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Analysis of Raritan Bay Bottom Waters for Polynuclear Aromatic Hydrocarbons

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Petrochemical hydrocarbons have been frequently reported in the marine environment. Although many laboratory studies have reported effects and pathways of degradation and weathering of petrochemicals in the environment, little is known of the mechanism of environmental transport or incident levels. Laboratory experiments by BOYLAN & TRIPP (1971) have indicated that the aromatic fractions of oils are the most soluble components.

Polynuclear aromatic compounds are frequent components of oils and toxic wastes. They are also relatively toxic (ANDERSON et al. 1974) and more soluble than the alkane fractions (FRANKENFELD 1973). Several field studies have reported the occurrence of polynuclear aromatic compounds in shellfish (DUNN & STICH 1976), sediments (HITES et al. 1977), and water (HARRISON et al. 1975). The method of dissemination of these compounds in the environment is still unclear. Although relatively high concentrations of polynuclear aromatic hydrocarbons are found in sediments and animals, very low concentrations occur in the water column. Recent experiments (LEE & ANDERSON 1977) have described potential pathways of naphthalene in the environment.

New York Harbor and its environs receives large inputs of petrochemical hydrocarbons from a variety of sources (i.e., upstream pollution, air pollution, spills, effluents, boat traffic, sewage, etc.). TANACREDI (1977) reported an input of aromatic material from sewage outlets in Jamaica Bay. SEARL et al. (1977) studied the occurrence of extractable organics and nonvolatile hydrocarbons in New York surface waters. They found measurable quantities of hydrocarbons in the surface waters. Most investigations reported surface pollution. This study was therefore designed to survey polynuclear aromatic hydrocarbon concentrations and types in the bottom waters of the Lower NY Bay - Raritan Bay Complex. Knowledge of the types and concentrations of polynuclear aromatic hydrocarbons may elucidate mechanisms of transport and dissemination of these compounds in the environment.

Sample analyses were performed using synchronous excitation (SE) fluorescence spectroscopy. This method entails derivation of spectra by simultaneously scanning the excitation and emission monochromators of a fluorescence spectrometer according to procedures described by LLOYD (1971), and FRANK & GRUENFELD (1978). The SE technique yields better spectral data than conventional single wavelength excitation (SWE) fluorescence methods (FRANK (1975), TANACREDI (1977). Use of the SE technique yields spectra of petroleum fractions and polynuclear aromatic compound (PNA) mix-

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tures that are resolved according to the number of aromatic rings. GORDON & KEIZER (1974), HORNIG (1974) and TANACREDI (1977) demonstrated that the fluorescence of environmental water samples derived from petroleum PNA constituents. SE fluorescence emissions were therefore used in this study as an indication of PNA's. Some PNA characterization was achieved by comparing sample spectra to standard spectra of individual and mixtures of PNA's.

MATERIALS AND METHODS

Bottom waters were sampled from 18 sites (Figure 1) during June, 1977. Replicate 1 liter samples of water were taken from 2-3 feet above the bottom utilizing a Kemmerer Water Sampler. Samples were usually taken just after flood or mid ebb tide. One sample was taken near the outfall of the Oakwood Sewerage Treatment Plant (OKWD). One surface sample was taken from a littoral station below a storm sewer in Great Kills Harbor (GK3). At each station, one liter of sample was stored in a pre-washed glass jar (one Freon 113 washed and one cyclohexane washed) with a tin foil lined cap. Samples were extracted immediately upon return to the lab.

One liter of water from each station was successively extracted with two 50 ml portions of glass distilled cyclohexane (BURDICK and JACKSON) Muskegon, Michigan for fluorescence spectroscopic analysis. A problem occurred initially with emulsion formation. This was later resolved by the addition of 5 ml of concentrated hydrochloric acid to the sea water prior to extraction. Anhydrous sodium sulfate (pre-cleaned by baking 3 hours at 450° C) was added (1-3 g) to each extract. SE spectra of the cyclohexane extracts were obtained by simultaneously scanning a fluorescence spectrometers excitation and emission monochromators and recording the fluorescence emission. The excitation monochromator was set ahead of the emission monochromator by a 25 nm interval. SE spectra of fused ring PNA's at concentrations of 1 mg/1 in cyclohexane were similarly obtained.

Confirmation of the samples' PNA content was obtained by high pressure liquid chromatography (HPLC). This was used to isolate PNA's from the sample matrix. Identification of each PNA was accomplished by collection of appropriate fractions and fluorescence analyses. HPLC analyses were performed with an ODS reverse phase column and a mobile phase of 2-propanol/water (50:50). Fluorescence analyses were performed using the synchronous excitation (SE) procedure and a micro-cuvette with a 10 mcl capacity.

In addition, one liter portions of water from each station were also extracted with Freon according to GRUENFELD and FREDERICK (1977) for quantitation by infrared spectroscopy.

RESULTS

Hydrocarbon contents of the sample extracts were below the

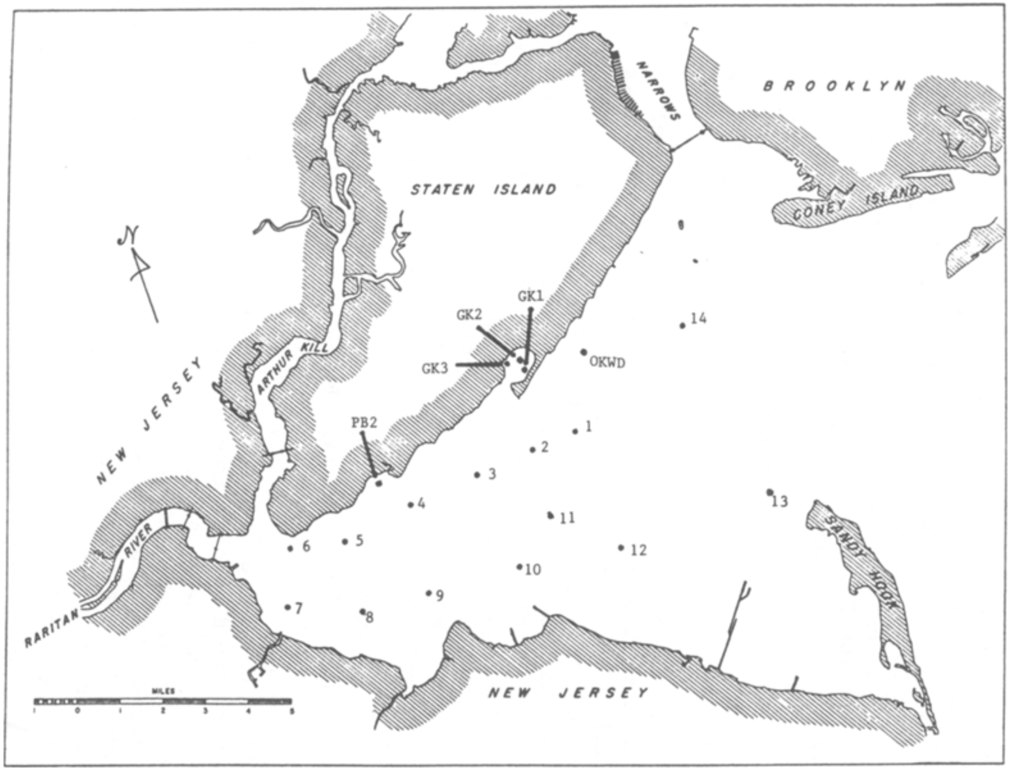

Fig. 1. Sampling stations in the Raritan Bay - Lower New York Bay Complex

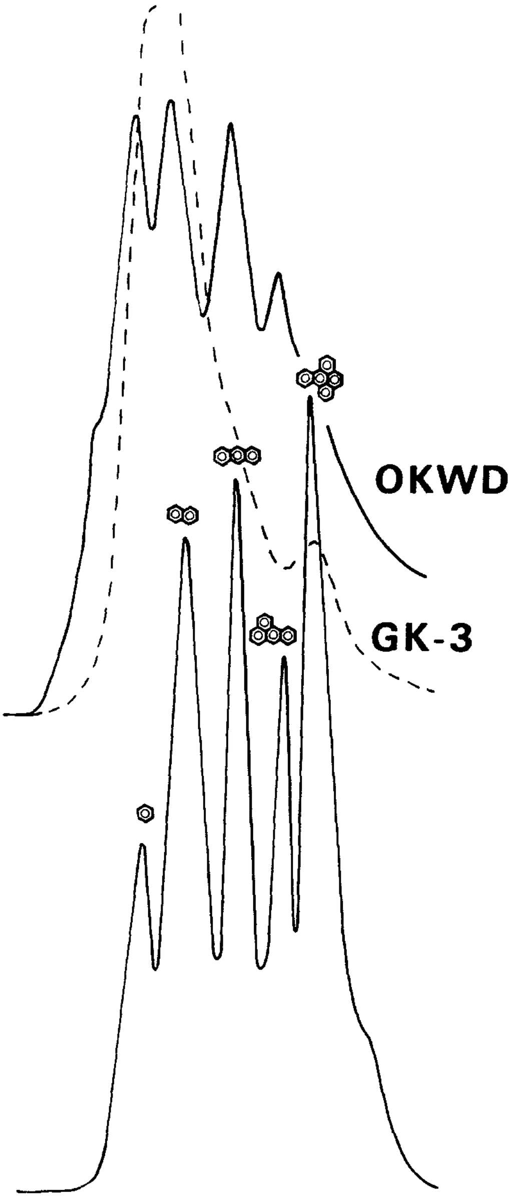

Fig. 2. The synchronous excitation (SE) fluorescence spectra of samples GK3 and OKWD with the SE spectrum of a PNA mixture used as standards.

level of detection by the infrared method used (< .2ppm). Fluorescing compounds were found in OKWD, GK2 and GK3 sample extracts. Detection was achieved at maximum sensitivity, indicating that the compounds were in the low ppb range. Sites 1 and 6 appeared to contain fluorescing material similar to methyl substituted isomers of naphthalene. Fluorescence spectra from the sample near the Oakwood Sewerage Treatment Plant (OKWD) indicated the presence of 1, 2 and 4 ring aromatic compounds, possibly naphthalenes and pyrenes. The spectra from site PB2 indicated the presence of three ring compounds. The spectra of site GK2 indicated the presence of isomeric methyl substituted naphthalenes and the spectra of GK3 contained approximately three times more fluorescing material than all the other samples. This extract was then analyzed by high pressure liquid chromatography and then re-examined by fluorescence spectroscopy. Known standards were also run concomittantly and benz-a-pyrene was identified.

Figure 2 illustrates SE spectra of samples GK3 and OKWD, and an SE spectrum of a mixture of PNA's used as standards. The OKWD sample spectrum exhibits a spectral profile which indicates the presence of 1, 2, 3 and 4 fused ring PNA's, each having an approximate concentration of 5-10 ppb. The GK3 and GK2 samples contained predominantly 2 and 5 ring PNA's; the concentration of the 2 ring aromatic compound was estimated to be 20 ppb and the 5 ring component was estimated to be 10 ppb.

Figure 3 illustrates SE spectra of a collected HPLC fraction of sample GK3, and a benz-a-pyrene standard. The similarity of these spectra and the retention times of peaks of sample and standard PNA chromatograms confirms the presence of PNA's in the samples.

DISCUSSION

One of the principal advantages derived from use of the SE approach in this study was the enhanced spectral resolution obtained from the sample spectra. In comparison to conventional SWE techniques, the SE procedure permits the characterization of the aromatic content of the water samples with respect to the number of aromatic ring systems. The advantage of the SE procedure for resolving mixtures of hazardous materials was previously demonstrated by FRANK (1978), and FRANK and GRUENFELD (1978). Their procedure utilized a three dimensional coordinate system incorporating the three interdependent variables: excitation wavelengths (x), emission wavelengths (y), and fluorescence intensity (z). Within this context, the fluorescence characterizations of PNA's are presented as "total fluorescence spectra" and the spectral information that is obtained by the SE and SWE techniques as appropriate portions of such spectra. Figure 4 illustrates hypothetical three dimensional total fluorescence spectra of various PNA's ring structures and the spectral information obtained by the SE and SWE techniques. The SWE approach measures only a portion of a total PNA spectrum. The SE approach, however, measures portions of all total PNA spectra and provides sufficient details for characterizing individual PNA's in mixtures.

The SE fluorescence spectra of the samples indicated the frequent occurrence and variation of PNA compounds. Fused ring PNA's were identified with respect to the number of rings. PNA isomers were not resolved.

The possibility that the fluorescence spectra emanated from fluorescent species other than PNA's was also considered. This was ruled out, however, by the following factors: (1) the PNA standard spectra matched the sample spectra, (2) the relative quantum efficiency of PNA's versus other possible compounds indigenous to the sampled area, (3) previously reported occurrence of PNA'a and, (4) additional compound isolation and characterization procedures.

The infrequent presence of PNA's and their low concentrations within the bottom waters sampled (sites 1, 6, OKWD, PB2 and GK2) was surprising with respect to the pollution input of the N.Y. - N.J. environs. The presence of PNA material in the surface sample (GK3) and the results of SEARL *et al*. (1977) suggest that much of the pollution is a surface phenomena. Those sites where PNA material was found were near ship channels or sewer outfalls implicating sewage and vessel traffic as sources of PNA material within the Raritan Bay area.

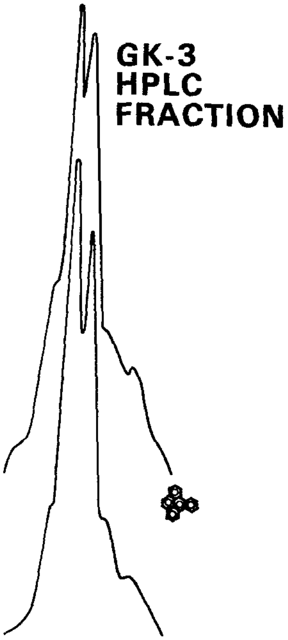

Fig. 3. The SE spectra of a collected HPLC fraction of sample GK3 matched with a benz-a-pyrene below.

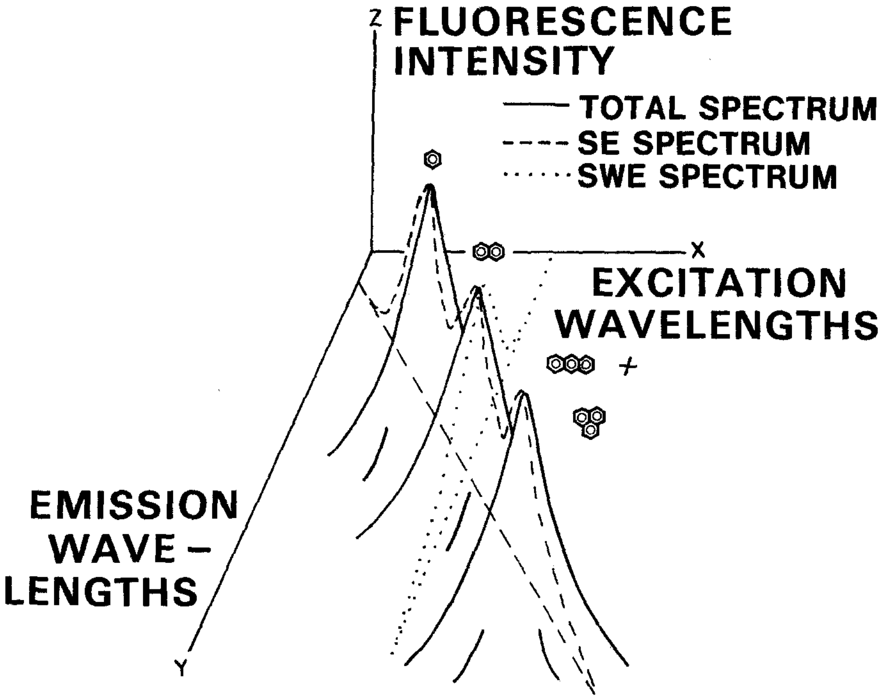

Fig. 4. Three dimensional total fluorescence spectra of various PNA ring structures obtained by the SE and SWE techniques.

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