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FINAL REPORT TO THE HUDSON RIVER FOUNDATION Apportioning PAH Sources to Sediments of the NY/NJ Harbor

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EXECUTIVE SUMMARY

Our Hudson River Foundation Project has two aims: (1) develop and refine an isotopic approach to PAH source apportionment and (2) apply coupled molecular and isotopic approaches to PAH apportionment of the NY/NJ Harbor Complex over the past century. We successfully developed a new high temperature pyrolysis reactor technique (i.e., using silica glass-lined alumina reactors at 1550 °C) that improved the hydrogen yield of conventional furnaces (i.e., unlined or carbon-lined alumina) for compound-specific δD analysis of PAHs five- to ten-fold. Unfortunately, our work appears to indicate that (unlike $\delta^{13}C$ measurements) *compound-specific D/H ratios are doubtful to be of value as a vector for discriminating PAH sources in real systems*. The key problem for source apportionment is the wide range of δD values for individual source types.

Sub-basins within the New York/New Jersey (NY/NJ) harbor host variable amounts and sources of polycyclic aromatic hydrocarbons (PAHs). Analyses of radionuclides ^{137}Cs and 7Be were used to assign approximate dates to individual sections of sediment cores collected from the four sub-basins of the Harbor complex. Parent and alkyl-substituted PAHs were identified and quantified by GC-MS and GC respectively. Gas chromatography - isotope ratio mass spectrometry (GC/IRMS) was applied to determine $\delta^{13}C$ values of pyrene ($\delta^{13}C_{Py}$), a principal 4 ring parent PAH. Two end-member PAH source components, petroleum-related PAHs (PRPAH) and combustion-related PAHs (CRPAH), were calculated by a carbon isotopic mass balance equation based on assumptions that petroleum-related $\delta^{13}C_{Py}$ is -29‰, and that combustion-derived $\delta^{13}C_{Py}$ is -24‰. Temporal trends of PRPAH in these cores are similar to those of the petroleum-derived unresolved complex mixture (UCM), whereas CRPAH resembled trends of "Total" PAH (TPAH). Three molecular ratios, fluoranthene to fluoranthene plus pyrene (Fl/(Fl+Py)), high molecular weight 4-6 ring PAH to total PAH (Ring456/TPAH) and parental to total (Par/(Par+Alkyl)), correlate strongly with each other, and shows a moderate to strong positive correlation with $\delta^{13}C_{Py}$. In contrast, the ratios of anthracene to phenanthrene plus anthracene (A/(Pa+A)), benzo[a]anthracene to benzo[a]anthracene plus chrysene (BaA/(BaA+Chy)), and indeno[1,2,3-cd]pyrene to indeno[1,2,3-cd]pyrene plus benzo[ghi]perylene (IP/(IP+Bghi)) show no, weak, or even negative correlation with the four well correlated ratios ($\delta^{13}C_{Py}$, Par/(Par+Alkyl), Fl/(Fl+Py), and Ring456/TPAH). Combined application of the four well correlated molecular indicators suggests that PAH contribution from combustion has become more important in most areas of the NY/NJ harbor in the last three decades.

Keywords: polycyclic aromatic hydrocarbons; compound-specific carbon isotope ratio; molecular source indicators; correlation analysis; source apportionment

RESEARCH OBJECTIVES

This HRF project is aimed at extending existing chronologies of PAH deposition from the NY/NJ Harbor to the mid to late 1990s (cf., Keane, 1998; Keane et al., 1997), developing complete chronologies at additional sites that have particular relevance to PAH source distinction at the Harbor; and application of compound-specific stable isotope ratio measurements and molecular indicators for the apportioning of PAH sources in space and time in the NY/NJ Harbor.

BACKGROUND

Sediments in the highly urbanized New York /New Jersey (NY/NJ) harbor complex are known to be contaminated by various chemical compounds and heavy metals (Bopp et al., 1993a; Crawford et al., 1995; Wolfe et al., 1996). Following estuary-wide multiyear intensive bioeffects surveys conducted by the National Oceanic and Atmospheric Administration (NOAA), PAHs have emerged as a leading concern in this area (Wolfe et al., 1996). These surveys have shown that among all contaminants analyzed (PAHs, pesticides, PCBs, and 16 trace and heavy metals), amphipod toxicity was most strongly associated with levels of PAHs in the NY/NJ harbor (Wolfe et al., 1996). Although a number of pioneering studies have investigated spatial and temporal distributions of PAHs in the NY/NJ harbor areas (Wolfe et al., 1996; Gigliotti et al., 2002), most were focused on concentrations of principal parent (unsubstituted) PAHs. Given the substantial variations in the distributions of alkyl substituted PAHs from different sources, alkyl-substituted PAHs can provide additional important information for PAH source apportionments (Sporstol et al., 1983; Pereira et al., 1999; Yunker et al., 2002).

Traditionally, PAH source apportionment studies have relied on a number of molecular criteria to distinguish between pyrogenic (combustion-derived, e.g. emissions from wood and motor vehicles) and petrogenic (petroleum-derived, e.g. oil spills, leakage of crankcase and lubrication oil) (Wakeham, 1996; Budzinski et al., 1997; Yunker et al., 1999). These criteria are based on overall PAH molecular fingerprints or relative concentrations of isomers with the same mass. Currently applied criteria include: $Fl/(Fl+Py)$, the ratio of fluoranthene (Fl) to fluoranthene plus pyrene (Py), both have a mass of 202; $A/(Pa+A)$, the ratio of anthracene(A) to PAHs with mass 178 (A and phenanthrene (Pa)); $BaA/(BaA+Chy)$, the ratio of benzo(a)anthracene (BaA) to the sum of mass 228 PAHs (BaA+ Chrysene(Chy)); $C_0/(C_0+C_1)_{P/A}$ and $C_0/(C_0+C_1)_{F/P}$, ratios of parent PAHs with mass 178 (Pa, A) or 202 (Fl, Py) to the parent PAHs plus C_1 alkyl homologues at the same mass respectively; and $IP/IP+Bghi$, the ratio of indeno[1,2,3-cd]pyrene (IP) to the sum of IP and Benzo(g,h,i)perylene (Bghi). In previous study of the 990s harbor surface sediments (Yan et al., 2004b), two other indicators were used: Ring456/TPAH, the ratio of high molecular weight 4-6 ring PAHs (including all alkylated 4-6 ring PAHs as well) to TPAH, the sum of all quantified parent plus alkyl PAHs (table 1); $Par/(Par+Alkyl)$, the sum of the parent PAHs with masses 128, 178, 202, and 228 (Na, Pa, A, Fl, Py, BaA, Chy) divided by these parent PAHs plus their related alkyl PAHs. Each of these ratios should theoretically increase with enhanced contributions from combustion (Yunker et al., 2002).

Compound-Specific Carbon Isotope Analysis (CSCIA) was introduced by O'Malley et al. (1994) as method of utilizing distinct carbon isotope differences between petrogenic and

Compounds	Abbreviations	Compounds	Abbreviations
*Naphthalene	Na	Benzo[ghi]fluoranthene	BghiF
Biphenyl	Bph	Benzo[c]phenanthrene	BcP
*Acenaphthylene	Acy	Tetramethyloctahydrochrysenes	C48HChy
*Acenaphthene	Ace	*Benzo[a]anthracene	BaA
Dibenzofuran	DBFu	*Chrysene+Triphenylene	Chy
*Fluorene	F	Trimethyltetrahydrochrysenes	C34HChy
Dibenzo(b,d)thiophene	DBT	*Benzo[b]fluoranthene	BbF
*Phenanthrene	Pa	*Benzo[k]fluoranthene	BkF
*Anthracene	A	Benzo[a]fluoranthene	BaF
4H-cyclopenta[def]phenanthrene	4HCP	Benzo[e]pyrene	BeP
2-Phenylnaphthalene	2PN	*Benzo[a]pyrene	BaP
*Fluoranthene	Fl	Perylene	Per
*Pyrene	Py	Indeno[7,1,2,3-cdef]chrysene + Dibenzo(aj)anthracene	IC+DjA
Benzonaphthofurans	BNFu	*Indeno[1,2,3-cd]pyrene	IP
Retene	Ret	Picene	Pi
1,2-Benzofluorene	12BF	*Dibenzo[ah]anthracene	DA
2,3-Benzofluorene	23BF	*Benzo[ghi]perylene	Bghi
Benzo(b)naphthothiophenes	BNTH	Anthracene	AA
Alkylated series			
C ₁ -C ₄ Naphthalene	C ₁ -C ₄ Na	C ₁ -C ₂ Dibenzo(b,d)thiophene	C ₁ -C ₂ DBT
C ₁ -C ₃ Phenanthrene/Anthracene	C ₁ -C ₃ P/A	C ₁ PAHs with mass 252	C ₁ m252
C ₁ -C ₂ Fluoranthene/Pyrene	C ₁ -C ₂ F/P		
C ₁ -C ₂ Benzo[a]anthracene/Chrysene	C ₁ -C ₂ B/C		

Table 1. Quantified PAHs and their abbreviations in sediment samples. The compounds denoted with * are EPA PAHs, the sum of all 16 EPA PAHs is calculated as Σ PAH. TPAH is the sum of all the PAH shown in this table.

pyrogenic PAH sources in sediments for source apportionment studies (O'Malley et al., 1994; Mazeas & Budzinski, 2001; Okuda et al., 2002a; Okuda et al., 2002b). Petrogenic sources (e.g. fresh fuel oil, crankcase oil) typically have a depleted $\delta^{13}\text{C}$ value for the principal parent PAH

pyrene (Py) (around -27 to -29‰), whereas pyrogenic (combustion-related, e.g. wood, or petroleum burning) Py has a heavier value around -24‰ (O'Malley et al., 1994; Abrajano et al., 2003). McRae and coworkers have observed significant variations in $\delta^{13}\text{C}$ value during coal conversion processes (McRae et al., 1996; McRae et al., 1998).

In our studies of dated NY/NJ harbor sediments, we have found the dominant PAH sources in recent sediments are from petroleum usage including direct oil-spill (petrogenic) and petroleum combustion (pyrogenic) sources (Yan et al., 2004b). In addition, we have shown recently, based on our study of Central Part (NY) sediments, that coal and petroleum combustion PAH can be distinguished using a combination of molecular indicators (Yan et al., 2004a). Typically, coal combustion products have abundant high molecular weight (HMW) PAH, limited amount of unresolved complex mixtures (UCM), and ratios of Fl/(Fl+Py) and 1,7/2,6-DMP around 0.58 and 1.96, respectively (Yan et al., 2004a). 1,7/2,6-DMP, the ratio of 1,7-dimethylphenanthrene to 2,6-dimethylphenanthrene was first used as an indicator of softwood combustion by Benner et al., 1995), but we suggested that this ratio could also be used to differentiate between pyrogenic sources (e.g. wood, coal, petroleum combustion) (Yan et al., 2004a). Petroleum-combustion derived hydrocarbon have abundant UCM, a ratio of around 0.45 for Fl/(Fl+Py), and a 1,7/2,6-DMP ratio around 0.5. Therefore, by using this molecular ratio, we can estimate relative contributions from various combustion source (petroleum, coal, and wood) (Yan et al., 2004c).

In this study, dated sediment cores were selected from a sediment archive maintained at LDEO and RPI over 20 years' extensive coring in the NY/NJ harbor areas. By comparing the pyrene $\delta^{13}\text{C}$ values with molecular ratios, we attempt to evaluate the usefulness and limitations of these widely used molecular indicators. The implications of the isotopic and molecular variations in sediment cores from the NY/NJ Harbor complex will subsequently be explored.

LABORATORY AND FIELDWORK

Experiments on PAHs:

We have employed an innovative method based on the measurement of carbon and hydrogen isotopic compositions of individual PAHs, utilizing a technique referred to as gas chromatography/isotope ratio mass spectrometry (GC/IRMS). Immediately after the installation of the RPI Isotope Facility in the summer of 1999, we commenced laboratory investigations of PAH δD isotope measurements and testing of D/H isotopic integrity during PAH weathering. We investigated hydrogen isotopic fractionation associated with extraction and chromatographic purification, and showed no isotopic fractionation accompanied incomplete extraction (30 to 100 %). Mixtures were prepared by dissolving the PAH standards in distilled hexane, and using this mixture to spike 15g portions of sterile sediments (i.e., exhaustively extracted). These sediments were Soxhlet extracted, and the recovery of each PAH was determined using external calibration curves constructed using a range of concentrations of the pure individual PAH. Our experiments showed that D/H isotope compositions were retained during the extraction process to within the experimental precision of compound-specific D/H measurement (<5 ‰). It is interesting to note that, although the differences in δD values for extracted and non-extracted PAH are within analytical precision, PAH that went through the extraction scheme are invariably depleted in deuterium compared to the non-extracted samples. In addition to negating analytical concerns of PAH isotopic integrity during sample preparation, these experiments also revealed that only very small fractionation can be

expected as a result of partial PAH losses during natural weathering. In particular, the dominant loss mechanisms during sample extraction are likely to be similar to loss mechanisms during weathering (e.g., volatilization, sorption, dissolution, D/H exchange, and photodegradation). Indeed, the lack of D/H isotope exchange between naphthalene and solvent was shown after over 4 hours of exposure:

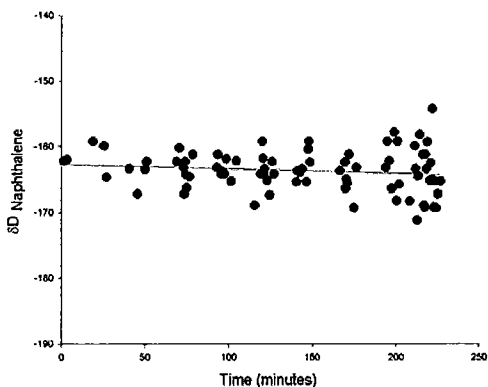


Fig. 1. D/H exchange between naphthalene and solvent over time.

Initial aerobic microbial degradation experiments with naphthalene were also completed at RPI last summer (using *Pseudomonas Putida*, Biotype B ATCC17484), and the results reveal the absence of D/H isotope shift in residual naphthalene after > 95% degradation:

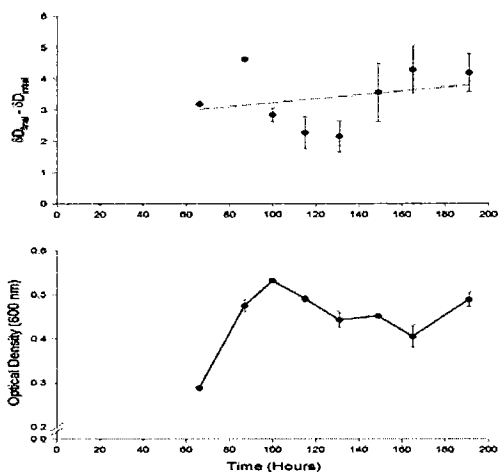


Fig. 2 δD shift in Naphthalene during aerobic degradation (*Pseudomonas Putida*, Biotype B ATCC17484).

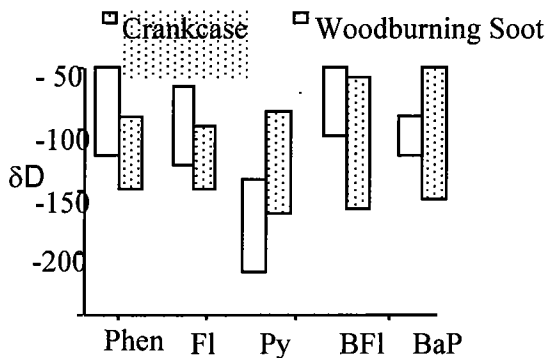


Fig. 3 Range of δD values for PAHs from wood burning sources ($n=23$) and crankcase oil ($n=34$).

These results are consistent with previous observation that PAH biodegradation is **not** accompanied by carbon isotopic fractionation (O'Malley, et al., 1994; Mazeas and Budzinski, 2001). Note that the $< 5 \text{ ‰}$ temporal shift in the measured δD for all the residual naphthalene (cf. initial δD_{Naph}) is in the direction of an isotopically heavier residue, which is consistent with expected shift due to kinetic isotope effect (KIE). We proceeded to characterize the range of compound-specific D/H ratios for various PAH sources, and showed them to overlap significantly (Figure 3). Figure 3 indicates that compound-specific D/H ratios are unlikely to be useful as a vector for discriminating PAH sources. The

δD values observed on pyrene was first thought to be a potential discriminant of sources (Figure 2), but our measurement of δD values in sediments dominated by combustion (e.g., sediments from Massena, Newark Bay) showed δD values between -80 and -100 ‰ , all within the range of the crankcase oil sources we measured.

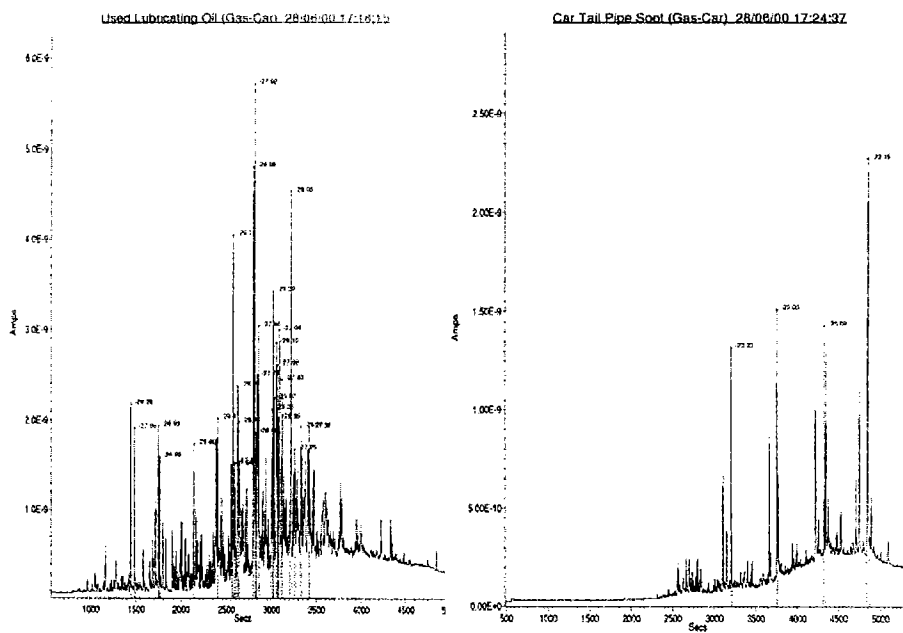


Fig. 4 Molecular signatures of lubricating oil and car emission sources from the Hudson watershed.

Observations on Hudson basin sources (e.g., car emission soot, lubrication oil) are broadly consistent with the carbon isotopic "signatures" for Canadian primary sources previously established by Dr. Abrajano and co-workers. Apart from the greater abundance of lower molecular weight and methylated PAHs in petroleum-derived PAH (left chromatogram) relative to the combustion-derived PAH (right chromatogram), the petroleum sources exhibit distinctly depleted ^{13}C relative to the combustion sources [Petroleum: -25.3 to -29.7; Combustion: -22.0 to -25.7 ‰].

Field Sampling and Analysis

Several sampling sites (Fig. 5) were selected from the NY/NJ Harbor areas including heavily contaminated areas like Newark Bay (NB) and the Passaic River (PR), and less contaminated sites such as Raritan Bay (RB), and Jamaica Bay (JB). Two cores (core JB6 and JB13) were collected from Jamaica Bay located south of John F. Kennedy International Airport (JFK) with one core (JB6) collected in 1982 and another taken 6 years later near the same location (Bopp et al., 1993b). The Passaic River (PR) core was collected in 1985 from an area containing petroleum refineries and storage facilities (Bopp et al., 1993b). Two Newark Bay cores (NB13 and NB20) were taken in 1984 and 1985 respectively (Keane, 1998) near the center of the bay (Bopp et al., 1991). In this study, we analyzed ^{137}Cs dated sediments from the upper 44 cm of core NB13, corresponding to deposition dates of ~1964 to 1996 and lower part of NB20 (36cm until bottom, deposition approximate from 1954 to 1964) (Bopp et al., 1991). Two Raritan Bay cores were collected in 1980 (RB17) and 1990 (RB29). Core RB17 was used to study deposition prior to 1980, while the surface sample (0-2cm) of RB29 with measurable ^7Be has been used to characterize deposition ca.1990 (Bopp et al., 1993b). Cores from sites of NB, PR and JB and core RB29 were segmented into 2 or 4 cm depth sections soon after collection. RB17 was sliced into 2.5-3 cm sections (Keane, 1998). Core sections were dried at 35°C under a flow of air filtered through Florisil to minimize contamination from laboratory air. Once dried, samples were homogenized to a fine powder with a mortar and pestle and stored in pre-cleaned aluminum cans until analysis.

Detailed descriptions of radionuclide dating methods have been discussed previously in previous publications (Bopp et al., 1991; 1993a). Briefly, activities of particle-associated radionuclides including ^{137}Cs and ^7Be were measured by Gamma-ray spectrometry using either a Lithium-drifted germanium or an intrinsic germanium detector. ^{137}Cs is derived from fallout from the atmospheric testing of nuclear weapons that began in 1954 and peaked in 1963 (Olsen et al., 1981). ^7Be is naturally created in the upper levels of the atmosphere through spallation of N_2 and O_2 by cosmic rays. Due to its short half-life (53.4 days), the presence of ^7Be in the top few centimeters in a sediment core is evidence of a recent deposition within one year of core collection. On the basis of three time horizons noted above (1954 and 1963 by ^{137}Cs and collection year by ^7Be), approximate dates of deposition were assigned to individual core sections.

Sediments were Soxhlet extracted using an azeotropic acetone/hexane mix (60/40 (v/v)) over night, then the extract was concentrated to 2-4mL in a Kuderna-Danish device. In order to remove the more polar compounds, alumina column chromatography was performed on the concentrated extracts. Following alumina cleanup, activated copper powder was added to remove

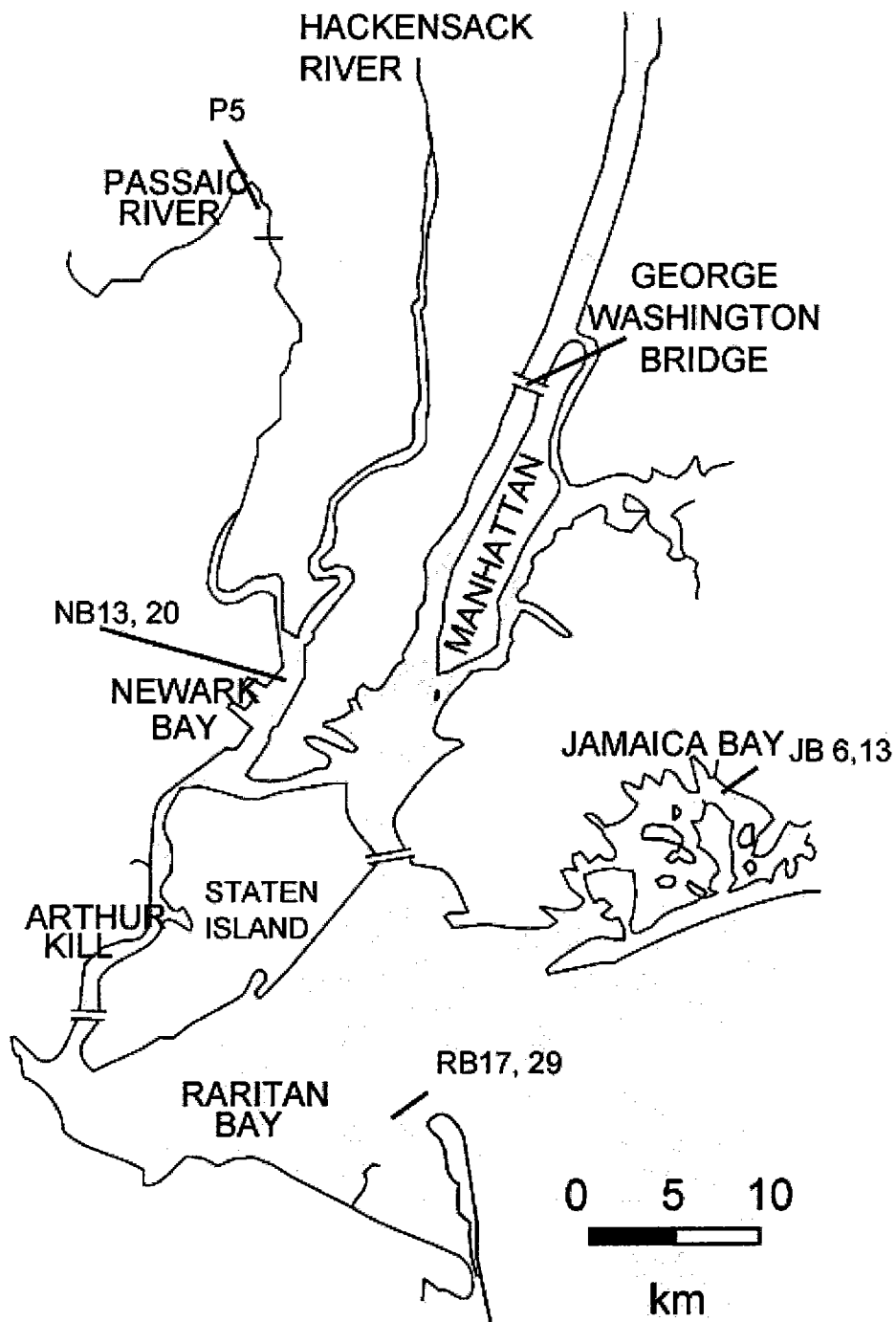


Figure 5. Sampling sites of seven sediment cores in this study from in the New York/New Jersey Harbor complex

elemental

sulfur. The extract was separated into two fractions on silica: the first fraction coeluted with hexane containing the low polarity saturated hydrocarbons, and PCBs; the second fraction with CH₂Cl₂ containing more polar compounds like PAHs and pesticides (Bopp, 1979).

Hydrocarbon compounds were identified by the GC, GC-MS with the help of various purchased standards and the Standard Reference Database of the National Institute of Standards and Technology (NIST). For the alkane fraction, total saturated hydrocarbons (TSH) were quantified by integrating all the resolved alkane peaks and "hump" UCM as one peak. Various high-purity PAH standards, which included the 16 EPA PAHs, C₁-C₄ alkyl PAHs homologues, thiophene series and retene were purchased from Accustandard, Chiron, or Supelco.

GC-FID analysis was performed on a Fisons Instruments 8000-series gas chromatograph equipped with an EL980 FID electrometer. Compound separation was done on a 0.32 mm ID, 60 meters, 0.25 micron film thicknesses, DB-5 capillary column with a temperature-programmed run (50-150°C at 10°C min⁻¹; 150-300°C at 4°C min⁻¹; isothermal at 300°C for 60 min). Flame ionization detector provides a linear detector response for a wide range of PAH concentrations along with a predictable decrease of area responses (peak area per ng carbon) with increased retention times. Area responses were used for calibration of most of the parental PAHs with available standards. For those without available standards, area responses were interpolated from the trend of the area response vs. retention time for known standards (R²=0.97). GC-MS analysis was done using a Shimadzu GCMS-QP5050 with the GC column oven programmed at from 50 to 280 at 5°C/min, held at 50°C for 3 min, and then at 280°C for 20 min. The column used for GC-MS analysis was similar to that used for GC/FID analysis but half the length (30 m). CSCIA was performed with a Hewlett Packard 5890 gas chromatography coupled with a combustion interface to a VG Optima isotope ratio mass spectrometer (IRMS) as previous reported (O'Malley et al., 1994; Smirnov et al., 1998). The temperature program is the same as the GC PAH program.

To assure data quality in the PAH analysis, over 5% of the total number of samples analyzed in our lab were extracted and analyzed more than once using different sample weights (cf. Keane, 1998). 10% of the sample extracts were injected twice, providing duplicate chromatographic runs. Analytical results from both types of duplicates showed a relative percent difference of less than 15% (Bopp, unpublished data). QA/QC methodology for the GC-IRMS follows that of O'Malley et al. (1994, 1996).

NEW YORK/NEW JERSEY HARBOR SEDIMENTS

Chronology in Brief

Forty miles upstream at Fort Edward and sixty miles downstream at Kingston, Be-7 bearing surface sediment samples have been collected that have allowed extension of existing PAH chronologies (Keane, 1998) to the late 1990s.

From the NY/NJ Harbor complex, we collected cores at seven sites - five along the main stem between mp -2 and mp 10, Newtown Creek, and the Kill van Kull. At each site, four cores were

collected and the surface (0-2 cm) sections were composited. All composited samples contained measurable activity of Be-7 and were used for extending chronologies to the late 1990s.

We have also collected and dated sediment cores that will provide a complete PAH chronology (1950 to the late 1990s) for the main stem of the Hudson at Albany. This is particularly significant because our best previous core upstream of Kingston and downstream of the confluence with the Mohawk only provided samples deposited between 1972 and 1977.

Spatial and temporal distributions of hydrocarbons from the NY/NJ harbor complex

"Total" PAH (Σ PAH) is commonly defined as the sum of sixteen 3-6 ring parental PAH compounds, but this measure clearly underestimates petrogenic sources that tend to have abundant alkyl PAHs. To better compare our results with other studies, we use Σ PAH as defined (Fig. 6), but we also present TPAH as sum of all quantified parent and alkyl PAHs (table 1, Fig. 7). The range of Σ PAH concentrations varies considerably, both spatially and temporally. For example, around 1980, the concentration sequence in four sites from highest to lowest is the Newark bay (70,000 ng/g), Passaic River (60,000 ng/g), Jamaica Bay (9,400 ng/g), and Raritan Bay (1,900 ng/g), which is consistent with other reports in these areas (Crawford et al., 1995; Gigliotti et al., 2002). The considerable geographic variations in PAH concentrations suggest that particle-associated contaminants in the Harbor Complex are not well-mixed and the PAH sources are likely localized.

In core PR, concentrations of principal PAHs (Fl, Py, BaA, Chy etc.) in all but the top section are higher than their effects range-medians (ERM) an amphipod toxicity guideline values. This suggests that PAHs in the Passaic River could have severe adverse effects on benthic organisms (Long et al., 1995). In all but the oldest sections of the NB cores, concentrations of these principal compounds are lower than their ERM, but greater than ERL (effects range-low) (Long et al., 1995). In contrast, most of above mentioned principal PAHs in core JB and RB are below their corresponding ERL values.

Σ PAH depth profiles from NB, RB and JB show elevated levels around 1940s-1950s, then generally decline to the date of collection. These decreasing temporal trends are consistent with those presented by Huntley et al., 1995) and elsewhere around the world (Sanders et al., 1993; Simcik et al., 1996; Fernandez et al., 2000; Okuda et al., 2002a). This substantial decline in PAH concentration since the 1950s has been attributed to a major shift in energy use (e.g. residential heating & power generation) from predominantly coal-derived energy to a greater petroleum and gas usage (Hites et al., 1980; Pereira et al., 1999). Evidence suggests that coal combustion has the potential to release more PAHs than petroleum or natural gas per unit of power generated (Rogge et al., 1993; Oros & Simoneit, 2000; Schauer et al., 2001).

In all four cores, the decrease in PAH concentrations towards the present was interrupted by a temporary increase around early to mid 1980s, which has also been shown for other contaminants such as heavy metals, γ -Chlordane and PCBs (Bopp et al., 1991). It has been suggested that this event may be a result of a major flood that occurred on April 4-5, 1984 after two consecutive years of drought (Bopp et al., 1991).

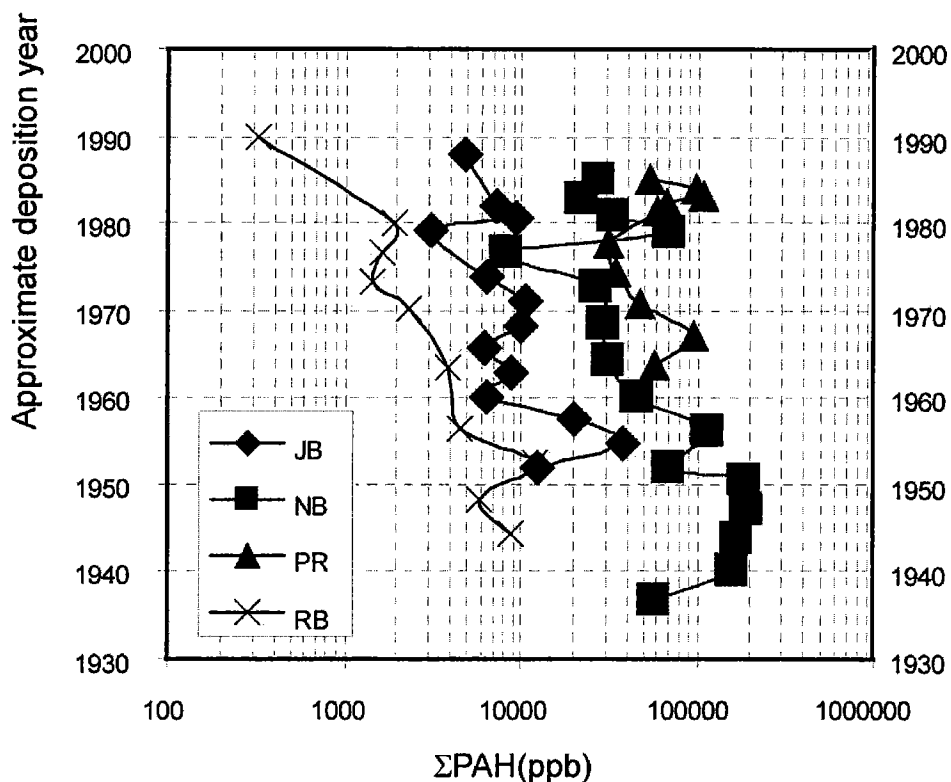


Figure 6. Σ PAH depth profiles in the four cores from NY/NJ harbor complex. Approximate deposition date prior to 1953 in cores NB and RB was estimated under the assumption that there is the same deposition rate before 1953 as that after 1953.

The UCM in the GC-FID chromatogram in the saturated hydrocarbon (SH) fraction – is mostly associated with degraded or weathered petroleum residues although it has also been observed in wood and coal combustion (Oros & Simoneit, 2000; Fine et al., 2001). In most of the sediments from cores RB and JB, the hump is generally broad and high compared with saturated hydrocarbon peaks indicating saturated hydrocarbon sources are mainly from petroleum usage. Temporal trends in UCM from all sites except RB do not follow the PAH profiles. Compared with a broad UCM range (i.e., large molecular weight range) in samples from other sites, elevated UCM in core JB tends to have a lower molecular weight distribution (C_{15} - C_{21}), probably indicating the input from biodegradation of jet fuel, whose alkane ranges mainly in the range C_{15} to C_{20} (Fig. 8). The John F. Kennedy (JFK) airport is adjacent to our sampling site (Fig. 5), and it is likely that there is a direct input from the airport (Bopp et al., 1993b). The carbon preference index (CPI), ratio of the sum of the odd carbon-numbered alkanes to the sum of the even carbon-number, is widely used to distinguish saturated hydrocarbon sources between higher plants (CPI >5), and petroleum (CPI~1) (Wakeham, 1996). In all our cores, CPI is mainly around 1-2, indicating dominant petroleum sources for the saturated hydrocarbons rather than higher plant sources.

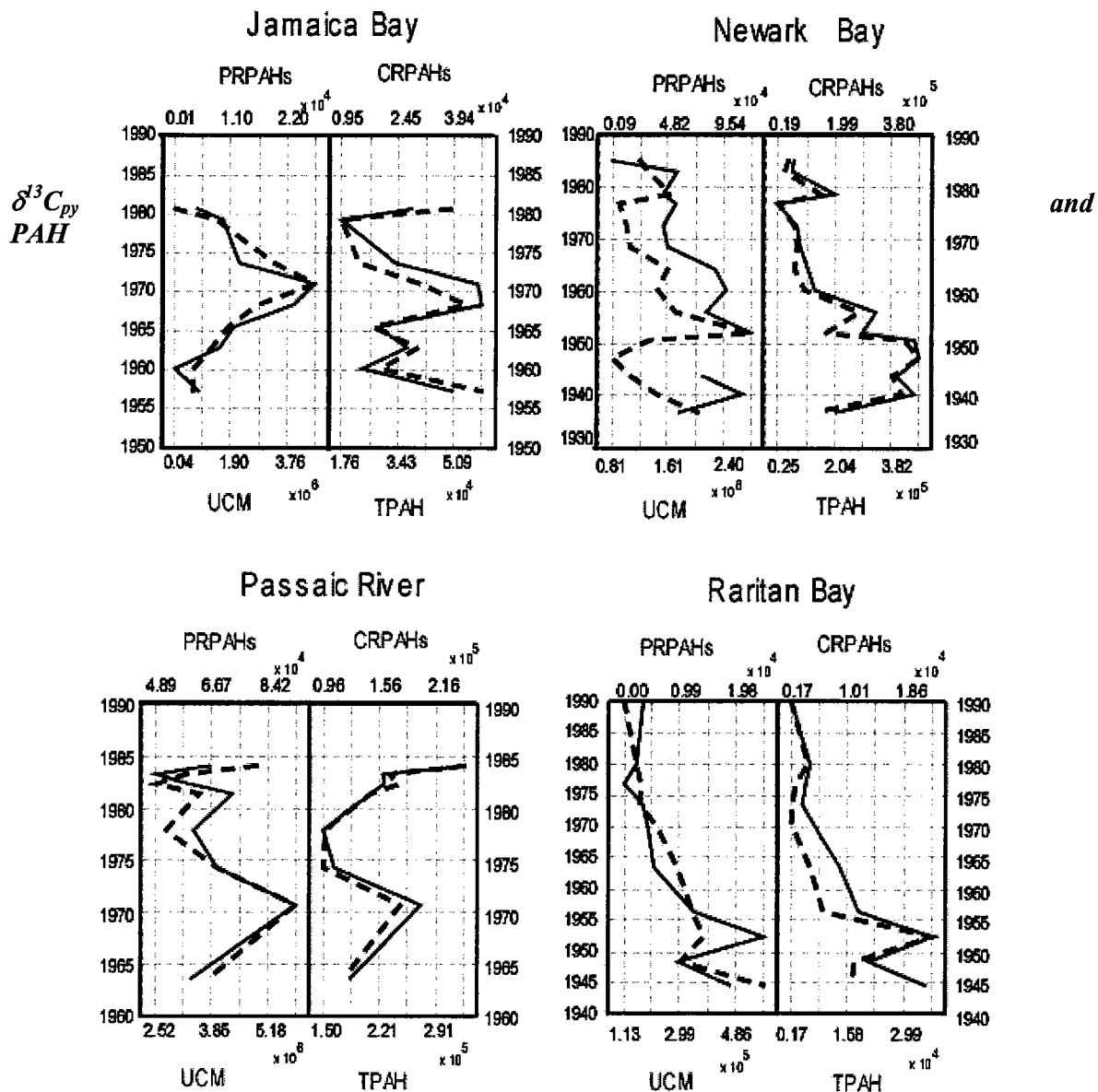


Figure 7. Temporal trends of UCM, TPAH, calculated petroleum derived PAHs and combustion derived PAHs (refer to text definitions) in four sub-basins in New York/New Jersey harbor complex. Trends indicated by dashed lines follow the top scale; solid lines follow the bottom scale.

Sources Over Time

We previously proposed a method for quantifying PAH sources from carbon isotopic mass balance equations (e.g., O'Malley et al., 1994; Abrajano et al., 2003). For the present work, an individual compound – Pyrene (Py) – is used to define the two end-members of petroleum related PAHs (PRPAHs) and combustion related PAHs (CRPAHs). Using this approach, we

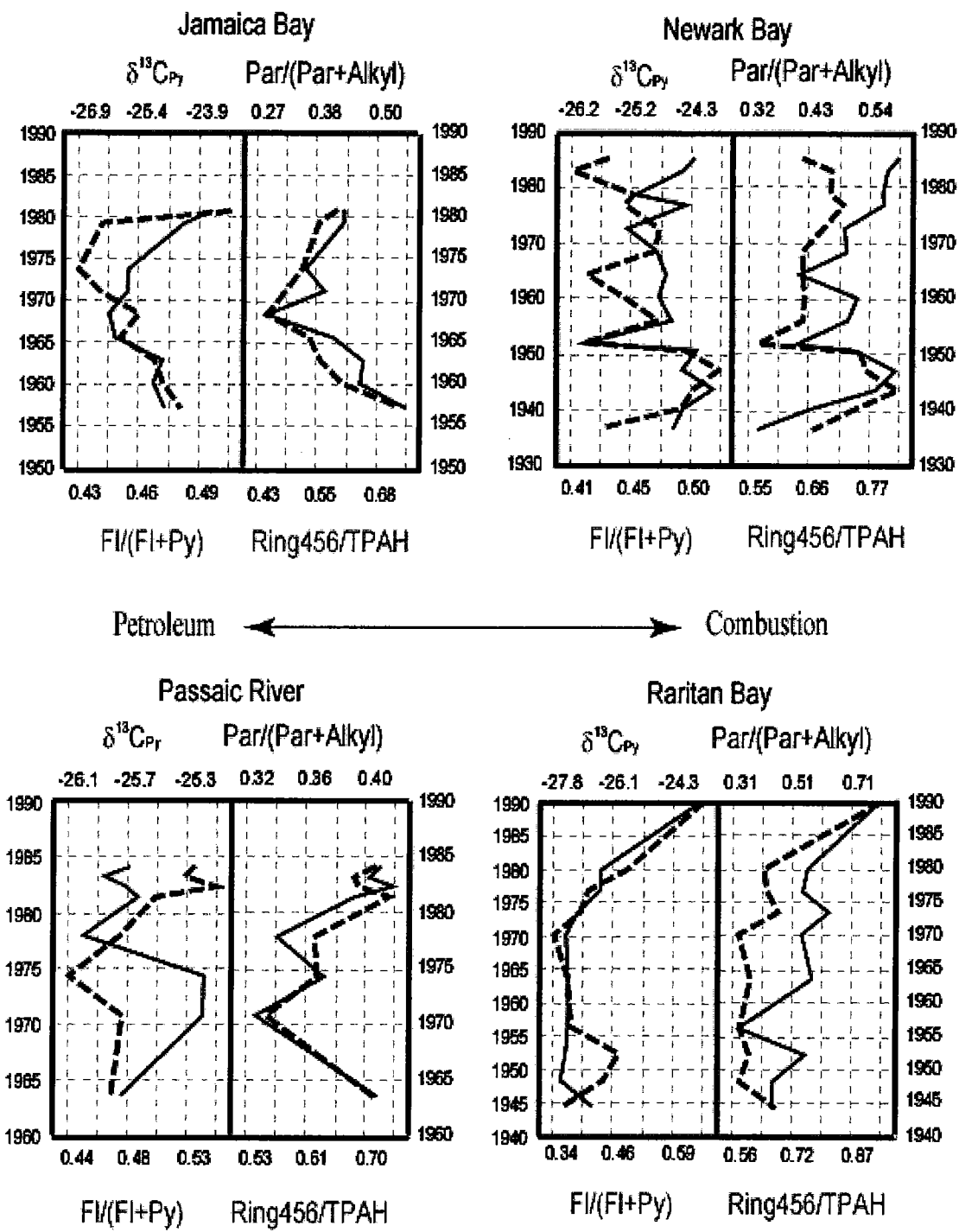


Figure 8. Temporal trends of correlated indicators (refer to text definitions) in samples from four cores in New York/New Jersey harbor complex. Trends indicated by dashed lines follow the top scale; solid lines follow the bottom scale. For all indicators, a tendency towards the right suggests increasing contributions from combustion, while to the left, petroleum.

Table 2. The Pearson correlation matrix of various concentrations

	TPAH	TESH	PRPAHs	CRPAHs
TPAH	1.00			
UCM	0.49	1.00		
PRPAHs	0.54	0.67	1.00	
CRPAHs	0.98	0.39	0.37	1.00

Note : TPAH is concentration sum of all quantified PAHs in samples, UCM is unresolved complex mixture; PRPAHs is the petroleum related PAHs, CRPAHs is the combustion related hydrocarbons, both are calculated from the mass balance of isotope ratios (detailed explanations in text).

assumed $\delta^{13}\text{C}$ of Py ($\delta^{13}\text{C}_{\text{Py}}$) from petroleum was -29‰ , while that from combustion sources was -24‰ (O'Malley et al., 1994; Abrajano et al., 2003). The mass balance equation is as follows:

$$\delta^{13}\text{C}_{\text{sample}} = -29\text{‰} * f_{\text{Petro}} + -24\text{‰} * (1-f_{\text{Petr}}) \quad (1)$$

where f_{Petro} is the proportion from petroleum. Equation 1 assumes 2-source mixing, hence the fraction from combustion should be $1-f_{\text{Petr}}$. If $\delta^{13}\text{C}$ of Py in the sample is known, then PRPAHs can be calculated from equation 1 and the following equation:

$$\text{PRPAHs} = \text{TPAHs} * f_{\text{Petro}} \quad (2)$$

where we use TPAH rather than ΣPAH because ΣPAH underestimates "total PAH" especially when there is input from petroleum related sources (Readman et al., 2002; Yan et al., 2004a). Depth profiles of PRPAHs and UCM from the four sites are shown in figure 3. Even minor fluctuations in these two profiles are similar, whereas the calculated combustion-related PAH resemble the profile of TPAH. PRPAHs show a stronger correlation with the UCM (Pearson correlation $R=0.72$, $n=42$) than CRPAH do ($R=0.39$) (table 2). Similar historical trends and strong correlation between PRPAHs and UCM in these four cores suggest that the trend of PRPAHs calculated by the carbon mass balance equation can reflect the relative importance of petroleum input.

Correlation of Pyrene $\delta^{13}\text{C}$ with Molecular Indicators

Pearson correlation analysis was used to elucidate the relationship of the aforementioned molecular criteria and $\delta^{13}\text{C}_{\text{Py}}$. As discussed above, if initial molecular characteristics are retained from sources to sediments, the molecular ratios should correlate with each other and with $\delta^{13}\text{C}_{\text{Py}}$. Theoretically, $\delta^{13}\text{C}_{\text{Py}}$ should be positively correlated with the molecular ratios as configured because $\delta^{13}\text{C}_{\text{Py}}$ will increase as petroleum combustion contribution increases (O'Malley et al., 1994).

Fl/(Fl+Py)

Fluoranthene and pyrene are two of the most abundant PAH compounds in sediment samples (Wakeham et al., 1979a, 1979b; Fernandez et al., 2000). Yunker et al. (2002) reviewed the

variation of Fl/(Fl+Py) ratios in petroleum/crude, single-source combustion and environmental samples. They proposed that the petroleum/crude to combustion boundary ratio appears closer to 0.4 than 0.5, the latter being the demarcation used by others previously. Yunker et al.'s (2002) work also suggests that petroleum combustion products has a range of Fl/(Fl+Py) of around 0.4-0.5, while PAH produced from plant biomass burning (including grass, wood or coal) have ratios typically greater than 0.50 (Yunker et al., 2002). Correlation coefficients among various indicators in this study are shown in table 3. Fl/(Fl+Py) correlates strongly with $\delta^{13}\text{C}_{\text{Py}}$ ($R=0.66$, $n=42$, $p<0.001$) when all samples from the four sampling sites are considered. However, the correlation coefficients between Fl/(Fl+Py) ratio with $\delta^{13}\text{C}_{\text{Py}}$ vary considerably from site to site when only the samples within individual sites are considered (table 4). It is likewise notable that the correlation appear to be weakest where TPAH are highest (i.e., Passaic River, Newark Bay). In core PR and the upper portion of core NB, very small variations in $\delta^{13}\text{C}_{\text{Py}}$ and Fl/(Fl+Py) ratios were observed, indicating a relative stable contribution from combustion and petroleum sources. In contrast, cores JB and RB showed larger temporal changes in both $\delta^{13}\text{C}_{\text{Py}}$ and Fl/(Fl+Py) ratios (Fig. 8), suggesting the fluctuations of major PAH contribution between petrogenic and combustion sources. The stronger correlation of $\delta^{13}\text{C}_{\text{Py}}$ and Fl/(Fl+Py) in cores JB and RB suggest that these two ratios are indeed sensitive enough to reflect major shifts in PAH sources between petrogenic and pyrogenic sources (cf. Abrajano et al., 2003). The weaker correlation in the more heavily polluted areas is presumably due to enhanced importance of within sources (e.g., amongst combustion sources such as motor vehicle emissions, combustion from oil refineries, residence heating, wood combustion, incinerator products, etc.) where no large shifts in petrogenic/combustion ratio occur or where combustion overwhelmingly dominates PAH sources (e.g., in highly industrialized areas). The poor correlation between $\delta^{13}\text{C}_{\text{Py}}$ and Fl/(Fl+Py) may also arise where the specific petrogenic and combustion PAH sources for an area overlap in their Fl/(Fl+Py) ratios. For example, the ratio of Fl/(Fl+Py) from kerosene (petrogenic PAH source) is around 0.46, while that from gasoline combustion has a similar value around 0.44 (Yunker et al., 2002, and reference therein).

A/(Pa+A)

The ratio of A/(Pa+A) has been considered as a sensitive indicator by Yunker and other scientists (Budzinski et al., 1997; Readman et al., 2002). Generally, a ratio < 0.1 is indicative of petrogenic sources, while greater than 0.1 implies combustion sources. In the present study, A/(Pa+A) has a different trend and weak correlation with $\delta^{13}\text{C}_{\text{Py}}$ and other molecular indicators (table 3). For instance, in all but surface sediments from sites RB, both the $\delta^{13}\text{C}_{\text{Py}}$ (ranging from -27.7 to -27.0 ‰) and Fl/(Fl+Py) ratio (0.34-0.4) indicate a dominant petrogenic source. However, A/(Pa+A) ratios are greater than 0.25 suggesting a dominant combustion source. The inconsistency of ratio A/(Pa+A) with the other ratios is also observed in 1990s harbor surface sediment study and Central Park Lake core (Yan et al., 2004a). We attribute this discrepancy to environmental behavior differences between two isomers Pa and A. Previous work have shown that anthracene (A) has a much higher potential for photolysis than Pa, hence the applicability of this molecular indicator in "weathered" PAHs may be questionable (Masclat et al., 1986; Sanders et al., 1993).

BaA/(BaA+Chy)

Yunker et al. (2002) proposed that a ratio of BaA/(BaA+Chy) less than 0.2 is indicative of petrogenic inputs, whereas ratios greater than 0.35 point to combustion sources. However, the

Table 3. The Pearson correlation matrix of isotope ratios and various molecular ratios(all the samples from NY/NJ Harbor)

	$\delta^{13}\text{C}_{\text{py}}$	Fl/(Fl+Py)	A/(Pa+A)	BaA/(BaA+Chy)	$\text{C}_0/(\text{C}_0+\text{C}_1)$ P/A	$\text{C}_0/(\text{C}_0+\text{C}_1)$ F/P	IP/(IP+Bghi)	Ring456/ TPAH	Par/ (Par+Alkyl)
$\delta^{13}\text{C}_{\text{py}}$	1.00								
Fl/(Fl+Py)	0.66	1.00							
A/(Pa+A)	0.09	-0.11	1.00						
BaA/(BaA+Chy)	-0.20	-0.47	-0.14	1.00					
$\text{C}_0/(\text{C}_0+\text{C}_1)$ P/A	0.01	0.00	0.33	-0.09	1.00				
$\text{C}_0/(\text{C}_0+\text{C}_1)$ F/P	0.49	0.60	0.06	-0.42	0.06	1.00			
IP/(IP+Bghi)	0.01	0.16	0.12	-0.43	0.20	0.11	1.00		
Ring456/TPAH	-0.29	-0.21	-0.40	0.39	-0.01	-0.17	-0.35	1.00	
Par/(Par+Alkyl)	-0.57	-0.56	-0.29	0.31	-0.16	-0.49	-0.11	0.76	1.00

Note: $\delta^{13}\text{C}_{\text{py}}$ is the stable carbon isotope composition of Py; See text for molecular indicator definition.

present study shows that BaA/(BaA+Chy) negatively correlates with $\delta^{13}\text{C}_{\text{py}}$ and Fl/(Fl+Py) when samples from all the four sites are considered. Indeed, the correlation coefficients varied substantially from site to site, but are very weak in general (table 4). BaA/(BaA+Chy) shows a low negative correlation with $\delta^{13}\text{C}_{\text{py}}$ in cores from Raritan Bay (RB17 and RB29) and Passaic River, but a low positive correlation in cores JB and NB. As with the ratio of A/(Pa+A), the weaker correlation and the aberrant variations in correlation coefficients between the ratio of BaA/(BaA+Chy) and $\delta^{13}\text{C}_{\text{py}}$ may be caused by the different environmental behaviors of these two isomers. BaA has a shorter half-life when exposed to sunlight, atmosphere, compared with chrysene (Masclat et al., 1986; Kamens et al., 1988). Regardless of the ultimate explanation for the observed results, they clearly imply that caution is necessary when using BaA/(BaA+Chy) as tracer to source PAHs.

IP/(IP+Bghi)

Yunker et al. (2002) proposed that IP/(IP+Bghi) ratios less than 0.2 may suggest a petrogenic input, between 0.20 and 0.50 likely imply liquid fossil fuel combustion, while over 0.5 may be indicative of plant biomass combustion (including coal combustion). Our correlation studies show that IP/(IP+Bghi) has little to no correlation with the $\delta^{13}\text{C}_{\text{py}}$ ($R=0.01$), and no or very weak correlation with other molecular ratios (e.g. Fl/(Fl+Py)) (table 3).

Alkyl PAH series ($\text{C}_0/(\text{C}_0+\text{C}_1)_{\text{P/A}}$; $\text{C}_0/(\text{C}_0+\text{C}_1)_{\text{F/P}}$)

High $\text{C}_0/(\text{C}_0+\text{C}_1)_{\text{P/A}}$; $\text{C}_0/(\text{C}_0+\text{C}_1)_{\text{F/P}}$ ratios generally indicate combustion contribution, whereas low ratios implicate petrogenic sources (Wakeham et al., 1979a; Sporstol et al., 1983; Yunker et al., 2002). Our post-1990 harbor sediment study showed that both these two indicators have good correlations with the Fl/(Fl+Py) ratio (R is 0.92 and 0.94 for P/A and F/P series respectively, $n=13$) (Yan et al., 2004b). In the NY/NJ Harbor sediments, $\text{C}_0/(\text{C}_0+\text{C}_1)_{\text{P/A}}$ showed poor correlation with $\delta^{13}\text{C}_{\text{py}}$ ($R=0.01$, $n=42$) and Fl/(Fl+Py) ($R=0.04$, $n=42$), whereas the $\text{C}_0/(\text{C}_0+\text{C}_1)_{\text{F/P}}$ is moderately correlated with $\delta^{13}\text{C}_{\text{py}}$ ($R=0.49$, $p<0.01$) and Fl/(Fl+Py) ($R=0.60$) (table 3). F/P series appears to be poorly correlated with $\delta^{13}\text{C}_{\text{py}}$ in Jamaica Bay ($R=0.04$, $n=9$)

Table 4. Correlation coefficients of $\delta^{13}\text{C}_{\text{py}}$ with Fl/Fl+Py and Par/(Par+Alkyl) and Ring456/TPAH from four sampling sites.

	Jamaica Bay(n=9)	Newark Bay(n=15)	Passaic Rive(n=8)	Raritan Bay(n=10)
Fl/(Fl+Py)	0.63	0.38	-0.48	0.83
BaA/(BaA+Chy)	0.16	0.46	0.03	-0.80
$\text{C}_0/(\text{C}_0+\text{C}_1)$ F/P	0.04	0.55	0.15	0.60
Ring456/TPAH	0.59	0.32	0.52	0.64
Par/(par+Alkyl)	0.52	0.66	0.48	0.72

despite the fact that other molecular ratios are correlated strongly (table 4). The stronger correlation of these two ratios with $\delta^{13}\text{C}_{\text{py}}$ and Fl/(Fl+Py) in post 1990s harbor sediment and weaker historical correlation in older sediment cores may be due to the alteration of engine types and catalytic conversion systems in the past several decades. It is well known that varied combustion temperature and ratios of air to fuel ratios in different engine types as well as post-engine pollution control devices could substantially alter the alkyl PAH composition in motor vehicle emissions (Simoneit et al., 1985, Baek et al., 1991).

Ring456/TPAH

Ratios or percentages of LMW (2-3 ring) to total or HMW (4-6 ring) parental PAHs has been applied in several studies to distinguish petrogenic and pyrogenic PAH sources (Bence et al., 1996; Wang et al., 1999; Mai et al., 2002). However, Bence et al. (1996) found that a few years after the Exxon Valdez oil spill, most of the 2-3 ring parent PAHs were lost due to evaporation and degradation. Hence, source apportionment assignments using 2-3 ring parent PAHs may become compromised after moderate weathering. Nevertheless, it is also known that some of the alkylated Na and Pa homologues especially the C_3 - C_4 homologues could remain after moderate weathering and deposition in anaerobic conditions (Wang, et al., 1999). For post-1990s sediments, Ring456/TPAH, the ratio of total 4-6 ring PAHs (including parent and alkylated homologues) to total PAH, was used as a proxy for the ratios of LMW to total or HMW parent PAHs (Yan et al., 2004b), and was found to strongly correlate with Fl/(Fl+Py) and two alkyl series molecular indicators. Further analyses have found that Ring456/TPAH is sensitive to inputs from fresh oil spills as long as no extensive degradation occurs (e.g. complete loss of the 2 and 3 ring parent and alkyl PAHs) (Yan et al., 2004b). After moderate to strong weathering, the ratio may become indifferent to petrogenic contributions. In the NY/NJ Harbor sediments, Ring456/TPAH correlated fairly with $\delta^{13}\text{C}_{\text{py}}$ ($R = \sim 0.29$, $p < 0.1$, $n = 42$) when all of sediment samples are included, but show similar trends were observed (Fig. 8) within each specific core site. The similar trends within each core site but fairly correlation in whole Harbor Complex would imply either that the molecular characteristics of petrogenic and combustion sources are distinct from site to site or there are distinct weathering pathways after PAH deposition in each specific site over the last several decades.

Par/(Par+Alkyl)

Dominance of alkyl substituted over parental PAHs from petrogenic sources is seen in the Pa/A, F/P Na and BaA/Chy series (Wang et al., 1999). LMW Na and P/A series degrade more

easily, leading to a prominence of HMW PAHs in sediments in general (e.g. Fl/Py and BaA/Chy series) (Wang et al., 1999). Despite of possible degradation, the BaA/Chy series from oil spills could retain their alkyl dominance even after extensive weathering (e.g., Bence et al., 1996). Consideration of all of four alkyl series (Na, P/A, F/P, and 228 series) may allow a determination of the presence of oil spills and the degree by which the oil has been degraded (Wang et al., 1999). Therefore a ratio like Par/Par+Alkyl, the total C₁-C₄ homologues of the masses 128, 178, 202, and 228 to the parent PAHs with these masses (Na, Pa, A, Fl, Py, BaA, Chy), can be used to distinguish petrogenic and pyrogenic sources even after extensive weathering in sediments (Yan et al., 2004b). In the Harbor sediments, correlation coefficient of 0.57 (p<0.001) between Par/(Par+Alkyl) and $\delta^{13}\text{C}_{\text{Py}}$ was observed. Par/(Par+Alkyl) also presents a very strong correlation with other molecular ratios (e.g. 0.56 with Fl/(Fl+Py) and 0.76 with Ring456/TPAH, p<0.001). As with Ring456/TPAH, correlation coefficients range from 0.48 in core PR to 0.72 in core RB (table 3), indicating its fairly stable correlation with $\delta^{13}\text{C}_{\text{Py}}$ in all of these four areas. The strong correlation in each individual area and whole Harbor Complex implies that Par/(Par+Alkyl) may be a reliable PAH source indicator over large geographic (or even temporal) scales.

Combined application of $\delta^{13}\text{C}_{\text{Py}}$, Fl/(Fl+Py), Par/(Par+Alkyl), and Ring456/TPAH

The above discussions suggest that $\delta^{13}\text{C}_{\text{Py}}$ and Fl/(Fl+Py), Par/(Par+Alkyl), and Ring456/TPAH are promising indicators that could be used as PAH tracers in the NY/NJ harbor areas. Figure 4 shows trends of those four ratios in each site. Despite the parallel trends of ΣPAH levels in most areas of the NY/NJ harbor from the 1950s to the 1980s (Fig. 6), depth profiles of $\delta^{13}\text{C}_{\text{Py}}$ and the three molecular ratios are completely different from site to site (Fig. 8), suggesting varied PAH sources in different areas. Generally, in most sediment samples, Fl/(Fl+Py) and 1,7/2,6-DMP ratios (not shown) are below 0.48 and 0.7 respectively. This is especially true for sediments deposited within the past half century, where the ratios are well below the corresponding ratios for coal-combustion (0.56, 1.9 respectively). Interestingly, these ratios are within the range of 1,7/2,6-DMP ratios of fossil fuel combustion products. In contrast, the top section of core RB29, Fl/(Fl+Py) show a high ratio of 0.65 and 1,7/2,6-DMP of 1.08, suggesting a high possibility for PAH input from coal combustion for these recent sediments. However, the ratio of U/R (UCM to resolved hydrocarbons) is 23, much higher than the coal generated ratio from coal smoke (2.9-3.3) (Oros & Simoneit, 2000), and comparable with petroleum dominant ratios (~20) seen in Central Park Lake, New York City (Yan et al., 2004a). Therefore, it is likely that in these four sites, petroleum-combustion related usage is the dominant PAH source in the several decades.

However, we note that prior to 1960, higher concentrations of TPAH are observed in the sediments from NB and RB. As mentioned above, the decreasing ΣPAH trends since the 1940s to the present have been attributed to a major fuel change from coal to petroleum combustion (Hites, et al., 1979). The energy shift probably can explain observations from Newark Bay sediments. From the 1930s to 1940s in core NB, $\delta^{13}\text{C}_{\text{Py}}$ is around -24 to -25.7‰ indicating a combustion dominant source. Fl/(Fl+Py) ratios are around 0.5, suggesting a possible source from coal or wood combustion. However, 1,7/2,6-DMP ratios would be higher (>1) than those determined in the 1940s (~0.64) if the major source was wood burning (Benner et al., 1995; Yan et al., 2004a). Therefore, the dominant PAH sources in Newark Bay around the 1940s were most

