



Mass Balances on Selected Polycyclic Aromatic Hydrocarbons (PAHs) in the NY/NJ Harbor Estuary

by

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I. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous organic compounds containing 2 to 8 fused aromatic rings. The entire range of PAH compounds can be produced naturally via volcanoes and forest fires, but PAHs in the atmosphere are dominated by those arising from anthropogenic sources, which include combustion of any kind (burning of wood, coal, gasoline, diesel, natural gas, municipal waste, etc) and evaporative emissions during petroleum refining. Naphthalene, unlike the other PAHs, is still used in many industrial applications (1). Humans are exposed to PAHs by breathing contaminated ambient air, eating grilled meat, and inhaling tobacco smoke. The U.S. Department of Health and Human Services has determined that some PAHs may reasonably be expected to be carcinogens. Some PAHs, most notably benzo[a]pyrene, are known or probable human carcinogens (2). Benzo[a]pyrene is on EPA's list of 12 priority Persistent Bioaccumulative Toxins (PBTs) currently being addressed under its PBT initiative (<http://www.epa.gov/pbt/cheminfo.htm>). PAHs are part of a group of 31 priority chemicals that EPA has identified for source reduction under the National Partnership for Environmental Priorities (NPEP).

Due to their ubiquitous presence and potential to cause adverse human health effects, PAHs are a concern in all urban watersheds. Previous attempts to assess PAH contamination in the NY/NJ Harbor Estuary have been hampered by a lack of data on ambient water concentrations of PAHs due to a limited number of studies and also due to difficulties associated with measuring PAHs in water (described in more detail below). Farley et al. (3) conducted a crude assessment of the fate of PAHs in the NY/NJ Harbor Estuary by using PAH concentration data from other systems. For example, Farley et al. used atmospheric data from the Great Lakes to estimate atmospheric deposition of many compounds to the NY/NJ Harbor Estuary. To our knowledge, this report represents the first attempt to construct a mass balance on PAHs in the NY/NJ Harbor Estuary based on data collected in the Estuary.

II. PAH CYCLING IN THE HUDSON RIVER

Physical properties of the different compounds that make up the larger category of PAHs vary over a wide range. Vapor pressures range from 11 Pascals (Pa) for naphthalene to 1.4×10^{-8} Pa for perylene (4). These values put them in the class of chemicals considered "semivolatile" meaning that they exist in the atmosphere in measurable quantities in both the gas and airborne particle phases. Naphthalene is found almost entirely in the gas phase, while perylene is found almost entirely in the particle phase in the atmosphere. Atmospheric PAHs are subject to deposition to water bodies (and other surfaces) via dry particle deposition, wet deposition, and absorption into water from the gas phase ("gross gas absorption"). They have relatively low water solubilities, ranging from about $10^{-3.6}$ g/L (naphthalene) to $10^{-8.8}$ g/L (perylene) (4). Their relatively low water solubilities and high vapor pressures render the lower molecular weight (MW) PAHs susceptible to volatilization from the dissolved phase in water to the gas phase (the opposite of gas absorption). The high MW PAHs are hydrophobic, and prefer to associate with organic matter in solid phases such as sediment and suspended sediment rather than remaining in the dissolved phase in water. In general, the lower the molecular weight of a PAH compound, the higher its vapor pressure, and the less pronounced its preference for organic matter. Because of the strength of their association with sediment, a comprehensive assessment of PAH fate in an aquatic system such as the NY/NJ Harbor Estuary requires that a mass balance

be developed on the solids (sediment) in the system. Such mass balances have been constructed previously, most notably by Farley et al. (3). Transport of PAHs with sediment will be addressed in this report by using “whole-water” PAH concentrations (the sum of PAHs in the dissolved phase plus those associated with suspended particulate matter in the water column) to develop tributary loadings and tidal exchange losses to the New York Bight.

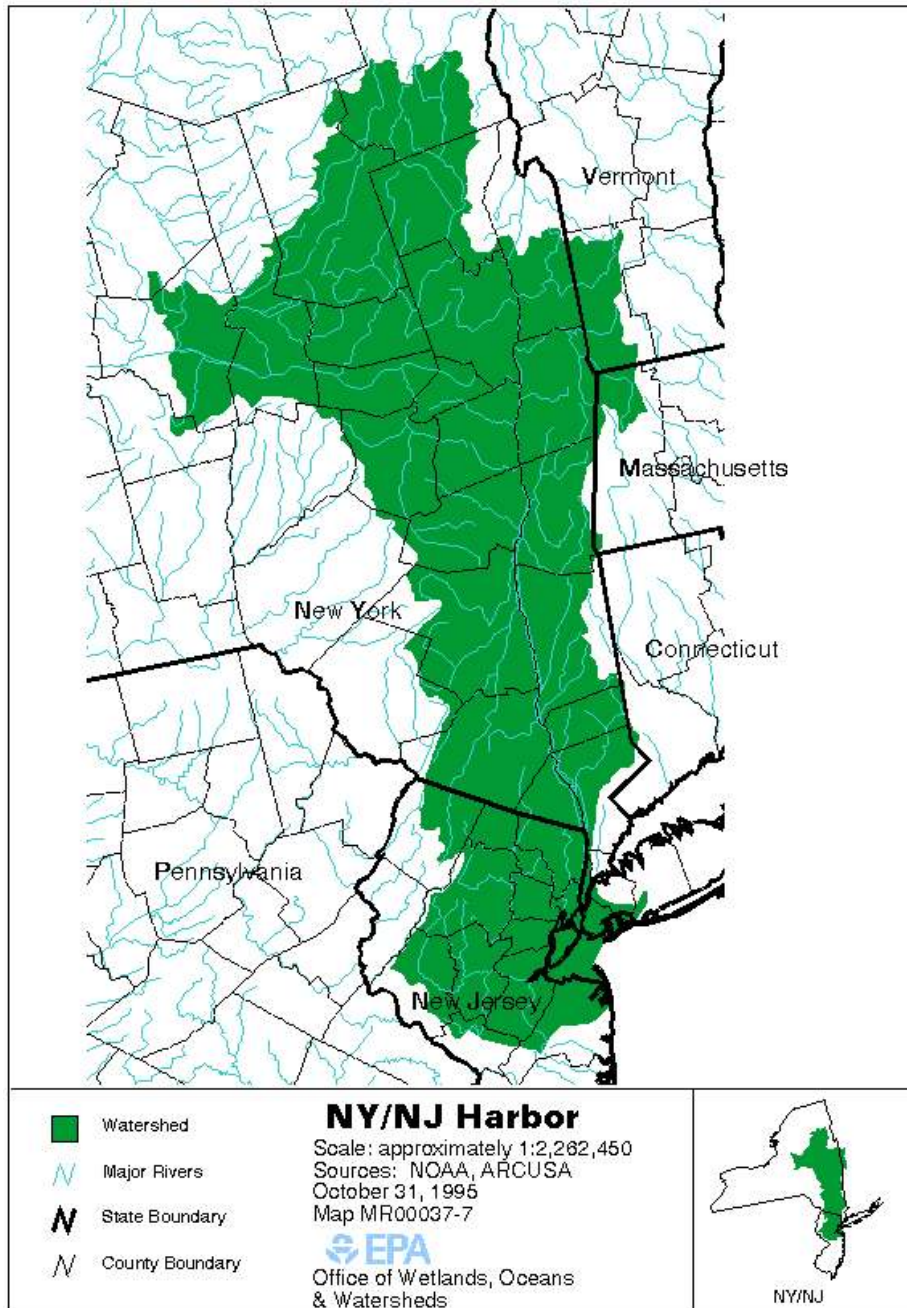


Figure 1. New York/New Jersey Harbor Drainage Basins.

III. APPROACH

The New York/New Jersey Harbor drainage system covers an area of 42,128 km² (16,456 square miles) (Figure 1). The water surface encompasses about 811 km². These mass balance calculations are based on the general 3-box model used to examine cadmium distributions in the estuary (5, 6). This model has been used in past to construct mass balances on mercury (7), cadmium (8) and PCBs (9) in the estuary. The model includes three boxes: *Hudson River*, *Estuary* and *New York Bight*. The River box includes all freshwater bodies (i.e. combined riverine inputs from the Hudson, Hackensack, Passaic, Raritan, Elizabeth, Rahway, and East Rivers). The River box is separated from the estuary by the zero salinity point. Note that the geographical location of this point depends on the water discharge; at low discharge the tidal tongue pushes the river upstream, whereas at high discharge, typically in March and April (3), the freshwater body extends further downstream. The Estuarine box extends from zero salinity seaward (for area calculation we designate the Newburgh Bridge as the northern extension of the estuary)(Table 1) and includes the Upper and Lower Harbor. The line connecting Sandy Hook with Long Island separates the Harbor from the New York Bight.

Table 1. Total water surface area used in this study (10).

Sub-basin	Area km²	% of area
Lower Harbor	318	39%
Upper Harbor	104	13%
Jamaica Bay	47	5.8%
Newark Bay	32	3.9%
Battery to Newburgh Bridge	310	38%
Total water surface area	811	100%

Sources of PAHs to the NY/NJ Harbor considered in this report include:

- Tributaries.
- Atmospheric deposition via wet and dry particle deposition and gross gas absorption.
- Wastewater treatment plant discharges.
- Combined sewer overflows (CSOs).
- Stormwater runoff.
- Oil spills.

This report will attempt to quantify the above processes. Other processes could be important sources of PAHs to the NY/NJ Harbor, but the data necessary to evaluate their importance are unavailable. These include: (a) unidentified point sources, (b) groundwater discharges from leaking underground storage tanks, and (c) runoff of PAH-laden soils and dust from contaminated sites (for example, superfund sites associated with creosote production, wood-treatment, manufactured gas production, etc.). Processes a and c are partially accounted for in the tributary inputs.

Processes considered in this report which remove PAHs from the water column of the NY/NJ Harbor include:

- Advection of dissolved or suspended sediment-bound PAHs out of the NY/NJ Harbor into the coastal Atlantic Ocean.
- Volatilization of dissolved PAHs into the atmosphere.
- Removal of sediment-bound PAHs via disposal of dredged sediments outside the NY/NJ Harbor.
- Aerobic biodegradation in surficial sediments
- Accumulation or burial of sediment-bound PAHs in the NY/NJ Harbor

Although accumulation of sediment-bound PAHs in the bottom sediments of the estuary removes them from the water column, it does not remove them from the estuary itself, and is therefore not truly a loss process. Storm events, disturbances to the sediments, areas of high turbidity can result in the resuspension of sediments and an opportunity to release contaminants back to the water column thereby making the sediments a source of PAHs rather than a sink.

This report relies on three main data sets for PAH measurements. The first is the CARP (Contaminant Assessment and Reduction Project) data, which includes measurements of 22 PAH compounds in ambient water (dissolved and particulate phases) as well as in combined sewer overflows, wastewater treatment plant effluent, and stormwater. CARP is a collaborative effort between the New York State Department of Environmental Conservation and the New Jersey Department of Environmental Protection. The NYSDEC CARP samples were collected during 1998-2001. The New York CARP data was provided by Simon Litten of the New York State Department of Environmental Conservation. The New Jersey CARP data was collected during 2000-2002 and was provided in draft form by Joel Pecchioli. Although unpublished, the CARP data has undergone an extensive QA/QC review. This review resulted in the recommendation for virtually all PAH measurements of “use with caution.” The reasons for and implications of this recommendation are discussed below. CARP data was used to construct PAH loadings from tributaries, wastewater effluents, CSOs, and runoff. In other words, most of the loads described here were derived from CARP data. CARP data was also used to construct losses associated with volatilization and tidal exchange.

The second important source of data is the R-EMAP (Regional Environmental Monitoring and Assessment Program), which includes measurements of 17 PAH compounds in sediment samples collected during 1993-1994 and 1998 at a variety of locations within the Estuary (10, 11). The R-EMAP data was used to calculate storage of PAHs within the sediments of the estuary, and losses of PAHs from the estuary due to dredging of the sediment. These two processes dominate the total losses of high molecular weight PAHs from the system.

The third data set is from the NJADN (New Jersey Atmospheric Deposition Network), which measured concentrations of 27 PAHs at three sites (Sandy Hook, New Brunswick, and Jersey City) near the Estuary in the atmosphere (gas, particle, and precipitation) starting in 1997 (12, 13). This data was used to estimate the atmospheric loads of PAHs to the system.

The PAHs selected for investigation in this report are listed in Table 2. These fourteen compounds were chosen because they represent a wide range of molecular weights, which are closely related to the physical properties of the compounds. In addition, these PAHs (except naphthalene and acenaphthene) were measured in all three of the data sets used to construct this report. Naphthalene was added because it is frequently the most abundant PAH in the dissolved phase, and the U.S. Department of Health and Human Services has concluded that it is reasonably anticipated to be a human carcinogen. Acenaphthene was added to the list because it has established USEPA and New York State water quality criteria. The NJADN project did not

measure these compounds due to their low molecular weight and high volatility, which renders them difficult to measure in the atmosphere via the methodologies used. Three small differences between data sets are apparent. First, the CARP measured benzo[b+j+k]fluoranthene, while NJADN measured benzo[b+k]fluoranthene, and R-EMAP measured benzo[k]fluoranthene. (The b, j, and k represent different configurations of the benzofluoranthene aromatic ring structure.) Similarly, CARP and R-EMAP measure dibenz[a,h]anthracene, while NJADN measures dibenz[a,h+a,c]anthracene. Because atmospheric deposition is small compared to the overall mass balance of this compound, this difference was not felt to be significant. Third, CARP and R-EMAP measured chrysene alone, while NJADN measured chrysene plus triphenylene. In all cases, the data from the three projects was felt to be comparable because the various isomers co-elute on most analytical systems and are therefore quantified together regardless of the nomenclature used.

Table 2. PAH compounds investigated and their air-water exchange mass transfer coefficients (K_{OL}).

	Molecular Weight (g/mol)	K_{OL} (m/d)	Rings
Naphthalene	128	0.91	2
Acenaphthene	154	0.71	3
Fluorene	166	0.53	3
Phenanthrene	178	0.35	3
Fluoranthene	202	0.21	4
Pyrene	202	0.18	4
Benz[a]anthracene	228	0.15	4
Chrysene	228	0.07	4
Benzo[a]pyrene	252	0.05	5
Perylene	252	0.05	5
Benzo[b+k]fluoranthene	252	0.07	5
Benzo[g,h,i]perylene	276	0.03	6
Indeno[1,2,3-cd]pyrene	276	0.03	6
Dibenz[a,h]anthracene	278	0.03	5

Measurement of PAHs in water samples is often problematic. The New York water samples were collected by pumping the water through a filter to capture the particulate matter and then through a column containing XAD-2 resin, which extracts the organic chemicals from the water. XAD-2 is an excellent choice for analysis of polychlorinated dioxins and furans (PCDD/Fs), and polychlorinated biphenyls (PCBs), but it unfortunately gives rise to high background levels of some PAH compounds. This is assumed to have caused overestimates of dissolved-phase concentrations of some compounds in the New York CARP data set. PAHs (and other organics) in the New Jersey CARP samples were typically measured in whole water samples and did not use XAD-2 resin. These samples were also subject to blank contamination, in part because the small sample size gave rise to small analyte masses such that even low levels of contamination could significantly impact the overall measured PAH levels. Naphthalene (and

associated methylated compounds), fluorene, acenaphthene, phenanthrene, indeno(1,2,3-cd)pyrene, and benz(g,h,i)perylene are most impacted by these issues (Joel Pecchioli, NJDEP, personal communication, 2004). As a consequence of this contamination and other sampling issues, virtually all of the PAH measurements in the CARP data set are flagged as “use with caution” by the QA/QC reviewers. In many instances, only a particle phase measurement is available in a given compartment for a given PAH. This is particularly a problem for dibenz[a,h]anthracene. For this compound, all measurements in the dissolved phase for ambient waters were used to calculate an average and standard error, which was used to estimate the dissolved phase concentration in compartments where no site-specific measurement was available. This leads to very high uncertainty in the mass balance for this compound. These sampling issues also affect the veracity of the measurements of PAHs in precipitation conducted by NJADN, which also use XAD-2 resin columns. However, wet deposition of PAHs is a comparatively small input to the system. The rest of the NJADN data and the R-EMAP data are not affected by these sampling issues.

There is some evidence that perylene is produced naturally in the sediments of the Estuary (14), which could lead to losses exceeding inputs to the system for this compound.

IV. SOURCES AND SINKS

A. Riverine Inputs

Tributaries considered include the Hudson, Passaic, Hackensack, Rahway, Raritan, and Elizabeth Rivers. Net transport of PAHs in the East River results in a loss to the system, which is described under Section G: Tidal Exchange. For the Hudson River, flow data from Fitzgerald and O'Connor (7) were used to assess inputs to the NY/NJ Harbor. In order to accurately estimate loadings of PAHs from the Hudson, the an average concentration of PAHs above the head of tide should be used, to ensure that tidal mixing of PAHs already present in estuary does not affect the measured concentration (and therefore the loading). For the Hudson River this is difficult, because the boundary of the Estuary for this report is taken to be the Newburgh Bridge, which is within the tidal portion of the Estuary, and not the Troy Dam, which is the head of tide for the Hudson. Thus PAH measurements within the tidal reach will be used to construct loadings estimates, due to the presence of PAH sources below the head of tide, such as the wastewater treatment plant at Poughkeepsie. The New York State Department of Environmental Conservation (NYSDEC) conducted several sampling campaigns from November 1998 to April 2000 in which ambient PAH concentrations in the Hudson were measured. This data has been kindly provided by Simon Litten (NYSDEC) via personal communication. The measurements from Kingston to Poughkeepsie best represent the condition of the River near the Newburgh Bridge, and will be used to calculate the PAH load to the NY/NJ Harbor. Because no clear relationship between river flow and PAH concentration is evident in this data set, the PAH concentrations measured are assumed to apply to all flow regimes. Thus the loading of PAHs from the Hudson to the NY/NJ Harbor (Table 5) is the concentrations in both the dissolved and particle phases (ng/L) multiplied by the flow of 650 m³/s. The uncertainty in the Hudson River load was estimated from the standard error of the mean dissolved and particulate PAH measurements. Because this load is based on measurements of PAHs taken below the head of tide, it may be an overestimate due to incursions of PAHs from downstream. Most of the

investigated PAHs displayed increases in concentration in the samples taken downstream of this location.

Draft loadings from the New Jersey tributaries (Table 5) generated by USGS were provided by Joel Pecchioli of NJDEP and did not include an estimate of uncertainty. Because they represent a major load to the system, it is important to estimate the uncertainty associated with this load. The Hudson River loads described above are associated with uncertainties ranging from 2 – 55%. Therefore we err on the side of caution and assume an uncertainty in the NJ tributary loads of $\pm 50\%$.

B. Atmospheric Inputs

Since October of 1997, Steve Eisenreich and researchers at Rutgers University have operated the New Jersey Atmospheric Deposition Network (NJADN). This network has consisted of as many as 13 sites scattered throughout NJ, PA, and DE where PAHs and other semivolatile organic compounds (SOCs) are measured in air, aerosol, and rain. The NJADN included three sites within the NY/NJ Harbor watershed at Sandy Hook, Jersey City (at the Liberty Science Center), and New Brunswick (at Rutgers Gardens). In general, atmospheric concentrations of PAHs are higher by about a factor of two at these three sites than at other less urban sites such as Chester, NJ (13). NJADN did not measure naphthalene or acenaphthene due to difficulties in sampling of these relatively volatile compounds. Thus the NJADN data can be used to calculate atmospheric loadings of all but these two PAHs. Naphthalene and acenaphthene are the most volatile of the fourteen PAHs addressed in this report. Due to their volatility, their atmospheric deposition is likely dominated by gas absorption, with wet and dry particle deposition of these two compounds being negligible. In the absence of information on the gas-phase concentrations of these two compounds, it is impossible to estimate their gas absorption fluxes. However, the gas absorption loading of these compounds would be partially or even totally offset by volatilization. Therefore a further discussion of the gas absorption of these two PAHs will be presented in the section on volatilization, below.

Higher atmospheric concentrations of PAHs contribute to larger deposition fluxes to the estuary via wet and dry particle deposition, and gross gas absorption. In order to translate these fluxes into a loading to the NY/NJ Harbor, it is necessary to make some judgment about the concentrations of PAHs likely to be present in the atmosphere over the waters of the estuary. Yan (15) reports PAH concentrations in the atmosphere at a location in the middle of Raritan Bay that were generally higher than those measured at Sandy Hook and lower than those measured at Jersey City. Thus the deposition fluxes calculated at Jersey City and Sandy Hook are assumed to represent the maximum and minimum fluxes, respectively, likely to prevail in the estuary. Multiplied by the surface area of the NY/NJ Harbor (811 km² from ref (6)), this translates to the loadings in Table 6.

C. Waste water loadings

The NY/NJ Harbor receives effluent from >30 water pollution control plants (WPCPs). Based on the average flow of these plants, the NY/NJ Harbor receives more than 2 billion gallons of treated effluent each day (16). This translates into a flow of 94 cubic meters per second. In comparison, flow of the Hudson River past Manhattan is about 430 cubic meters per second for most of the year (3).

The NYSDEC sampled 18 WPCPs in New York. These 18 plants discharge about 1,700 MGD (million gallons per day) of effluent to the estuary. Concentrations of each PAH compound in each effluent sample were provided by Simon Litten of NYSDEC. To construct the loading estimate, the average dissolved and particulate PAH concentrations were multiplied by the average total 2001 flow for all WPCPs. (WPCP flow data are available for 2002, but this data was not used because flows were generally lower than in previous years, assumedly due to the extensive drought of 2002.) The range of estimates was obtained from the standard error of the mean concentrations. The range of estimates encompasses the estimate that could be obtained by summing the individual loads for each of the sampled WPCPs (i.e. by pairing each effluent measurement with the treatment plant at which the sample was collected).

NYDEP sampled another 12 plants in New Jersey that discharge about 575 MGD of treated effluent to the estuary. A draft of this data was provided in the form of average (\pm standard deviation) concentrations in small and large WPCPs. This data was multiplied by the total flow of all of the large or small WPCPs in NJ to give the total load. The error in this load was propagated from the error (standard deviation) of the concentrations provided.

D. Combined sewer overflows

The total flow from combined sewer overflows (CSOs) to the Harbor is about 424 cfs (cubic feet per second) (17). Simon Litten (NYSDEC) collected 16 samples of wet-weather influents to represent NYC CSOs. The CSO load is estimated by multiplying the average PAH concentration in the NY CSOs by the total CSO (NY+NJ) flow. The uncertainty in this load was calculated from the standard error of the mean CSO PAH concentrations (dissolved and particulate).

E. Runoff

The flow of stormwater into the NY/NJ Harbor Estuary is highly uncertain. The EPA used a flow of 1,000 cubic feet per second (893 million cubic meters per year) in a report from 1997 (18). Robin Miller (personal communication, 2004) from HydroQual kindly provided estimates of stormwater flows to the "Harbor Core Area", which is essentially the same as the Estuary as defined in this report except that in it, the Hudson River begins at Piermont Marsh as opposed to Newburgh Bridge. These estimates are based on the detailed hydrodynamic model of the Hudson River and its Estuary developed by HydroQual over the last ~25 years. Stormwater flows were calculated based on the rain that actually fell and the ground cover type in the drainage area on an hourly basis for six different water years: 1988-1989, 1994-1995, 1998-1999, 1999-2000, 2000-2001, and 2001-2002. (A water year begins in October). The estimated stormwater flows range from 462 to 1062 million cubic meters per year and average 710 million cubic meters per year. The standard error of the mean is $\pm 12\%$, and this uncertainty was used to propagate the uncertainty in the stormwater load.

Draft stormwater data was provided by NJDEP. Five New Jersey stormwater outfalls were sampled three times each by NJDEP for PAH analysis. Total PAHs in these samples ranged from 597 to 598,000 ng/L. The lowest and two highest concentration samples were discarded and an average and standard deviation for the remaining 12 samples was provided by Joel Pecchioli of NJDEP. These concentrations were multiplied stormwater flow to determine the low and high estimates of stormwater loads to the Estuary

For many of the PAHs investigated, the present estimates suggest that runoff is one of the largest sources of PAHs to the estuary. However, the size of the stormwater load is highly uncertain. Very few measurements of PAH concentrations in runoff in the Estuary exist. Also, the flow of runoff into the Estuary is expected to exhibit significant temporal variability, as changes in precipitation rate and ground permeability will change the amount of rainfall that is absorbed into the groundwater vs. the amount that runs off into the Estuary.

The sources of PAHs in runoff are not known, but could include indirect atmospheric deposition (dry and wet deposition of PAHs to land surfaces which is then collected in the runoff), erosion of PAH-contaminated soils, and runoff of spilled oil or gas.

F. Oil spills

Estimation of the amount of PAHs entering the Harbor due to oil spills is extremely difficult. The authors of the Industrial Ecology report for PAHs constructed loads of PAHs to the Harbor from oil spills based on information from the Coast Guard's National Response Center (<http://www.nrc.uscg.mil/download.html>). This information is provided in the report "Pollution Prevention and Management Strategies for Polycyclic Aromatic Hydrocarbons in the New York/New Jersey Harbor" in section 3.4. and Appendix A tables. The estimated maximum inputs are reproduced in summary Table 5. Oil spills were not found to be a significant source of PAHs to the Harbor.

G. Tidal exchange

To evaluate the effect of tidal exchange on the PAH budget in the NY/NJ Harbor, the estimates of tidal exchange of Rosenthal and Perron-Cashman (8) were used for the flows into and out of Raritan Bay and the NY/NJ Bight. They report the flow of water from the Estuary to the Bight to be $1,971 \text{ m}^3/\text{s}$, and the flow of ocean water into the Estuary to be $726 \text{ m}^3/\text{s}$. For flows in the East River, the measurements of Caplow were used (21), which indicate that the flow from the Long Island Sound to the Harbor is about $630 \text{ m}^3 \text{ s}^{-1}$, and the flow from the Harbor to the Sound is about $430 \text{ m}^3 \text{ s}^{-1}$. Even though the net flow of water is from the Sound to the Harbor at a rate of about $200 \text{ m}^3 \text{ s}^{-1}$, the higher concentrations of contaminants in the Harbor results in net transport of most contaminants from the Harbor to the Sound. PAH concentrations from Simon Litten (NYSDEC) measured in Raritan Bay, New York Bight, Long Island Sound, and Hudson River below the Harlem River were used to calculate the tidal exchange terms. The uncertainty in the tidal exchange loss was estimated by propagating the variance in the concentration measurements.

H. Dredging

Dredging is a loss process because the dredged material is usually removed from the Harbor. Dredging to maintain the shipping channels of the NY/NJ Harbor is conducted by the US Army Corps of Engineers in conjunction with the Port Authority of New York and New Jersey. The estimates of the volume of sediments dredged each year are taken from Farley et al. (3), who estimate that 656,000 metric tons of dry sediment are removed from the NY/NJ Harbor annually. The source of this material by sub-basin in the Estuary is shown in Table 3 (3). In order to estimate the amount of PAHs removed due to this dredging, a PAH concentration in the surface

sediment was assigned to each portion of the Estuary, based on the REMAP data of Adams et al. (10, 11). Data from 1998 were used for all compounds except dibenz[a,h]anthracene, which was not measured in the 1998 data set. Dibenz[a,h]anthracene concentrations were taken from the 1993-1994 REMAP data set. Also, the 1998 data set did not include measurements in Long Island Sound, so this data was taken from the 1993-1994 data set. The 90% confidence limits on these PAH concentrations were used to generate the high and low estimates of the PAHs removed from each sub-basin.

Table 3. Solids removed from the Estuary by dredging by sub-basin.

Sub-basin	Sediment removed
	% of total Ref (3)
Battery to Newburgh Bridge	20%
Newark Bay	20%
Lower Harbor	23%
Upper Harbor	21%
W. Long Island Sound	13%
Other	3%
Total	656,000 Metric tons (dry)

I. Volatilization

Estimation of the volatilization flux of PAHs for any aquatic ecosystem is fraught with a great deal of uncertainty. The approach used here is to take the dissolved concentration of PAHs (C_{diss}) times the mass transfer coefficient (K_{OL}) (Table 2) times the surface area of the system (A):

$$\text{Volatilization Loss} = C_{diss} \cdot K_{OL} \cdot A \cdot 365 \text{ days}$$

Of the parameters in the above equation, only A is reasonably certain. C_{diss} and K_{OL} all change with both time and space in the Estuary. In addition, the procedure for estimating K_{OL} is complex (see refs (22, 23) for details) and the resulting values are thought to be associated with an uncertainty ranging from 40% to 200% (22, 24). In this report, a yearly average K_{OL} value (Table 2) was calculated for each PAH based on an average temperature of 15°C and a yearly average wind speed (about 5 m/s). The greatest error in the estimation of K_{OL} occurs at low wind speeds, where the different models for estimation the mass transfer coefficient across the stagnant water boundary layer diverge significantly. At the yearly average wind speeds used here (~5 m/s), the uncertainty in K_{OL} is thought to be less than 200%. Herein the uncertainty in K_{OL} will be assumed to be 40%, in accord with the recommendations of other researchers (22, 24). A conservative estimate of the uncertainty in the flux was obtained by propagating this error with the error in C_{diss} , which was assumed to equal the standard error of the mean C_{diss} concentration in each sub-basin. This uncertainty was used to generate the high and low estimates of volatilization for all PAHs investigated here.

As described in the section on atmospheric deposition, the volatilization fluxes of naphthalene and acenaphthene will be offset to some degree by the gas absorption of these compounds from the atmosphere. Air-water exchange could potentially be at equilibrium, with the flux in from the atmosphere being perfectly balanced by the volatilization out from the Estuary, but this does not represent a limiting case of maximum atmospheric deposition, because the input via atmospheric deposition could actually exceed the loss due to volatilization.

J. Aerobic degradation in sediments

Microbial degradation of PAHs under aerobic and anaerobic (including sulfate reducing and denitrifying conditions) has been demonstrated in laboratory cultures (see (25) for a summary). Anaerobic degradation of PAHs in sediments is generally much slower than aerobic degradation (25), and for this report, will be assumed to be negligible. Measuring such degradation in the field is difficult, especially in the Harbor, where constant inputs of PAHs support the sediment concentrations at relatively constant levels. Biodegradation of any contaminant is always a function of the contaminants inherent biodegradation potential and its bioavailability. Unfortunately, there are several data gaps that make modeling of PAH degradation difficult. For example, environmental fate databases such as Syracuse Research Corporation's CHEMFATE database (<http://www.syrres.com/esc/chemfate.htm>) and the extensive compilation of Mackay (4) do not include parameters for degradation in sediments of PAHs other than naphthalene. Rate constants for PAH degradation in sediments are lacking, as are measurements of PAH bioavailability in Harbor sediments.

Wammer and Peters (26) suggest that the inherent aerobic biodegradation potential of a range of two- to four-ring PAHs is relatively constant, varying over only an order of magnitude, whereas degradation rates measured in the field can vary over many orders of magnitude, suggesting that bioavailability is controlling the fate of these compounds in sediments. Partitioning of PAHs into different organic carbon fraction in sediment, and particularly the role of black carbon in sequestering PAHs, is an area of active research. Several recent studies (27-30) have indicated that unburned coal and black carbon dominate the phase partitioning/distribution of PAHs in sediments, such that these carbon fractions should control the rates of desorption and bioavailability of sediment-bound PAHs. The association of PAHs with black carbon can also be related to whether their primary sources are pyrogenic or petrogenic. Pyrogenic PAHs (those derived from combustion) are more likely to be associated with black carbon and have been shown to be protected from degradation reactions (31, 32).

Tabak et al. (25, 33) investigated PAH degradation in sediments from the East River and concluded that hydrogen sulfide in the sediment consumes most of the available oxygen, but once that demand is met, aerobic degradation of PAHs does occur. Over a 24-week incubation, a maximum disappearance of ~80% of some low MW PAHs (acenaphthene) was observed (25), although other heavier PAHs (benzo[g,h,i]perylene, indeno[1,2,3-cd]pyrene, dibenz[a,h]anthracene) were not degraded over this time frame. This corresponds to pseudo first-order rate constants (k_{deg}) of 0 – 3.5 y^{-1} . Their results for naphthalene indicate relatively little degradation (10% in 24 weeks), whereas the CHEMFATE database lists several references in which significant degradation of naphthalene was observed, especially in contaminated sediments. In uncontaminated sediments, Saylor and Sherrill (34) observed a first-order degradation rate constant of 3.2 y^{-1} .

Farley et al. (3), in their model of PAH fate in the NY/NJ Harbor, assumed degradation was negligible. This model was primarily constructed to investigate the fate of PCBs, and a general lack of data on PAH concentrations in the various input streams severely limited the predictive value of the model. These researchers noted, however, that model results were generally in good agreement with R-EMAP sediment data. This may suggest that degradation of PAHs in the Harbor is indeed negligible. In contrast, Greenfield and Davis (35) used pseudo-first order degradation rate constants derived from an extensive literature review (Table 4) in their fate model for PAHs in San Francisco Bay. These researchers found that use of these rate constants causes the model to predict that degradation is the most important loss process for PAHs in San Francisco Bay. They also note, however, that estimates of degradation are highly uncertain.

Table 4. Pseudo first-order rate constants from Greenfield and Davis (35) and estimated degradation of PAHs in Harbor sediments.

	Greenfield and Davis 2005	
	Rate constant	Degradation
	k (y⁻¹)	kg y⁻¹
Naphthalene	11	7273
Acenaphthene	3.7*	1613
Fluorene	3.7*	2643
Phenanthrene	3.7	9283
Fluoranthene	0.73	2198
Pyrene	0.73*	2270
Benz[a]anthracene	0.73	1440
Chrysene	0.73*	1611
Benzo[a]pyrene	0.11*	135
Perylene	0.11*	148
Benzo[b+k]fluoranthene	0.11	347
Benzo[g,h,i]perylene	0.11	134
Indeno[1,2,3-cd]pyrene	0.11*	129
Dibenz[a,h]anthracene	0.11	35

*Assumed based on structure.

The rate constants of Greenfield and Davis (35) were used to estimate degradation of PAHs in the Harbor. For the PAHs not included in the Greenfield and Davis model, the rate constant of the PAH most similar in MW was used. These rate constants (k_{deg}) are multiplied by the sediment PAH concentrations (C_{sed}) (10) and the mass of sediment to yield a degradation loss in kg/y. The mass of sediment is determined from the sediment volume and density (ρ_{sed}). The volume was determined by multiplying the surface area of each sub-basin (Table 1) by the depth over which aerobic degradation could conceivably occur. We take this depth to be 10 cm. Thus:

$$\text{Degradation Loss} = C_{sed} \cdot k_{deg} \cdot A \cdot 10 \text{ cm} \cdot \rho_{sed}$$

These estimates of the degradation of PAHs in the sediment of the Harbor are listed in Table 6.

K. Storage in Sediments

In order to estimate storage of PAHs in the sediments deposited to the estuary, it is necessary to estimate both a sediment PAH concentration and a sedimentation rate. Woodruff et al. (36) estimate that an annual sedimentation rate of 2-3 mm/y over the entire estuary is required in order to keep a constant river depth with respect to current sea-level rise. Assuming the same sediment surface area as for the water (i.e., 811 km²)(Table 1) and a solids concentration of 50 g/L, 2-3 mm/y equals $0.8-1.2 \times 10^9$ kg/y. The median sedimentation estimate is therefore taken to be 1×10^9 kg/y, and the uncertainty in the sedimentation rate is assumed to be 20%.

Assuming that sedimentation is uniform over the entire surface of the Estuary, the amount of PAHs stored in the various sub-basins may be estimated by applying the appropriate sediment PAH concentration from the 1998 REMAP data set (11) (Table 6). Data for dibenz[a,h]anthracene were not available for the 1998 REMAP study, so the 1993-1994 sediment concentrations were used instead (10). The uncertainty in the storage estimate is propagated from the uncertainties in the sediment PAH concentrations and the sedimentation rate. Much of the PAHs stored in the sediments remain available for resuspension and transport out of the estuary. A portion of the deposited sediments will eventually become permanently buried in the deep sediments.

V. PAH ANNUAL BUDGET

The loadings and losses estimated above can be assigned into one of three groups based on the level of uncertainty. Processes with low uncertainty are those for which a substantial amount of concentration data are available (usually from the CARP program) and for which the flows are well known. These include loads from tributaries, wastewater treatment effluents, and CSOs. Processes with medium uncertainty are those for which concentration data are available, but mass or water flows are not as well characterized. These include loadings from atmospheric deposition and runoff and losses due to tidal exchange, dredging, and volatilization. Processes with high uncertainty are those for which relatively little concentration data is available (oil spill loads) or for which processes are not well understood (biodegradation). The CARP program, despite the data limitations of the PAH measurements, has vastly expanded the amount of data available on PAH concentrations within the Harbor and reduced the uncertainty associated with most of the loadings and losses. The processes associated with the greatest uncertainty, therefore, are those for which CARP data is not helpful. These are the PAH inputs due to oil spills and the biodegradation losses. These two terms are so uncertain that they throw the entire mass balance into question for many of the low MW PAHs. For the high MW PAHs, these two terms are relatively unimportant, such that the mass balance is more meaningful. Tables 5 and 6 present the annual budget for PAHs in the NY/NJ Harbor. Storage in the sediments is included in Table 6, but it must be remembered that this is not a loss process, because it does not represent a removal of PAHs from the system, but rather an accumulation of PAHs within the estuary. Table 7 attempts to examine the big picture of PAH cycling in the Harbor by summing the inputs and outputs (except biodegradation) from Tables 5 and 6 and comparing them with the losses due to aerobic degradation. This table suggests that if degradation is neglected, the mass balance

is closed for 12 of the 14 PAHs studied. For PAHs with MW < 250 g/mol, aerobic degradation could be significant. For higher MW PAHs (benzo[a]pyrene and above, excluding perylene), the mass balance is closed regardless of whether biodegradation is included.

To check the validity of the mass balance loadings, the median loading estimate was divided by the total mass of sediment entering the Harbor each year (Table 6). Since the sedimentation in the Harbor is estimated to be 1×10^9 kg/y, the PAH load in kg/y is, by coincidence, equal to the sediment PAH concentration in ppb. This value represents the PAH concentration that would be expected in the sediments of the Harbor in the absence of degradation. These predicted sediment concentrations are at the high end of the range of concentrations measured in the various regions of the Harbor (10), and are similar to the sediment concentrations in the Upper Harbor, for all compounds except naphthalene. This analysis, as well as the loading instead of loss of naphthalene from tidal exchange with the East River, suggest that the mass balance for naphthalene may be seriously in error. This is perhaps not surprising since naphthalene is one of the PAHs thought to be most prone to blank contamination in the CARP samples. For the other PAHs, this analysis suggests that our loading estimates are reasonably accurate.

A closed mass balance suggests a system at steady state, one in which inputs equal outputs and there is no long-term change in PAH concentrations in the waters of the Estuary. A mass balance that is not closed suggests one of two things: (1) sources or sinks (or both) are inaccurate or (2) the system is not at steady state. Do we have any reason to believe that the Estuary is at steady state with respect to PAH contamination? Yan (37) measured Σ PAH (Σ PAH = the 16 EPA listed PAHs) in sediment cores from several locations in the Harbor and concluded that Σ PAH levels dropped substantially from the 1950's to the 1970's in all areas of the Harbor. However, the trends from 1970 to 1990 (when the cores were collected) were not as clear. Some cores (Passiac River) showed an increase in Σ PAH concentrations, while others (Raritan Bay) showed a decrease. A comparison of the 1993-1994 and 1998 REMAP data sets (10, 11) shows that in Raritan Bay, for the 16 PAHs for which enough data was available to determine the trends, 9 showed a decrease from 1993-1994 to 1998, while 7 increased in concentration. The trend for the sum of all 16 PAHs was a decline of 13%, which is probably not significant given the uncertainties involved. Thus it is likely that PAHs in the Harbor are near steady state and the mass balances should be closed.

Keeping in mind the many limitations of the data, it is possible to draw some conclusions from these mass balances. The losses and loadings are very different for the high molecular weight (MW) PAHs (MW > 202) than for the low MW PAHs (MW \leq 202).

High MW PAHS

Perhaps the most important conclusion of this report is that for the high MW PAHs, inputs to the system are dominated by stormwater runoff, which contributes on average ~50% of the total load to the Estuary. Additional stormwater sampling to confirm the importance of the stormwater load is warranted. It implies, however, that controlling PAH levels in the Estuary will require the implementation of strict stormwater management plans. The relative loadings of the high MW PAHs are remarkably constant, with average (\pm standard deviation) percentage loadings of: 51 \pm 4% from stormwater, 21 \pm 2% from the NJ tributaries, 11 \pm 6% from the Hudson River, 9 \pm 1% from CSOs, 4 \pm 1% from atmospheric deposition, and 4 \pm 2% from wastewater.

The losses of high MW PAHs from the Estuary are driven by their association with sediments. Typically a majority of all losses are due to dredging, and a significant portion of the

mass that enters the Harbor remains stored in the sediments. The losses of high MW PAHs are again remarkably similar: $55\pm 8\%$ are lost to dredging, $22\pm 8\%$ are flushed out to the Bight, $15\pm 5\%$ are flushed out to the Long Island Sound via the East River, and $8\pm 5\%$ volatilize (uncertainties represent one standard deviation).

Low MW PAHs

Loads of fluorene and phenanthrene are dominated by atmospheric deposition, comprising about 45% of the total load. It is unclear whether these two PAHs are representative of the lower MW PAHs in general. If they are, it suggests that the atmosphere could be a major source of naphthalene and acenaphthene as well. Relatively few measurements exist of acenaphthene in ambient air. One study observed less than $0.01 \mu\text{g}/\text{m}^3$ acenaphthene in outdoor samples from Taiwan (38). This level would result in an atmospheric deposition load of less than 225 kg/y, which could make atmospheric deposition the largest source of acenaphthene. A recent review of airborne naphthalene concentrations (1) suggests that urban concentrations of naphthalene could be on the order of $1 \mu\text{g m}^{-3}$. This level would result in atmospheric deposition (mostly via gaseous absorption) $\sim 300 \text{ kg/y}$, a level which is smaller than many other loadings, but not insignificant, especially in light of the high degree of uncertainty associated with the naphthalene mass balance in general. Controls on the atmospheric emissions of low MW PAHs such as fluorene and phenanthrene will be necessary to achieve significant reductions in their ambient water concentrations.

The losses of low MW PAHs are dominated by volatilization. For naphthalene and fluorene, volatilization is calculated to represent $>90\%$ of the total losses. Sedimentation and dredging are also important for phenanthrene and acenaphthene. It is possible that aerobic degradation is a significant loss process for some of the low MW PAHs.

Conclusions

This report has identified several data gaps that should be addressed in order to enable a better understanding of PAH cycling in the Harbor. The two processes associated with the highest degree of uncertainty in this mass balance are biodegradation losses and oil spill loads. Additional research on the rates of biodegradation of PAHs in the Harbor should be conducted. This mass balance suggests that biodegradation may not be as important in the NY/NJ Harbor as Greenfield et al. (35) assumed it was in San Francisco Bay. This could be due to differences in the two ecosystems or it could suggest that the rate constants for aerobic biodegradation of PAHs that Greenfield et al. (35) derived from literature sources (which are mostly the results of laboratory, not field, studies) are not applicable to real-world conditions in estuarine systems. Oil spill loads are also highly uncertain, but they appear to constitute a relatively small and localized input of PAHs to the Harbor.

Although atmospheric deposition is relatively well characterized in the Harbor region, the lack of data on atmospheric concentrations of low MW PAHs such as naphthalene and acenaphthene is problematic. Since this analysis suggests that atmospheric deposition is an important source of low MW PAHs to the system, atmospheric measurements of these low MW species should be performed. In addition to naphthalene and acenaphthene, alkylated low MW PAHs should also be measured.

Despite the data gaps, one important conclusion of this investigation is that, with the exception of naphthalene, the CARP PAH data appears to provide a reasonable picture of the cycling of PAHs in the Harbor is therefore perhaps more reliable than initially feared. One

important measure of the validity of the mass balance loadings (and therefore of the CARP PAH data) is the good match between estimated loads and sediment concentrations (Table 8). This good match between the CARP PAH data, which may be subject to severe blank contamination, and the sediment data, which is not, provides good evidence that the CARP PAH data are reasonably reliable.

The portions of this mass balance that are associated with medium or low uncertainty have revealed some important points concerning the cycling of PAHs in this system:

- Stormwater is an important source for all PAHs investigated, and is the dominant source of high MW PAHs ($MW \geq 202$ g/mol). Thus stormwater management plans will be required to manage PAH contamination in the Harbor.
- Atmospheric deposition is the dominant source of some low MW PAHs in the Harbor.
- Biodegradation is probably unimportant for high MW PAHs ($MW > 250$ g/mol) in the Harbor. Further investigation is required to determine whether biodegradation is an important loss process for lower MW PAHs.

Table 5. Loadings of PAHs to the NY/NJ Harbor in kg/y.

	Rivers				Atmospheric Deposition		Wastewater		CSOs		Runoff		Oil Spills
	Hudson		NJ Tribs		low	high	low	high	low	high	low	high	Max
	low	high	low	high									
Naphthalene	744	772	79	236	?	?	300	1752	0	874	0	917	3021
Acenaphthene	32	37	6.0	18	?	?	58	119	1.9	17	21	234	0.00036
Fluorene	22	63	4.0	12	177	483	102	195	14	44	57	213	2674
Phenanthrene	124	131	96	288	541	1531	148	281	60	204	213	909	398
Fluoranthene	113	196	183	548	132	427	70	114	35	353	334	1684	1729
Pyrene	94	297	147	441	75	284	145	216	34	288	355	1336	34
Benzo[a]anthracene	56	98	59	176	5.8	40	28	44	5.6	110	85	568	21
Chrysene	105	131	121	362	16	75	46	70	21	211	206	1059	47
Benzo[a]pyrene	77	80	90	270	7.2	32	17	32	9.3	148	114	782	11
Perylene	33	103	28	84	2.0	10	5.2	10	3.7	37	21	220	5.1
Benzo[b+k]fluoranthene	141	179	210	630	27	105	43	77	32	320	283	1606	0
Benzo[ghi]perylene	58	87	92	275	13	62	18	32	13	133	171	710	0.00042
Indeno[1,2,3-cd]pyrene	48	78	87	261	19	83	16	27	11	120	99	639	0.45
Dibenz[a,h]anthracene	3.8	13	13	38	2.1	8.8	7.9	15	1.9	28	25	146	0

Table 6. Losses of PAHs from the NY/NJ Harbor in kg/y.

	Tidal Exchange				Dredging		Volatilization		Storage in Sediments		Aerobic Degradation
	Raritan Bay		East River		low	high	low	high	low	high	Max
	low	high	low	high							
Naphthalene	118	156	-291	-162	44	103	2061	6433	21	143	7273
Acenaphthene	11	13	36	41	20	67	63	146	6	68	1613
Fluorene	26	31	17	23	15	64	1242	3192	4.6	72	2643
Phenanthrene	188	204	44	75	166	402	112	666	81	535	9283
Fluoranthene	385	411	67	120	251	867	82	493	107	1100	2198
Pyrene	214	237	98	150	294	1046	114	406	123	1372	2270
Benz[a]anthracene	86	90	92	121	145	682	46	120	55	817	1440
Chrysene	145	233	82	120	175	691	16	89	66	877	1611
Benzo[a]pyrene	137	145	102	137	208	821	6.9	18	79	1065	135
Perylene	87	90	103	156	118	380	21	56	48	493	148
Benzo[b+k]fluoranthene	204	208	111	183	326	1140	23	61	100	1487	347
Benzo[ghi]perylene	105	112	12	43	72	247	12	33	35	317	134
Indeno[1,2,3-cd]pyrene	120	128	39	74	41	247	9.6	25.1	11	277	129
Dibenz[a,h]anthracene	24	27	12	20	41	102	12	36	40	121	35

Table 7. Sum of inputs and losses of PAHs from the NY/NJ Harbor in kg/y. Losses do not included aerobic degradation, which is listed separately. The mass balance is closed for most PAHs when degradation is excluded.

	inputs		outputs		balanced?	aerobic degradation
	lo	hi	lo	hi		
Naphthalene	1156	3131	2014	6610	Yes	7273
Acenaphthene	120	365	166	304	Yes	1613
Fluorene	377	918	1338	3348	No	2643
Phenanthrene	1194	3223	818	1655	Yes	9283
Fluoranthene	872	3282	1389	2495	Yes	2198
Pyrene	851	2792	1468	2586	Yes	2270
Benz[a]anthracene	243	1023	805	1449	Yes	1440
Chrysene	516	1885	889	1605	Yes	1611
Benzo[a]pyrene	315	1329	1025	1693	Yes	135
Perylene	94	460	599	952	No	148
Benzo[b+k]fluoranthene	737	2884	1456	2385	Yes	347
Benzo[ghi]perylene	365	1285	377	611	Yes	134
Indeno[1,2,3-cd]pyrene	281	1197	353	618	Yes	129
Dibenz[a,h]anthracene	54	242	169	264	Yes	35

Table 8. Comparison of mass balance median estimates (kg/y = ppb) to sediment concentrations (ppb) (10, 11).

	Median Input Estimate	Battery to Newburgh Bridge ("Harbor")	Jamaica Bay	Newark Bay	Lower Harbor	Upper Harbor
Naphthalene	2143	82	32	140	37	224
Acenaphthene	242	37	4	67	2	148
Fluorene	647	38	3	79	7	138
Phenanthrene	2209	308	129	677	118	852
Fluoranthene	2077	603	274	1341	202	1748
Pyrene	1822	747	289	1284	207	2431
Benz[a]anthracene	633	435	134	755	107	1476
Chrysene	1200	471	174	807	121	1567
Benzo[a]pyrene	822	571	124	1023	160	1889
Perylene	277	270	117	550	89	806
Benzo[b+k]fluoranthene	1810	176	79	299	67	515
Benzo[ghi]perylene	825	793	432	1664	255	2329
Indeno[1,2,3-cd]pyrene	739	144	33	249	33	500
Dibenz[a,h]anthracene*	148	79	17	146	27	248

* 1993-1994 data. All other PAHs are 1998 REMAP data.

References

- (1) Preuss, R.; Angerer, J.; Drexler, H. Naphthalene - an environmental and occupational toxicant. *International Archives of Occupational and Environmental Health* **2003**, *76*, 556-576.
- (2) Agency for Toxic Substances and Disease Registry (ATSDR). "Toxicological Profile for Polycyclic Aromatic Hydrocarbons (PAHs).," Public Health Service, U.S. Department of Health and Human Services, 1995.
- (3) Farley, K. J.; Thomann, R. V.; Cooney, T. F. I.; Damiani, D. R.; Wands, J. R. "An Integrated Model of Organic Chemical Fate and Bioaccumulation in the Hudson River Estuary," The Hudson River Foundation, 1999. March 1999.
- (4) Mackay, B.; Shiu, W.-Y.; Ma, K.-C. *Physical-Chemical Properties and Environmental Fate Handbook*; Chapman & Hall: 1999.
- (5) Yang, M.; Sañudo-Wilhelmy, S. A. Cadmium and manganese distributions in the Hudson River estuary: interannual and seasonal variability. *Earth and Planetary Science Letter* **1998**, *160*, 403-418.
- (6) Klinkhammer, G. P.; Bender, M. L. Trace metal distributions in the Hudson River estuary. *Estuarine, Coastal and Shelf Science* **1981**, *12*, 629-643.
- (7) Fitzgerald, W. F.; O'Connor, J. S. "Mercury Cycling in the Hudson/Raritan River Basin," New York Academy of Sciences, 2001.

- (8) Rosenthal, Y.; Perron-Cashman, S. "Cadmium Cycling in the Hudson/Raritan River Basin," New York Academy of Sciences, 2002.
- (9) Totten, L. A. Present-Day Sources and Sinks for Polychlorinated Biphenyls (PCBs) in the Lower Hudson River Estuary. In *Pollution Prevention And Management Strategies For Polychlorinated Biphenyls In The New York/New Jersey Harbor*; Panero, M., et al., Eds.; New York Academy of Sciences: New York, 2005, 18.
- (10) Adams, D. A.; O'Connor, J. S.; Weisberg, S. B. "Sediment Quality of the NY/NJ Harbor System," US EPA, Final Report. 902-R-98-001. 1998.
- (11) Adams, D.; Benyi, S. "SEDIMENT QUALITY OF THE NY/NJ HARBOR SYSTEM: A 5-Year Revisit: 1993/4 - 1998," US EPA, Final Report. EPA/902-R-03-002. 2003.
- (12) Gigliotti, C. L.; Dachs, J.; Nelson, E. D.; Brunciak, P. A.; Eisenreich, S. J. Polycyclic Aromatic Hydrocarbons in the New Jersey Coastal Atmosphere. *Environ. Sci. Technol.* **2000**, *34*, 3547-3554.
- (13) Eisenreich, S. J.; Reinfelder, J.; Totten, L. A. "The New Jersey Atmospheric Deposition Network (NJADN)," New Jersey Department of Environmental Protection, Final Report. 2004.
- (14) Venkatesan, M. L. Occurrence and possible sources of perylene in marine sediments-a review. *Marine Chemistry* **1988**, *25*, 1-27.
- (15) Yan, S. Air-water exchange controls phytoplankton concentrations of polychlorinated biphenyls in the Hudson River Estuary. Master's Thesis, Rutgers University, 2003.
- (16) Durell, G. S.; Lizotte, R. D. PCB levels at 26 New York City and New Jersey WPCPs that discharge to the New York/New Jersey Harbor Estuary. *Environ. Sci. Technol.* **1998**, *32*, 1022-1031.
- (17) Hydroqual "Assessment of Pollutant Loadings to the New York-New Jersey Harbor.," USEPA Marine and Wetlands Protection Branch Region 2., Job Number WOCL0302. 1991.
- (18) TAMS Consultants, T. C. G., Inc., and the Gradient Corporation "Phase 2 Report - Further Site Characterization And Analysis Volume 2C - Data Evaluation And Interpretation Report Hudson River PCBs Reassessment RI/FS," USEPA and US Army Corps of Engineers, **1997**. February 13, 1997.
- (19) Irwin, R. J.; VanMouwerik, M.; Stevens, L.; Seese, M. D.; Basham, W. *National Park Service Environmental Contaminants Encyclopedia*; National Park Service, Water Resources Division.: Fort Collins, Colorado, 1998.
- (20) Potter, T. L.; Simmons, K. E. "Total Petroleum Hydrocarbon Criteria Working Group Series," Association for Environmental Health and Sciences, 1998.
- (21) Caplow, T. New Insights On The Transport Of Solutes In A Large Estuary Revealed With SF6 Tracer. PhD Thesis, Columbia University, 2004.
- (22) Bamford, H. A.; Ko, F. C.; Baker, J. E. Seasonal and annual air-water exchange of polychlorinated biphenyls across Baltimore Harbor and the northern Chesapeake Bay. *Environ. Sci. Technol.* **2002**, *36*, 4245-4252.
- (23) Totten, L. A.; Brunciak, P. A.; Gigliotti, C. L.; Dachs, J.; IV, G. T. R.; Nelson, E. D.; Eisenreich, S. J. Dynamic Air-Water Exchange of Polychlorinated Biphenyls in the NY-NJ Harbor Estuary. *Environ. Sci. Technol.* **2001**, *35*, 3834-3840.
- (24) Nelson, E. D.; McConnell, L. L.; Baker, J. E. Diffusive Exchange of Gaseous Polycyclic Aromatic Hydrocarbons and Polychlorinated Biphenyls Across the Air-Water Interface of the Chesapeake Bay. *Environ. Sci. Technol.* **1998**, *32*, 912-919.
- (25) Lei, L.; Khodadoust, A. P.; Suidana, M. T.; Tabak, H. H. Biodegradation of sediment-bound PAHs in field contaminated sediment. *Water Research* **2005**, *39*, 349-361.

- (26) Wammer, K. H.; Peters, C. A. Polycyclic Aromatic Hydrocarbon Biodegradation Rates: Structure-Based Study. *Environ. Sci. Technol.* **2005**, *39*, 2571-2578.
- (27) Accardi-Dey, A.; Gschwend, P. M. Assessing the Combined Roles of Natural Organic Matter and Black Carbon as Sorbents in Sediments. *Environ. Sci. Technol.* **2002**, *36*, 21-29.
- (28) Xiao, B.; Yu, Z.; Huang, W.; Song, J.; Peng, P. Black Carbon and Kerogen in Soils and Sediments. 2. Their Roles in Equilibrium Sorption of Less-Polar Organic Pollutants. *Environ. Sci. Technol.* **2004**, *38*, 5842-5852.
- (29) Cornelissen, G.; Gustafsson, O. Sorption of Phenanthrene to Environmental Black Carbon in Sediment with and without Organic Matter and Native Sorbates. *Environ. Sci. Technol.* **2004**, *38*, 148-155.
- (30) Talley, J. W.; Ghosh, U.; Tucker, S. G.; Furey, J. S.; Luthy, R. G. Particle-Scale Understanding of the Bioavailability of PAHs in Sediment. *Environ. Sci. Technol.* **2002**, *36*, 477-483.
- (31) Simo, R.; Grimalt, J. O.; Albiages, J. Loss of Un-Burned Fuel Hydrocarbons from Combustion Aerosols During Atmospheric Transport. *Environ. Sci. Technol.* **1997**, *31*, 2697-2700.
- (32) Farrington, J. W.; Goldberg, E. D.; Risebrouhg, R. W.; Martin, J. H.; Bowen, V. T. U.S. "Mussel Watch" 1976-1978: An overview of trace-metal, DDE, PCB, hydrocarbon, and artificial radionuclide data. *Environ. Sci. Technol.* **1983**, *17*, 490-496.
- (33) Tabak, H. H.; Lazorchak, J. M.; Lei, L.; Khodadoust, A. P.; Antia, J. E.; Bagchi, R.; Suidan, M. T. Studies On Bioremediation Of Polycyclic Aromatic Hydrocarbon Contaminated Sediments: Bioavailability, Biodegradability, And Toxicity Issues. *Environ. Toxicol. and Chem.* **2003**, *22*, 473-482.
- (34) Saylor, G. S.; Sherrill, T. W. "Bacterial Degradation Of Coal Conversion By-Products (Polycyclic Aromatic Hydrocarbons) In Aquatic Environments," Tennessee Univ. Water Resources Research Center, Report No. 39535. (NTIS PB 83-187161). 1981.
- (35) Greenfield, B.; Davis, J. A. A PAH fate model for San Francisco Bay. *Chemosphere* **2005**, *60*, 515-530.
- (36) Woodruff, J. D.; Geyer, R. W.; Sommerfield, C. K.; Driscoll, N. W. Seasonal variation of sediment deposition in the Hudson River estuary. *Marine Geology* **2001**, *179*, 105-119.
- (37) Yan, B. PAH Sources and Depositional History in Sediments from the Lower Hudson River Basin. PhD Thesis, Rensselaer Polytechnic Institute, 2004.
- (38) Lin, T.-C.; Chang, F.-H.; Hsieh, J.-H.; Chao, H.-R.; Chao, M.-R. Characteristics of polycyclic aromatic hydrocarbons and total suspended particulate in indoor and outdoor atmosphere of a Taiwanese temple. *J. Haz. Mat.* **2002**, *A95*, 1-12.