

## **Naphthalenes Associated with Treated Wastewater Effluents in an Urban National Wildlife Refuge**

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Our coastal environments have become the invariable recipient of petroleum and petroleum wastes. Demands for petroleum products coupled with a lack of economic incentive to recycle waste oil, will increase the probability of greater concentrations of petroleum derived hydrocarbons entering our estuaries (CEQ Report, 1983).

The sources of waste petroleum in municipal sewage systems and their receiving waters, range from individuals changing oil in automobiles and dumping wastes into sewers, to larger establishments sporadically discarding accumulated waste stocks (Tanacredi and Maltezou, 1980).

Due to existing municipal sewage treatment technology, waste petroleum will not be prevented from getting into a receiving body of water. This is based upon (1) most petroleum hydrocarbons are more resistant to degradative processes than other compounds found in sewage, and (2) skimming and settling operation disregard the finely dispersed portion of hydrocarbons (48-96% total HC's removed) [Farrington and Quinn, 1973].

Previous investigations (Tanacredi, 1977) to detect waste crankcase oil in wastewater effluents strongly suggested that appreciable quantities of polynuclear aromatic hydrocarbons (PAH) were remaining in suspension in near-surface waters of the Bay and that compounds isolated from tissue extracts of marine benthic bivalves collected in Jamaica Bay, were attributed to the PAH portion of automotive petroleum products.

This project demonstrates the polynuclear aromatic hydrocarbon character of Jamaica Bay sediments and the wastewater effluents entering the Bay from four major water pollution control facilities [320 million gallons of effluent per day]. Jamaica Bay, is a part of the Hudson-Raritan estuarine ecosystem and is incorporated into the Gateway National Recreation Area. Jamaica Bay, because of its hydrological characteristics, affords a long residence time for introduced pollutants.

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This study was conducted to further characterize the PAH character of the wastewater effluents. These fused ring structures are of interest in that they represent the carcinogenic, mutagenic, and toxic components of petroleum compounds to marine organisms (Peake and Parker, 1980; Pruell, Hoffman and Quinn, 1984; Farrington, et. al. 1986).

Because of their high molecular weight, the solubility of PAH in water, is of a very low order (Davis, Drahla, and Clowens, 1942). Consequently, in estuarine environments, PAH compounds will be found associated with suspended solids and sediments. Although PAH degrading microorganisms are known to occur in estuarine environments, the degradation rates of these compounds are very slow; ranging from 11 days for naphthalene to 3500 days for benzo(a)pyrene, both present at the part per billion level (Lee, 1977). These compounds have been shown to become incorporated into the tissue of marine organisms (Dunn and Stitch, 1976; Malins, et. al. 1987). Coupled with the low degradation rates and known carcinogenicity of many of these compounds, investigations (Payne and Martins, 1978) have exhibited results that fish and other organisms taken from areas with a history of oil contamination have been found to exhibit elevated levels of compounds which "bioactivate" complex PAH compounds found in waste crankcase oils into mutagens. The possible long-term adverse effects on human health requires greater scrutiny in-light of this potential mutagenic burden.

#### MATERIALS AND METHODS

Environmental samples considered containing petroleum hydrocarbons were determined by its fluorescence profile's ability to "correlate" visually with profiles generated by reference sample oils under the same analytical conditions (Frank and Gruenfeld, 1978). Reference standard waste crankcase oil (WCCO), excited at 290 nm, provided unique "profiles" for correlation. A synchronous excitation fluorescence spectroscopic technique was implemented for environmental sample analysis.

Standards were excited at successive wavelengths (20 nm intervals) from 240 nm to 440 nm while scanning for the maximum fluorescence emission at each of the respective excitation wavelengths. Each maxima peak can be utilized as a point to be plotted graphically generating a "fluorescence maxima profile" (FMP) for each sample. Once the FMP's for reference standards are obtained and the environmental sample FMP's generated, a simple correlation can be made.

Final effluent from each of the four New York City Municipal Water Pollution Control Facilities discharging into Jamaica Bay were collected in 980 ml., wide-mouth glass jars with aluminum foil lined lids. All sample jars were detergent washed, oven baked and solvent rinsed (hexane) prior to sample collection.

The extraction method was similar to that used by Miles, et. al. (1977) for liquid chromatographic analysis of oil in water. All laboratory procedures were conducted in appropriately washed, solvent rinsed glassware. The resulting extracts were stored under refrigeration at 4 degrees celsius until analysis. The samples of Jamaica Bay surficial sediments were taken immediately below the intertidal zone and placed in 980 ml. wide jars with aluminum foil lined lids.

A technique of reverse phase, high-performance liquid chromatography (HPLC) was used. Environmental sample extracts of 5 to 20  $\mu$ l. were injected into a DuPont Model 830 HPLC with a Whatman Parisil - 10 ODS 25 cm long, 4.6 mm ID column packed with a C(18) - type bonded phase for reverse phase chromatography. Major peaks of the sample chromatogram were collected and subjected to a UV-fluorescence technique which provides resolution of parent PAH compounds by simultaneously varying the excitation and emission monochromators.

The compounds responsible for the major peaks on each chromatogram generated from the HPLC analysis of the effluent and sediment extracts, were collected via a fraction collection valve and subject to further analysis by a Perkin-Elmer model. MPF -3 UV-fluorescence spectrophotometer. The instrument had two independent monochromators, a 150 watt xenon arc light source and a 10 mm path length. Synchronous excitation of the individual fraction was accomplished by exciting the sample at 20 nm wavelength intervals between 200 and 500 nm. The excitation wavelength was maintained 20 nm less than the emission wavelength. The emission monochromator was rapidly scanned at each excitation wavelength resulting in a spectra of emission vs. excitation wavelength.

Peak height measurements of the individual chromatograms were compared to PAH standards for quantification purposes. Calibration curves were checked for linearity of response and curves that passed through zero. The fluorescence data along with comparison of HPLC retention times to known standards were used to aid in the verification of the chemical composition of the individual peaks.

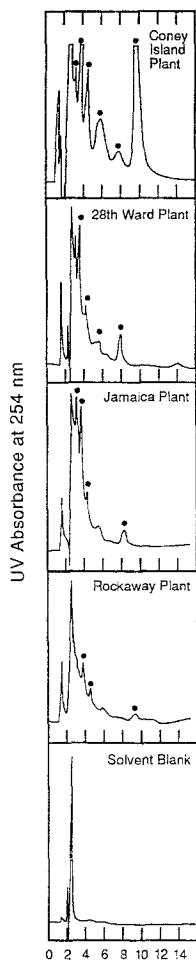


Figure 1. HPLC Sewage Effluent Extracts with UV-fluorescence confirmation of peaks (•).

## RESULTS AND DISCUSSION

The instrumental approach provided the capabilities for separation and detection of PAH in both the effluent and sediment. The HPLC sample chromatograms appeared to contain from one to five ring PAH compounds based on comparison of retention times to those of known standards (Figure 1).

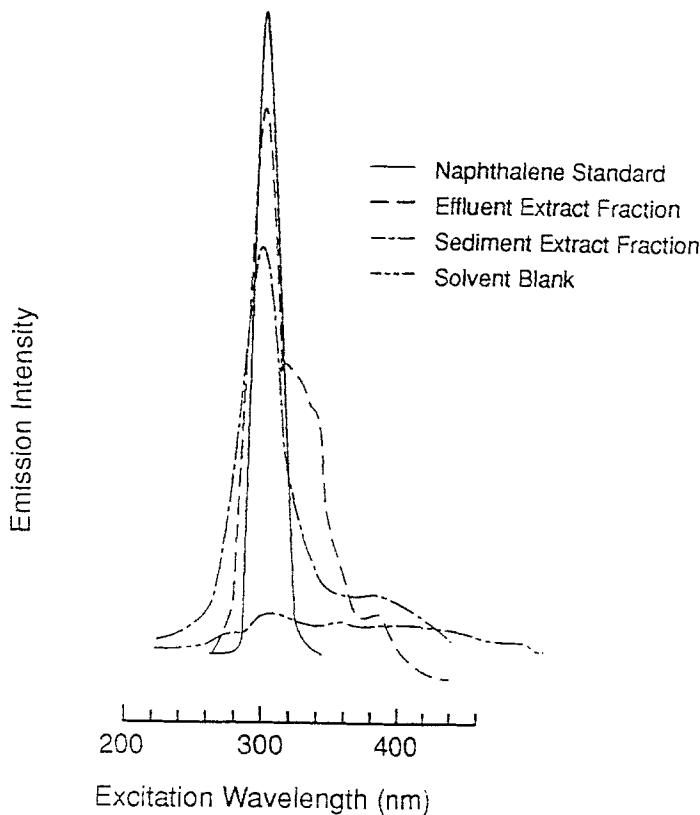


Figure 2. Representative correlation of effluent and sediment sample fractions to synchronous fluorescence spectra of naphthalene standard

Examination of fluorescence data of the individual fractions revealed that the emission maxima of the naphthalene standard of 300 nm (Figure 2).

Fluorescence data of several fractions indicated the presence of more than one PAH compound. In all cases, except naphthalene, the correlation was too weak to classify the nature of the PAH. Figure 2 demonstrates the type of correlation necessary between a sample fraction and the naphthalene standard for an individual

Table 1. Concentrations of Extracted Substituted Naphthalenes (ppb) in Individual Water Pollution Control Facility Effluents

SAMPLE EFFLUENT	DATE (1978)	APRIL 11	JUNE 8	JUNE 28
Coney Island Plant	42.9		63.7	26.9
26th Ward Plant	22.9		10.9	5.7
Jamaica Plant	24.6		11.5	6.8
Rockaway Plant	13.7		3.0	5.5

Concentrations of Extracted Substituted Naphthalenes (ppb) from Sediment Samples		
Jamaica Bay Sample Sites	DATE	
	JUNE 17	JUNE 23
1	N. D.	N. D.
2	10.8	12.1
3	N. D.	N. D.
4	N. D.	N. D.
5	12.6	18.9
6	N. D.	N. D.

N. D. = no identifiable quantity detected

peak to be quantified as a naphthalene compound. Because most sample peaks indicated to be naphthalene by fluorescence data had retention times greater than the unsubstituted parent and as synchronous fluorescence data makes no differentiation between substituted and unsubstituted PAH, the data is quantified in terms of substituted naphthalenes (Table 1).

Calculations of the total yearly burden of naphthalene attributable to wastewater on Jamaica Bay based on the 1987 discharge figures (approximately 320 million gallons per day from the 4 STP's) indicates a potential input of over 10 metric tons per year. Other inputs of PAH's to this ecosystem such as urban runoff, urban fallout, pleasure craft, marine oil transport, runoff from adjacent John F. Kennedy International Airport and local landfill leachate require further investigation.

Numerous authors have suggested that naphthalenes represent the most toxic fraction of petroleum hydrocarbons to marine organisms (Lee and Anderson, 1977). It has been demonstrated that mammalian metabolism of naphthalene involves the generation epoxides as an intermediary metabolite which has been shown to exhibit greater mutagenic activity than the parent PAH compounds (Huberman, et. al. 1971). A more extensive survey characterizing the PAH of Jamaica Bay ecosystem and detailed biological tissue analysis is required in light of recent requests for the commercial utilization of the bay's shellfish resources.

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#### REFERENCES

Council on Environmental Quality Report (1983) Oil and hazardous materials spills in U. S. waters 1971-1982. Table A048 Water Quality, p. 311

Davis WW, Drahil ME, Clowes GHA (1942) Solubility of the carcinogenic and related hydrocarbons in water. Journal Amer Chem Soc 64:108

Dunn BP, Stich HF (1976) Release of the carcinogen benzo(a)-pyrene from environmentally contaminated mussels. Bull Environ Contamin and Toxicol 15(4):398

Farrington JW (1986) Aromatic hydrocarbons in New York Bight polychaetes: ultraviolet fluorescence analyses and gas chromatography/GC-MS analyses. Env Sci Tech 20:69-72

Farrington J, Quinn J (1973) Petroleum hydrocarbons and fatty acids in wastewater effluents. Jour Wat Poll Control Fed 45:705

Frank U, Gruenfeld M (1978) Use of synchronous excitation fluorescence spectroscopy for in-situ quantification of hazardous materials in water. In: Proceedings of USCG/USEPA (ed) API National Conference on Control of Hazardous Materials Spills, pp119

Huberman E, Lourdes A, Heidelberger C, Grover P, Sims P (1971) Mutagenicity to mammalian cells of epoxides and other derivatives of polycyclic hydrocarbons. In: National Academy Sciences (ed) 68(12):3195

Lee RR, Anderson JW (1977) Fate and effect of naphthalenes: Controlled ecosystem pollution experiment. Bull Mar Sci 27(1):127

Lee RF (1977) Fate of petroleum components in estuarine waters of the Southeastern United States. In: Proceedings Conference on Prevention and Control of Oil Pollution (ed) Amer Petrol Inst, Washington DC pp611-616

Malins DC, McCain BB, Brown DW, Myers MS, Krahn MM, Chan SL (1987) Toxic chemicals, including aromatic and chlorinated HC's and their derivatives and liver lesions in white croaker (Genyonemus lineatus) from vicinity of L. A. Calif. Env Sci Tech, Vol. 21, No. 8, pp1987

Miles DH, Coign MJ, Brown LR (1977) A liquid chromatographic fluorescence technique for estimating crude oil in water, sediment and biological material. In: Joint Conference on Prevention and Control of Oil Pollution (ed) Amer Petrol Inst, Washington DC, pp179-182

Payne JF, Martins I (1978) Crankcase oils: Are they a major mutagenic burden in aquatic environments? Science 200:329

Peake E, Parker K (1980) Polynuclear aromatic hydrocarbons and the mutagenicity of used crankcase oils. In: Polynuclear Aromatic Hydrocarbons: Chemistry and Biological Effects, Fourth International Symposium (ed) Battelle Press, pp1025

Pruell RJ, EF Hoffman, JG Quinn (1984) Total hydrocarbons, polycyclic aromatic hydrocarbons and synthetic organic compounds in the hard shell clam, Mercenaria mercenaria purchased at commercial seafood stores. Mar Env Res 11: 163-181

Tanacredi JT (1977) Petroleum hydrocarbons from effluents: Detection in marine environment. Jour Wat Poll Control Fed, March: pp216

Tanacredi JT, Maltezou S (1980) Waste oil recycling: Are there any Incentives out there? Proceedings 1980 Year of the Coast Conference, Dowling College, Sponsored by New York State Marine Educators Association (NYSMEA) pp3

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