition, methods used in the present study may not be sensitive enough to detect PAH fluxes from anthracite coal combustion because of the lack of reliable studies on PAH emission from anthracite, an important coal source in New York City. Finally, sediment-derived fluxes can be very sensitive to the age model used to date the different sections of the core, so any detailed comparison between studies must be undertaken with extreme caution.

Despite these limitations, we believe we have successfully estimated fluxes from specific combustion sources using ratios based on component compounds that have been widely identified around the world and are easily quantified by traditional GC and GC/MS analysis.

In addition, the consistency between trends of calculated coal and petroleum combustion and the historical data provides confidence in the soundness of this method. This method was also used to reconstruct the PAH contamination history in sediment cores collected from the western New York and New Jersey harbor complex, specifically Newark Bay, a highly contaminated depositional system. Consistent with results from Central Park Lake, coal combustion was a significant contributor to PAH contamination in the 1930s and declined rapidly thereafter, with no detectable signal by the mid 1960s [46,47].

In summary, source-specific tracers based on PAH ratios provided detailed information about the combustion history and energy shift in the New York City environment. Consistency with historical records of fuel use indicates that these ratios can be quite useful for PAH source apportionment in other environments. The heating fuel change in residential buildings surrounding Central Park Lake greatly influenced PAH fluxes in the New York City area. The shift from coal to petroleum in New York City occurred from the 1930s to 1960s but did not result in a sharp decline in total PAH fluxes. A rapid decrease in total PAH fluxes in New York City occurred in the 1970s, most likely as a result of a combination of declining petroleum consumption, adoption of emission control techniques, and the shift toward low-sulfur content fuel.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Temporal profiles of fluxes of 16 US Environmental Protection Agency parental polycyclic aromatic hydrocarbons ($\Sigma_{16}\text{PAH}$; solid line) and total polycyclic aromatic hydrocarbon (TPAH; dotted line) in the Central Park Lake sediment core. [Color figure can be viewed in the online issue which is available at wileyonlinelibrary.com]

Figure 2.

The strong relationship between total polycyclic aromatic hydrocarbons (TPAH) and the sum of 1,7-dimethylphenanthrene (DMP) and 2,6-DMP.

Figure 3.

The calculated fractions of polycyclic aromatic hydrocarbons (PAHs) from wood, coal, and petroleum combustion (A) and fluxes (solid lines in B–E) of various pyrogenic sources by the ratio of retene to retene plus chrysene and that of 1,7-dimethylphenanthrene (DMP) to 1,7-DMP plus 2,6-DMP. For comparison, the energy consumption data are provided in dotted lines and follow the top scales (B–D). The PAHs from petroleum combustion are compared with excess vanadium level (dotted line in E) in another Central Park Lake core (5). NYS = New York State. [Color figure can be viewed in the online issue which is available at wileyonlinelibrary.com]

Table 1

Diagnostic ratios of 2 indicators from references and representative ratios in 3 CPF sections dominated by a single source

Sources	CPF sections dominated by a single source	Ret/(Ret +Chy)		1,7/(1,7+2,6)-DMP		Fl/(Fl+Py)	
		Literature ratios	CPF	Literature ratios ^a	CPF	Literature ratios ^e	CPF
Wood	46–48 cm	0.83–0.96 ^b	0.82	0.9	0.89	>0.5	0.72
Coal (low-volatile grade)	38–40 cm	0.24±0.06 ^c	0.22	0.65–0.68	0.67	>0.5	0.58
Petroleum	6–8 cm	0.24±0.22 ^d	0.22	0.40	0.40	0.40–0.5	0.47

CPF=Central park core F; Ret=retene; Chy=chrysene; DMP=dimethylphenanthrene; Fl=fluoranthene; Py=pyrene.

^aBenner et al. [35].

^bFine et al. [48].

^cBi et al. [49].

^dSjogern et al. [38].

^eYunker et al. [24].