Bull. Environ. Contam. Toxicol. (1993) 51:865–872

Bulletin of Environmental Contamination and Toxicology

Distribution of Polycyclic Aromatic Hydrocarbons (PAHs) in Three Northern New Jersey Waterways

S. L. Huntley,[1] N. L. Bonnevie,[1] R. J. Wenning,[1] and H. Bedbury[2]

[1]ChemRisk, A Division of McLaren/Hart, 1685 Congress St.,
Portland, Maine 04102, USA and [2]Maxus Energy Corporation, 717 North
Harwood Street, Dallas, Texas 75201, USA

The accumulation of polycyclic aromatic hydrocarbons (PAHs) in the sediments of harbors and rivers located in industrialized and heavily populated areas has been well established (NOAA 1988). As a result of their hydrophobicity and strong affinity for particulates, PAHs may accumulate in sediments and bioaccumulate in fish and shellfish at levels several orders of magnitude greater than found in source effluents (Herbes and Schwall 1987). Consequently, the vertical and spatial distribution of these persistent chemicals in bottom sediments provides useful information for evaluating the toxic potency of PAHs to aquatic life and for identifying historical and current sources of pollution. The presence of numerous industrial and municipal sources such as former creosote wood preserving facilities, petroleum and chemical storage and refinery facilities, paint and chemical manufacturers, combined sewer and stormwater outfalls, and municipal sewerage treatment facilities along shores of Newark Bay and its major tributaries suggests the potential for widespread PAH contamination (NOAA 1982).

In this study, the concentrations of PAHs and total extractable petroleum hydrocarbons (TEPH) were determined in sediment cores collected from the Arthur Kill, Hackensack River, and Passaic River. Temporal distributions were examined in each core based on the activities of radionuclides ^{210}Pb and ^{137}Cs. From this information, it is possible to identify current and historical sources of contamination and identify sediments in each waterway that may pose a toxic hazard to fish and shellfish.

MATERIALS AND METHODS

Thirty-one 10- to 20-foot sediment cores were collected during November and December of 1991 at locations throughout the Arthur Kill, Hackensack River, and Passaic River (Figure 1). Sampling stations were located outside of shipping channels in stable depositional reaches to minimize the impacts associated with dredging activities and ship traffic in an effort to obtain undisturbed sedimentation profiles. At all stations, except A3, P1, P2, and P3, cores were collected using a Model 1400 Vibracore unit with either a 10 ft or 20 ft stainless steel core barrel with a Lexan liner. At stations A3, P1, P2, and P3, a portable vibracore unit equipped with a 10 ft unlined aluminum core barrel was utilized. Prior to core collection, all field sampling and sample processing equipment, aluminum core barrels, and Lexan liners were rinsed with acetone and hexane (50:50), analyte-free

Send reprint requests to Steve L. Huntley at the above address.

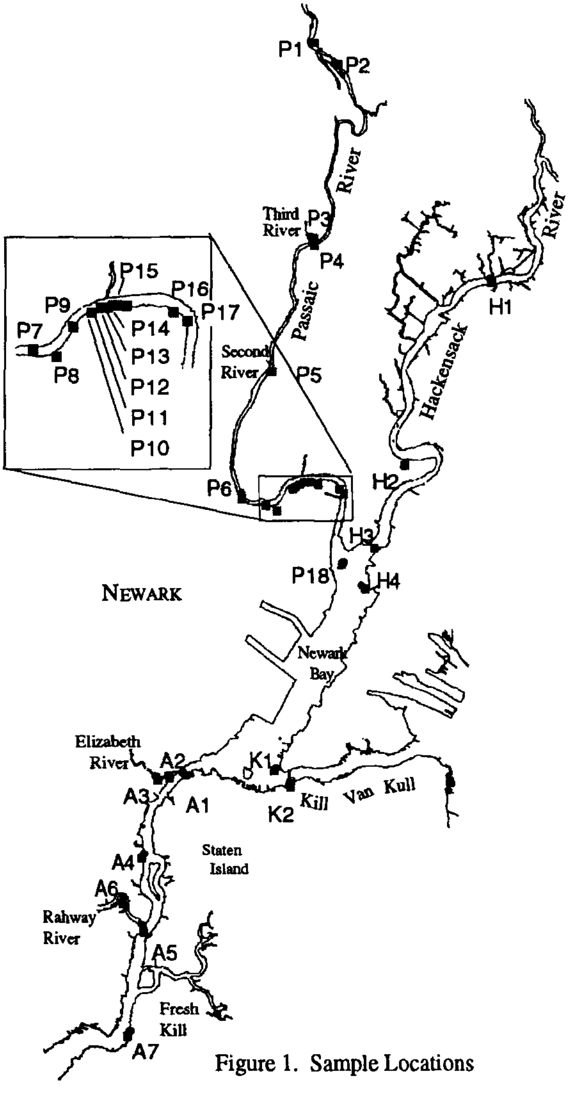

Figure 1. Sample Locations

trichloroethylene, and analyte-free deionized water. Core barrels and liners were sealed with aluminum foil until use in the field. Field and rinsate blanks were utilized to verify the levels, if any, of residual contamination. Sediment samples were collected from the intact Lexan liner at predetermined depths for chemical (2 in. segment) and radionuclide (1 in. segment) analyses. The outermost layer of sediment was discarded to minimize vertical mixing. Samples were transferred to pre-cleaned glass containers, sealed, and maintained at 4°C prior to analysis in accordance with USEPA Contract Laboratory requirements. Sediments were analyzed for base, neutral, and acid extractable (BNA) organic compounds by gas chromatography/mass spectroscopy using USEPA Method 8310. Total extractable petroleum hydrocarbons (TEPH) were determined using a modification of SW-848 USEPA Method 8015. For TEPH analysis, samples were extracted with methylene chloride by sonication and analyzed on a gas chromatograph equipped with a flame ionization detector. Diesel was used as the standard for GC calibration. All chemical analyses were performed by S-Cubed Laboratory (San Diego, CA).

Radiochemistry samples were analyzed for ^{210}Pb and ^{137}Cs activity by Teledyne Isotopes (Westwood, NJ). ^{210}Pb activity was determined by radiochemical separation and assay of the ^{210}Bi daughter product. Samples were leached with 6M hydrochloric acid together with stable lead and bismuth carriers. Sample filtrate was evaporated, oxidized with nitric acid, and dissolved in 1.8M hydrochloric acid. Using an anion exchange column, lead was eluted with 0.05M hydrochloric acid followed by 9M hydrochloric acid and deionized water. Bismuth was then eluted with 2M sulfuric acid. The bismuth was precipitated as the oxychloride and collected on a 1-inch glass fiber filter. Bismuth yield was determined gravimetrically. Beta activity of the bismuth precipitate was measured using a low level, gas-flow proportional counter. ^{137}Cs activity was determined by gamma spectral analysis of the sample using lithium-drifted germanium and high purity germanium detectors. Samples were dried and crushed, and then weighed into standard 150 ml or 300 ml counting containers. The containers were then analyzed for 5 hours or longer on large (>55 cc) germanium detectors connected to a nuclear data acquisition and analysis system. ^{137}Cs activity was measured by integrating its gamma emission at 661.6 KeV.

RESULTS AND DISCUSSION

The concentrations of PAHs and TEPH in sediment cores are summarized in Table 1. The frequency of detection for some PAHs in sediments such as carbazole and acenaphthylene was highly variable because of the relatively high analytical detection limits required for analysis. This was largely attributed to matrix effects associated with significant chemical and organic interferences in these contaminated sediments. For example, the sample quantitation limit for carbazole in one core collected at station P14 on the lower Passaic River ranged from 0.77 to 110 mg/kg (n=7). Pyrene and fluoranthene were the most frequently detected PAHs in Passaic River sediments. These compounds were detected in all upper Passaic River samples (stations P1, P2, and P3; n=9), 89% of middle Passaic River samples (P4, P5, and P6; n=9), and 69% of lower Passaic River samples (stations P7 through P18; n=77). The most frequently detected PAH in the upper Arthur Kill (stations A1 through A5) was pyrene, which was detected in 78% of all samples (n=15); however, pyrene was not detected in sediments from the lower Arthur Kill (station A7; n=3). Pyrene, fluoranthene, chrysene, and benzo(a)pyrene were the most frequently detected PAHs (58%) in Hackensack River sediments (n=15).

Table1. Summary of PAH and TEPH Sediment Concentrations[b]

	Arthur Kill (n=21)			Hackensack River (n=12)			Passaic River (n=95)		
Chemical	Freq.[b] (%)	Range (mg/kg)	Median (mg/kg)	Freq.[b] (%)	Range (mg/kg)	Median (mg/kg)	Freq.[b] (%)	Range (mg/kg)	Median (mg/kg)
Acenaphthene	28.6	0.26 - 34.0	1.95	33.3	0.38 - 3.10	0.56	38.9	0.19 - 1000	1.20
Acenaphthylene	14.3	0.36 - 3.40	0.48	33.3	0.32 - 1.10	0.47	33.7	0.18 - 80.0	0.91
Anthracene	42.9	0.61 - 31.0	1.40	50.0	0.66 - 4.70	1.33	36.7	0.18 - 500	1.30
Benzo(a)anthracene	38.1	0.30 - 12.0	1.60	41.7	1.30 - 5.00	1.70	61.1	0.37 - 320	2.55
Benzo(a)pyrene	57.1	0.31 - 11.0	0.86	58.3	0.50 - 4.70	1.70	62.1	0.22 - 210	2.30
Benzo(b)fluoranthene	76.2	0.29 - 8.70	0.90	33.3	0.69 - 4.80	2.50	65.3	0.24 - 110	2.35
Benzo(ghi)perylene	9.9	0.33 - 2.80	0.62	41.7	0.91 - 2.20	1.40	61.9	0.37 - 46.0	1.60
Benzo(k)fluoranthene	76.2	0.20 - 9.30	1.05	33.3	1.40 - 2.70	2.10	63.5	0.20 - 110	2.05
Carbazole	9.5	0.34 - 2.50	1.42	0.0	N/A	N/A	4.2	0.26 - 0.94	0.40
Chrysene	76.2	0.39 - 14.0	1.35	58.3	0.49 - 6.60	2.20	69.5	0.18 - 340	2.85
Dibenzo(a,h)anthracene	9.5	0.69 - 1.20	0.95	25.0	0.35 - 0.75	0.75	28.4	0.18 - 29.0	0.82
Dibenzofuran	19.0	0.48 - 6.00	0.61	0.0	N/A	N/A	21.9	0.23 - 74.0	2.60
Fluoranthene	76.2	0.59 - 66.0	2.40	58.3	0.67 - 8.30	3.70	72.6	0.18 - 420	4.10
Fluorene	28.6	0.74 - 17.0	1.09	41.7	0.34 - 2.20	0.67	35.8	0.16 - 530	1.04
Indeno(1,2,3-cd)pyrene	61.9	0.30 - 33.0	0.58	41.7	0.82 - 2.30	1.10	60.0	0.29 - 55.0	1.40
2-Methylnaphthalene	5.4	0.46 - 22.0	1.95	25.0	0.28 - 1.60	0.78	17.9	0.20 - 850	1.50
Naphthalene	19.0	0.37 - 54.0	2.05	25.0	0.32 - 3.00	1.00	22.1	0.28 - 1300	2.50
Phenanthrene	52.4	0.36 - 89.0	2.30	50.0	0.72 - 12.0	2.05	67.4	0.28 - 1200	2.40
Pyrene	81.0	0.17 - 27.0	1.80	58.3	0.57 - 8.40	3.20	72.6	0.21 - 650	5.10
TEPH	71.4	50 - 5130	450	50.0	60 - 270	170	58.9	30 - 61380	1140

a. Summary statistics are based on detectable concentrations only.

b. Frequency of detection.

The highest concentrations of PAHs were found in sediments from the upper Arthur Kill and the lower Passaic River (Table 2). Elevated concentrations at stations P10 to P17 on the lower Passaic River, located in an area found to have the highest sedimentation rates south of Dundee Dam (IT 1986), are likely due to the numerous petroleum storage tanks, stormwater and sewer outfalls, and industrial sites located along the river (Brydon 1974). Furthermore, the Roanoke Street and Brown Street sewer outfalls located in this reach are among Newark, New Jersey's most contaminated discharge sewers (PVSC 1970). In sediments collected 18 inches deep at station P14, the concentrations of naphthalene, phenanthrene, and acenaphthene exceeded 1,000 mg/kg, while the maximum concentrations of anthracene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)-fluoranthene, chrysene, fluoranthene, fluorene, 2-methylnaphthalene, and pyrene exceeded 100 mg/kg. The concentrations of PAHs in sediments from the Arthur Kill did not exceed 100 mg/kg, despite the waterway's proximity to the Bayway Refinery complex and the high frequency of petroleum spills recorded for this region (Gunster et al. 1993). In general, fluoranthene, naphthalene, and phenanthrene were detected at the highest concentrations in the Arthur Kill, ranging from 54.0 to 89.0 mg/kg. Of the three waterways investigated, Hackensack River sediments had the lowest PAH concentrations; the maximum concentration was 12.0 mg/kg for phenanthrene.

Table 2. Mean Total PAH and TEPH Sediment Concentrations (mg/kg) by Sampling Station [a]

Sampling Station	A1	A2	A3	A4	A5	A6	A7	H1	H2	H3
Mean Total PAH	139	34.4	1.74	13.3	14.2	6.74	9.39	0.74	46.2	17.1
Mean TEPH	2150	580	70	240	2647	323	1177	60	177	210
Sampling Station	H4	P1	P2	P3	P4	P5	P6	P7	P8	P9
Mean Total PAH	0.0	156	31.7	18.7	10.5	22.7	19.6	6.25	151	3.61
Mean TEPH	0.0	3873	345	85	390	490	645	50	1980	140
Sampling Station	P10	P11	P12	P13	P14	P15	P16	P17	P18	
Mean Total PAH	25.7	31.6	55.3	161	125	77.9	50.6	14.2	1.40	
Mean TEPH	1353	1701	2193	3385	13480	1376	768	282	0.0	

a. All means are based on detectable concentrations at all depths in a core; PAH means include detectable concentrations for all PAHs listed in Table 1.

Mean total PAH sediment concentrations exceeded 100 mg/kg at one station in the Arthur Kill and four sampling stations in the Passaic River (Table 2). At station A1, located downstream of the Chemical Control Superfund site at the confluence of the Elizabeth River and the Arthur Kill, the mean total PAH concentration was approximately 139 mg/kg. The corresponding mean TEPH concentration was 2,150 mg/kg. At station P1, located above the Dundee Dam on the Passaic River, the mean total PAH and TEPH concentrations were 156 mg/kg and 3,873 mg/kg, respectively. In the lower Passaic River in the vicinity of the Brown Street sewer sink area, extremely high mean total PAH and mean TEPH concentrations were found at sampling stations P8, P13, and P14 (Table 2).

At several sampling stations, high PAH concentrations occurred in sediments with high TEPH concentrations. To evaluate the relationship between PAH and TEPH concentrations, simple linear regression was used to determine the significance of PAH/TEPH correlations in each waterway; samples in which either a PAH compound or TEPH was not detected were excluded in order to eliminate bias associated with nondetect measurements. As shown in Table 3, a highly significant correlation ($p<0.05$) was found between TEPH concentrations and individual

PAHs in Passaic River sediments. However, with the exception of benzo(ghi)perylene, correlations between PAHs and TEPH were poor in sediments from the Arthur Kill and Hackensack River. The high correlations in Passaic River sediments suggests that PAH contamination may be related to industrial and municipal sources involved in the use of diesel fuels.

Table 3. Correlation between PAH and TEPH Concentrations[a]

	Arthur Kill		Hackensack River		Passaic River	
PAH	n^b	r^2	n	r^2	n	r^2
Acenaphthene	5	0.127	4	0.035	31	0.934 *
Acenaphthylene	3	0.233	3	0.296	30	0.943 *
Anthracene	4	0.086	4	0.013	47	0.938 *
Benzo(a)anthracene	4	0.287	4	0.060	48	0.918 *
Benzo(a)pyrene	7	0.088	5	0.025	47	0.928 *
Benzo(b)fluoranthene	10	0.085	2	-	52	0.900 *
Benzo(ghi)perylene	8	0.139	3	0.926	47	0.919 *
Benzo(k)fluoranthene	10	0.092	2	-	52	0.900 *
Carbazole	2	-	0	-	3	0.999 **
Chrysene	10	0.073	5	0.014	54	0.925 *
Dibenzo(a,h)anthracene	2	-	2	-	24	0.958 *
Dibenzofuran	3	0.222	0	-	12	0.966 *
Fluoranthene	10	0.052	5	0.047	55	0.919 *
Fluorene	4	0.250	4	0.019	29	0.954 *
Indeno(1,2,3-cd)pyrene	8	0.162	3	0.332	50	0.919 *
2-Methylnaphthalene	4	0.087	2	-	15	0.969 *
Naphthalene	4	0.105	2	-	18	0.973 *
Phenanthrene	7	0.095	4	0.004	53	0.937 *
Pyrene	11	0.052	5	0.015	55	0.917 *

* Statistically significant (one-tailed), $p=0.0001$

** Statistically significant (one-tailed), $p<0.05$

a. All correlations are based on pooled data for each waterway. Samples were included in the analysis only if a PAH compound and TEPH were detected in the same sample.

b. n = number of PAH-TEPH pairs tested.

The relationship between PAH contamination in sediments and sources of this contamination also was considered in this study. Mueller et al. (1989) investigated the extent of PAH contamination at creosote-contaminated sites and found that anthracene, 2-methylnaphthalene, naphthalene, and phenanthrene accounted for about 52%, by weight, of the total PAHs found in coal tar creosote. Fluorene, acenaphthene, fluoranthene, chrysene, pyrene, and benzo(a)pyrene were present in creosote residues in lower proportions. The heterocyclic compounds carbazole and dibenzofuran are also substantial components of coal tar creosote (Mueller et al. 1989). According to API (1978), phenanthrene is a major component of some crude oils. Minor components of crude oil include fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, and benzo(ghi)perylene. Typical sources of petrogenic hydrocarbons include tanker washings, storage transfer spills, outboard motors, sewage treatment plant effluent, and stormwater runoff (Pierce et al. 1986). Based on U.S. Coast Guard records, Gunster et al. (1993) reported that 67% of the petroleum released to Newark Bay during the past decade as a result of accidental spillage was discharged as diesel fuel.

The vertical distributions of PAHs in sediments cores were examined to investigate historical changes in anthropogenic loadings to bottom sediments. At most sampling stations, higher PAH concentrations occurred with greater depth, suggesting that more recent inputs have declined relative to historical sources (Table 4). Radiochemistry results support sedimentation rates ranging from 0.23 (A5) to 3.5 (P10) inches/year in the three waterways. Sediment cores from the lower Passaic River were found to have the highest depositional rates in the watershed (2.8 - 3.5 inches/year), confirming those reported in a previous study (IT 1986). The lower Passaic River has not been dredged since before 1950 (IT 1986); therefore, the high sedimentation rates calculated from this study indicate that more than 8 ft of sediment has accumulated in the Brown Street outfall sink area since that time.

Table 4. Range of Detected Concentrations (mg/kg) at Specified Depths

Depth (inches)	Total PAHs	Acenapthene	Naphthalene	TEPH
Arthur Kill				
0 - 2	3.35 - 414	ND - 34.0	ND - 54.0	ND - 2150
8 - 10	1.71	0.26 - 1.60	0.37 - 2.20	ND - 310
18 - 20	ND - 35.7	ND - 2.30	ND - 1.90	ND - 5130
38 - 40	0.31 - 19.5	ND	ND	ND - 2320
Hackensack River				
0 - 2	ND - 46.6	ND	ND - 3.00	ND - 190
18 - 20	ND - 68.8	ND - 3.10	ND - 1.00	ND - 250
38 - 40	ND - 23.3	ND - 0.72	ND - 0.32	ND - 270
Passaic River				
0 - 2	4.21 - 64.5	ND - 1.90	ND - 2.60	ND - 800
8 - 10	4.40 - 15.5	ND	ND	ND - 110
18 - 20	ND - 7824	ND - 1000	ND - 1300	ND - 61380
38 - 40	ND - 72.6	ND - 57.0	ND - 19.0	ND - 11330
>40	ND - 941	ND - 43.0	ND - 290	ND - 15690

Using sedimentation rates calculated from radioisotope measurements, pollution profiles of total PAH and TEPH concentrations in sediments at stations P10 - P15 were determined and plotted according to decade (Figure 2). In the Arthur Kill, ^{210}Pb and ^{137}Cs results for station A2 indicate that sediments at the 8 and 18 inch depths correlate to approximately 1978 and 1964, respectively. A survey of industrial development indicates that several creosote wood preserving industries and numerous petroleum refineries operated in the upper Arthur Kill during the 1960s and 1970s.

In the lower Passaic River, radiodating results indicate that the extremely high PAH concentrations and correspondingly high TEPH concentrations found at 18 inches at station P14 were deposited in the early 1930s. At this depth, the concentration of phenanthrene was 1,200 mg/kg. With the exception of benzo(ghi)perylene, the concentrations of the other minor components of crude oils found in this sample all exceeded 100 mg/kg and contained 6% TEPH. Radiodating results for stations P15 and P16 indicate that sediments at the 18, 38, and 92 inch depths correlate approximately to the years 1983, 1975, and 1952, respectively. In the Passaic River, station P14 (8 and 18 in), station P15 (146 in), and station P16 (92 in) showed the highest PAH and TEPH concentrations. Although there appears to be a fairly strong argument that PAHs are related to a petroleum source for sample P14 (18 in), other PAHs not necessarily associated with petroleum (naphthalene, fluoranthene, and anthracene) were also present in high concentrations in this sample suggesting that there may have been non-petroleum related sources such as paint and chemical manufacturing, which are major industrial activities on this portion of the Passaic River.

Petroleum hydrocarbon contamination in sediments from the Arthur Kill and the Passaic River is significant and suggests a potential hazard to fish and shellfish. Benchmark sediment toxicity values for aquatic organisms published by the National Oceanic and Atmospheric Administration (NOAA 1990) range from 0.035 mg/kg for fluorene to 0.60 mg/kg for fluoranthene. For total PAHs, the toxicity to aquatic biota at the 50th percentile occurs at 35.0 mg/kg. Comparisons to these toxicity values indicate that PAH concentrations in sediments in the Arthur Kill, Hackensack River, and Passaic River pose a potential hazard to fish and shellfish. Recent sediment bioassay studies have shown that toxicity to fish is greater for polyaromatic compounds such as PAHs than for mono- or diaromatic compounds such as PCBs and PCDD/Fs (Brunstrom et al. 1992). The occurrence of sediments

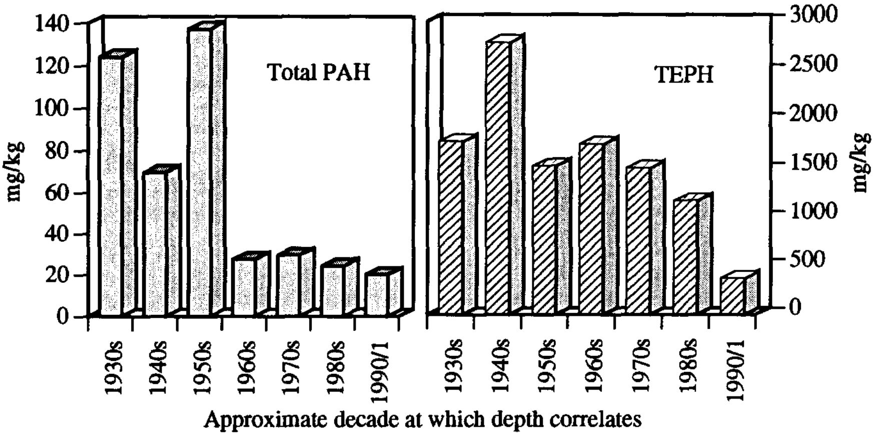

Figure 2. Mean PAH and TEPH Concentrations in the Lower Passaic River

in Newark Bay with PAH concentrations that exceed available sediment quality guidelines is indicative of the presence of on-going and historical sources of contamination. Although low-level, widespread PAH contamination is most often attributed to atmospheric deposition and other nonpoint sources (Menzie et al. 1992), sediment hot spots are more likely the result of localized point sources (NOAA 1982).

The results of this study support the association between the highly industrialized shoreline along the lower Passaic River and the upper Arthur Kill and relatively high PAH concentrations in sediments. Based on comparisons to benchmark toxicity values, petroleum hydrocarbon and PAH contamination in these waterways pose a significant hazard to aquatic life. The high PAH and TEPH concentrations found throughout the Arthur Kill, Hackensack River, and Passaic River indicate the need for further source identification research. Future source investigations should include historical petroleum, creosote wood treatment, and paint manufacturing sources along these waterways in order to evaluate their relative contributions to the presence of petroleum hydrocarbon and PAH contamination in sediment.

REFERENCES

API (1978) Fate and effects of polynuclear aromatic hydrocarbons in the aquatic environment. American Petroleum Institute, Washington DC, Publication No. 4297

Brunstrom B, Broman D, Dencker L, Naf C, Vejlens E, Zebuhr Y (1992) Extracts from settling particulate matter collected in the Stockholm archipelago waters: Embryolethality, immunotoxicity, and EROD-inducing potency of fractions containing aliphatics/monaromatics, diaromatics, or polyaromatics. Environ Toxicol Chem 11:1441-1449

Brydon NF (1974) The Passaic River past, present, future. Rutgers University Press, NJ

Gunster DG, Bonnevie NL, Gillis CA, Wenning RJ (1993) Assessment of chemical loadings to Newark Bay, New Jersey from petroleum and hazardous chemical accidents occuring from 1986 to 1991. Ecotox Environ Safety 25:202-213

Herbes SE, Schwall LR (1987) Microbial transformation of polycyclic aromatic hydrocarbons in pristine and petroleum-contaminated sediments. Appl Environ Micro 35:306-316

IT Corp (1986) Passaic River sediment study. Final Report. Prepared by International Technology Corporation, Pittsburgh, PA for the New Jersey Department of Environmental Protection, Trenton, New Jersey, March

Menzie CA, Potocki BB, Santodonato J (1992) Exposure to carcinogenic PAHs in the environment. Environ Sci Technol 26:1278-1284

Mueller JG, Chapman PH, Pritchard (1989) Creosote-contaminated sites. Environ Sci Technol 23:1197-1201

NOAA (1982) Contaminant inputs to the Hudson-Raritan Estuary. NOAA Technical Memorandum OMPA-21. Office of Marine Pollution Assessment. Boulder, Colorado

NOAA (1988) A summary of selected data on chemical contaminants in sediments collected during 1984, 1985, 1986, and 1987. NOS OMA-44. Rockville, Maryland

NOAA (1990) The potential for biological effects of sediment-sorbed contaminants tested in the National Status and Trends Program. National Oceanic and Atmospheric Administration, Seattle, Washington, March

Pierce RH, Brown RC, Van Vleet ES, Joyce RM (1986) Hydrocarbon contamination from coastal development. In: Sohn MC (ed) Organic Marine Geochemistry in ACS Symposium Series 305, American Chemical Society, Washington DC

PVSC (1970) Annual report to commissioners. Passaic Valley Sewerage Commissioners, Newark, New Jersey, pp 12-13

Received December 30, 1992; accepted May 1, 1993.