MOLECULAR TRACERS OF POLYCYCLIC AROMATIC HYDROCARBON SOURCES IN CENTRAL PARK LAKE, NEW YORK CITY

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) can have natural or anthropogenic sources, with natural biogenic sources (e.g. sedimentary early diagenetic processes) being relatively minor contributor to PAH inventories compared to anthropogenic sources. Anthropogenic sources include pyrogenic sources, such as the incomplete combustion of fossil fuels (petroleum and coal) or biofuels (e.g. grass, trees, or duff), and petrogenic sources, such as the direct release of these fossil fuels and the leakage of crankcase oil.

Different PAH sources have different molecular distribution patterns[1-4]. For example, combustion-derived PAHs are predominately parental and HMW PAHs (4-6 ring), whereas petroleum-related PAHs are largely alkylated homologues and LMW. In addition, ratios of some isomer pairs, vary from source to source. For instance, fluoranthene and anthracene are preferentially produced in combustion sources in respect to their corresponding isomers pyrene and phenanthrene[2]. Based on these differences, previous workers have employed various molecular ratios as PAH source indicators[5]. Two ratios derived from compound groups, Ring456/TPAH and Par/(Par+Alkyl), have been suggested and successfully applied as PAH source indicators[6]. Pyrogenic PAHs can originate from many source types including wood, coal and petroleum combustion (e.g. space heating, and motor vehicle emissions). It has been observed that 1,7–dimethylphenanthrene (DMP) is preferentially produced in softwood combustion emissions, and 2,6-DMP is found with comparable concentrations in emissions from both fossil-fuel and softwood combustion. The ratio of 1,7- DMP to 2,6-DMP in air particulate matter has been proposed and successfully used to distinguish softwood combustion from motor vehicle emissions[7]. Another compound, retene (1-methyl-7-isopropylphenanthrene), has also been proposed as a "fingerprint" of softwood combustion[8].

Materials and Methods

This study takes advantage of radionuclide-dated sediment cores collected from Central Park Lake that appear to have archived ca. 130 years of history, a time period during which there have been large changes in the predominant fuel type used in NYC. Estimates of NYC's historical fuel usage are derived from data provided by the Energy Information Administration (EIA)[9] scaled to changes in NYC's population, allowing evaluation of the usefulness and limitations of the PAH source indicators and current widely applied indicators in the saturated fraction (CPI, LMW/HMW, U/R etc., see text for detailed descriptions) to identify major PAH sources and reconstruct the combustion history in New York City over the past century. In a companion paper, estimation of SH & PAH depositional fluxes as well as a semi-quantitative estimation of the proportion of various combustion sources will be developed from the more reliable source-indicator ratios identified in this paper. Central Park Lake sediment cores have been used previously to investigate the history of atmospheric deposition of trace metals[10] and chlorinated organics[11].

Samples were Soxhlet-extracted using dichloromethane (DCM) overnight, after which the extracts were concentrated to 0.5 mL under a gentle flow of N_2. Following alumina column cleanup to remove the more polar compounds, activated copper powder was added to remove elemental sulfur. The extracts were separated into two fractions using silica chromatography: the first fraction eluted with hexane, containing the low polarity saturated hydrocarbons and PCBs; the second fraction with CH_2Cl_2 containing more polar compounds such as PAHs and pesticides.

Aliphatic and aromatic hydrocarbon compounds were identified by capillary gas chromatography with a mass spectrometer (GC-MS) detector. High purity PAH standards were purchased from Accustandard, Chiron, and Supelco. Standards include normal saturated hydrocarbons from C_{13}-C_{35}; 16 EPA parent PAHs, some C_1-C_4 alkyl PAHs homologues, thiophene series and retene. The quantification of both saturated and unsaturated fractions was carried out by GC Flame Ionization Detector (FID) due to its high linearity for different PAH concentrations and its predictable decrease of area responses (peak area per ng carbon) with retention times. For most of the parent

PAHs with available standards, area responses were used for calibration of these standards. For those without available standards, area responses were interpolated from the trend of the area response vs. retention time (r^2=0.97). GC FID analysis was performed on a Fisons Instrument (8000 series) gas chromatograph, equipped with a Restek DB-5 capillary column (0.32 mm ID, 60m, 0.25 micron film thickness) and an EI980 FID. Mass spectrometry utilized a Shimadzu GCMS-QP5050 in selective ion mode.

Results and Discussion

Yunker et al.[6] have summarized diagnostic ratios for some PAH source indicators. Ratios of Fl/(Fl+Py) are larger than 0.44 throughout the core CPF, indicating dominantly pyrogenic PAH sources. Despite their considerable variations, ratios of $C_0/(C_0+C_1)$F/P, $C_0/(C_0+C_1)$P/A are both greater than 0.5 throughout core CPF, also suggesting prevalently pyrogenic PAH sources. Furthermore, parent PAHs dominate throughout the core, indicating the combustion sources as the dominant PAH sources into CP Lake since the late 19th century. Although a predominantly pyrogenic PAH source is implicated for much of the history of deposition, ratios of A/(Pa+A) and BaA/(BaA+Chy) in three bottom samples (~ 0.04 and ~0.27) are lower than their pyrogenic to combustion diagnostic values (0.1, 0.35, respectively), indicating petrogenic sources. According to the EIA report[9], petroleum was not used widely in the USA prior to 1900, thus the only possible petrogenic source is fresh coal, which typically contains abundant alkyl PAHs. However, the late 1800's petrogenic signal is not apparent in the levels of parent PAHs, which, as mentioned previously, indicate that combustion sources were the dominant PAH throughout the core.

A ratio of 1,7/2,6-DMP ranging from ~2.4 to ~10 was observed in emissions from softwood combustion, ~ 0.74 from motor vehicle exhaust, ~ 1.7 in emissions from brown-coal-fired residential stoves and around 2 in sub-bituminous and bituminous coal smoke (Simoneit, pers. com.). Although elevated 1,7/2,6-DMP ratios (3-10) can be observed in fresh bituminous coal and brown-coal smoke (Simoneit, pers. com.), the distribution patterns of dimethylphenanthrene isomers (DMPs) from these fresh coals and sub-bituminous and bituminous coal-generated smokes differ from that in softwood combustion. 1,7-DMP is at a comparable level to its nearby isomers such as 1,6-DMP in bituminous related sources (Simoneit, pers. com.), and overwhelmingly higher than 1,6-DMP in softwood combustion emissions.

After 1900, 1,7/2,6-DMP and Fl/(Fl+Py) ratios decline gradually until the 1940s. A similar decrease is also observed in some remote lake cores[11]. Despite the different rates of decline, ratios of 1,7/2,6-DMP and Ret/Chy decrease in the early 1900s indicating the decreased contributions from softwood combustion. At the same period, PAH concentrations increases rapidly (~ 31-fold), whereas SH and UCM levels remain low with CPI ratios around 5, all indicating a minor petroleum-related hydrocarbon source. An increase in hardwood combustion could lead to the reduction of 1,7/2,6-DMP and Ret/Chy ratios due to their relative lower ratios in hardwood combustion emissions than softwood; however, the extremely rapid increase in PAH levels over just fifteen years together with the fact that NYC population only increased by ~20% during this period suggests that conversion to hardwood burning cannot account for the hydrocarbon signatures preserved in core CPF. We attribute this rapid PAH increase to coal combustion for residential heating and industrial usage at this period.

From ~1915 until ~1935, gradual decrease in 1,7/2,6-DMP ratios suggest a continuous reduction in coal and/or wood combustion. Ret/Chy remains constantly low, indicating negligible contributions of softwood combustion. Thus the decline in Fl/(Fl+Py) and DMP ratios most likely resulted from either a decrease in coal combustion, a relative increase in petroleum combustion, or both. Additionally, temporal profile of U/R exhibits a first-order increase in this period, indicating a continuous increase in petroleum combustion. The gradual enhancement in petroleum combustion input from the 1910s to 1930s probably results from the rapid increase in motor vehicle numbers after the first car assembly line was put into operation in 1913.

From the 1930s to 1960s, major PAH sources are from combustion of petroleum and coal according to the ratios of Fl/(Fl+Py), Ret/Chy and 1,7/2,6-DMP. Unlike TSH level profile, PAH levels do not peak at ~ 1945 and ~1964, demonstrating that SH and PAH may have different major combustion sources to CP Lake. From ~1935 to ~1944, SH levels increase over 10 times, whereas PAH levels remain relative constant, suggesting that the rapid increase in SH levels mostly likely is not caused by an increase in motor vehicle emissions. If they had been, PAH levels should have increased dramatically too. Therefore, another hydrocarbon source is probably responsible for this rapid SH increase. One potential source is from incineration of municipal solid waste (MSW). Chillrud et al[10] attributed very elevated levels of Pb, Sn and Zn observed in another CP Lake core (CPH) between the late 1930s and the mid

1960s as in indication of MSW emissions prior to the advent of effective pollution controls. Given that the disagreement between model-derived ages for depth sections from the 1930s and 1940s is about 10 years, the time periods for elevated levels of TSH and MSW-derived metals are very similar. Based on this similarity in time periods, emissions from MSW incinerators would appear to contain high abundance of UCM and comparable PAHs relative to other combustion sources. Abundant UCM was observed in a study, of emissions from waste incineration plants.

Although various ratios indicate that petroleum combustion was the dominant pyrogenic source in the 1970s, some variations in molecular ratios are noteworthy: PAH ratios increased towards the present with a corresponding slight reduction of U/R ratio. The substantial increase in 1,7/2,6-DMP indicates an increase in either coal or softwood combustion; however, the concurrent rise in Ret/Chy ratios, which is only responsive to wood combustion, suggest the various observed ratio increases are due to increased wood combustion. EIA data record increased combustion of wood in the late 1970s in the US. Estimation of the relative coal contribution is more complicated. Using mass balance equations based on these indicators, little to no increase in the coal combustion contribution was found in the 1970s. Qualitatively, the trends observed in the 1970s continue in the 1980s and 1990s, with all three of these PAH ratios increasing slightly and with a minor decline in the U/R ratio. However, in the 1980s and 1990s, the semi-quantitative analyses suggest that minor increases in both coal and wood combustion contribute to the observed trends[6].

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