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Determination of Polynuclear Aromatic Hydrocarbons in the New York Bight Area

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With increased offshore oil drilling along the eastern coast of the United States, the monitoring of organic contamination in this area has received greater attention (BROWN & PANCIVOV 1979). Polynuclear aromatic hydrocarbon (PAH) contamination is of particular concern, since many of these compounds are known or suspected carcinogens (SERRELL & REDING 1979, HANUS et al. 1979). Sources of PAH contamination in the marine environment other than drilling and oil spillage include creosote impregnated wooden piles, untreated sewage, and contamination with airborne particulates from the combustion of fossil fuels (DUNN & FEE 1979, ZITKO 1975). These contaminants are taken up by the fish and shellfish which inhabit contaminated areas. When the fish are harvested, a human health hazard may result.

The National Marine Fisheries Service, Gloucester Laboratory, has undertaken a study of PAH levels in specimens found in the New York Bight and Long Island Sound region for comparison with future levels. Samples of winter flounder, windowpane, red hake, rock crab, lobster, and sea scallops were collected from 25 sites by the Kelez Research Vessel during the Kelez-8008 cruise of July through August, 1980. The samples of five animals were collected by standard otter trawl, wrapped in pre-washed aluminum foil, and stored at -30C for future analysis. These specimens have been analyzed quantitatively for the presence of 15 PAHs.

MATERIALS AND METHODS

Materials. Toluene, 2,2,4-trimethylpentane and dimethylsulfoxide of "Distilled in Glass" grade were procured from Burdick and Jackson* for use in sample extraction. The ethanol was of "Absolute" grade, from International Chemical Company. The KOH was from Fisher Scientific. HPLC solvents were also from Burdick and Jackson. The acetonitrile was "UV" grade and the water was "High Purity." PAH standards were from Supelco, Inc.

Method. Sample extraction was done by the method of DUNN &

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ARMOUR (1980). The edible portions of the samples were homogenized and digested at reflux in ethanolic KOH and extracted with 2,2,4-trimethylpentane. The extract was washed with water and displaced into toluene. A florisil column was deactivated with 5% water and covered with sodium sulfate to dehydrate the extract which was eluted through the column with toluene. The eluant was displaced into dimethylsulfoxide and partitioned between aqueous dimethyl-sulfoxide and 2,2,4-trimethylpentane. The 2,2,4-trimethylpentane layer was dehydrated and displaced back into 0.5 mL of dimethyl-sulfoxide, to which 1.5 mL of acetonitrile was added. The samples were analyzed by high performance liquid chromatography (HPLC).

Instrumentation. HPLC was performed using a Perkin Elmer LC unit including a Series 3B pump module, an LC 100 column oven, and a Model 420 autosampler. The column was a 25 cm X 4.1 mm i.d. Supelco LC PAH column with a particle size of five microns. Detection was accomplished by Perkin Elmer LC 75 UV and 3000 fluorescence detectors connected in series. The programmable pump ran a system of acetonitrile and water (Figure 1). The column was eluted at 1.0 mL/min and was kept at 30C. The UV detector was operated at 254 nm. The fluorescence detector was operated at an excitation wavelength of 280 nm and emission wavelength of 389 nm.

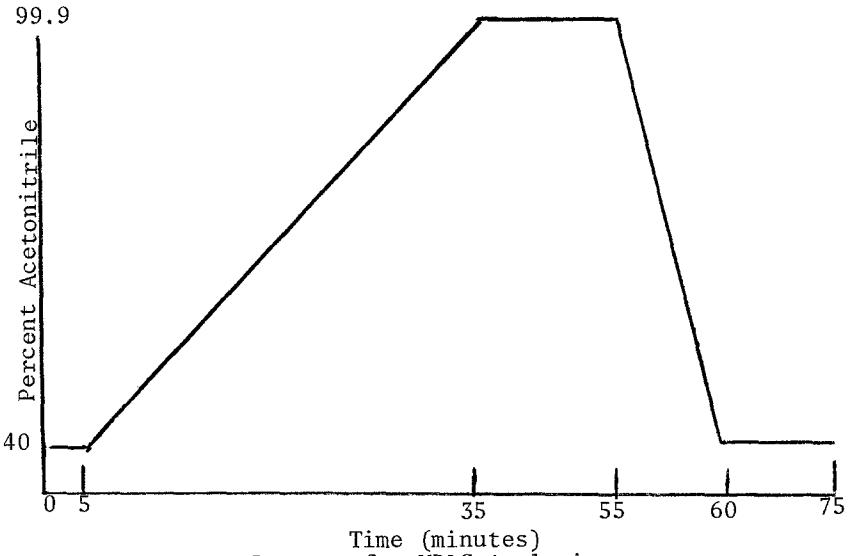

Figure 1. Solvent Program for HPLC Analysis

Method Verification. Seven 50-g samples of cod containing natural levels of 7 ppb (ng/g) phenanthrene and no other detectable levels of PAH were fortified with 500 ng of PAH. A control sample was also run (Table 1).

The linearity and detection limits for the HPLC method were tested by graphing concentration versus peak area curves for the 15 PAHs measured in this study. Good linearity and detectability was found from 2 to 20 PPb.

Table 1. Experimental Yields Of Selected PAHs

	Average Yields, %	Standard Deviation	Coefficient of Variance, %
Naphthalene	26	6	23
Acenaphthylene	53	5	9
Acenaphthlene	73	24	33
Fluorene	42	5	12
Phenanthrene	81	10	6
Anthracene	84	9	11
Pyrene	90	3	3
Chrysene	95	4	4
Benzo(a)pyrene	40	5	13
Benzo(g,h,i)perylene	77	10	13

RESULTS AND DISCUSSION

The low yields for benzo(a)pyrene observed in the method verification study (Table 1) are possibly attributable to two factors. Primarily benzo(a)pyrene is the most strongly retained PAH of the ones tested for on a polarity-differentiating column such as florisil. Further, benzo(a)pyrene is rapidly degraded photochemically.

The New York Bight samples were analyzed for naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene, and indeno(1,2,3-c,d)pyrene. The largest PAH concentrations found were for phenanthrene which were primarily in the 50-200 ppb range. Concentrations of other PAHs ranged from 0-50 ppb in most samples. The least typically found PAHs were naphthalene, acenaphthylene, acenaphthene, dibenzo(a,h) anthracene and benzo(g,h,i)perylene. Each of these PAHs were found in 25% or less of the samples studied.

The benzo(a)pyrene and total PAH concentrations for each sample are included in Table 2. The values for indeno(1,2,3-c,d) pyrene were excluded because artifacts in the UV spectrum complicated the interpretation of this peak. Benzo(a)pyrene is singled out because it is the most carcinogenic of the compounds measured in this study. Benzo(b)fluoranthene, benzo(a)anthracene, and chrysene have also been shown to have significant carcinogenic activity.

No overall geographic significance has been placed on these results since the sample size within species is small. However, the overall interpretation of these data indicates that the New York Bight area is a site of measurable and significant PAH contamination. The extent to which this contamination represents a health hazard is unknown.

Since this is a baseline study, the full significance of these results will be realized when a follow-up study is undertaken.

Table 2. Benzo(a)pyrene (BaP) and Total PAH Concentrations (ppb)

Finfish						
Capture Stations (Stations from Figure 2)	Winter Flounder (*Pseudopleuronectes americanus*)		Windowpane (*Scophthalmus aquosus*)		Red Hake (*Urophysate chuss*)	
New York Bight	BaP	Total PAH	BaP	Total PAH	BaP	Total PAH
1	ND	66				
6	ND	14	ND	87		
9	21	133				
12	ND	118	ND	85		
14						
15						
16	ND	193			2	143
18						
30	ND	174	ND	136	ND	412
31						
33	7	304				
34						
36					ND	323
38					4	168
41			1	18		
46	ND	80	4	136	2	149
47					8	178
50	ND	151	ND	189		
51	ND	315				
53			ND	78	22	244
57			ND	536		
58	ND	62				
59				131		
Long Island Sound						
8	ND	103	ND	73		
88	ND	72	ND	86	5	124

ND = NOT DETECTED

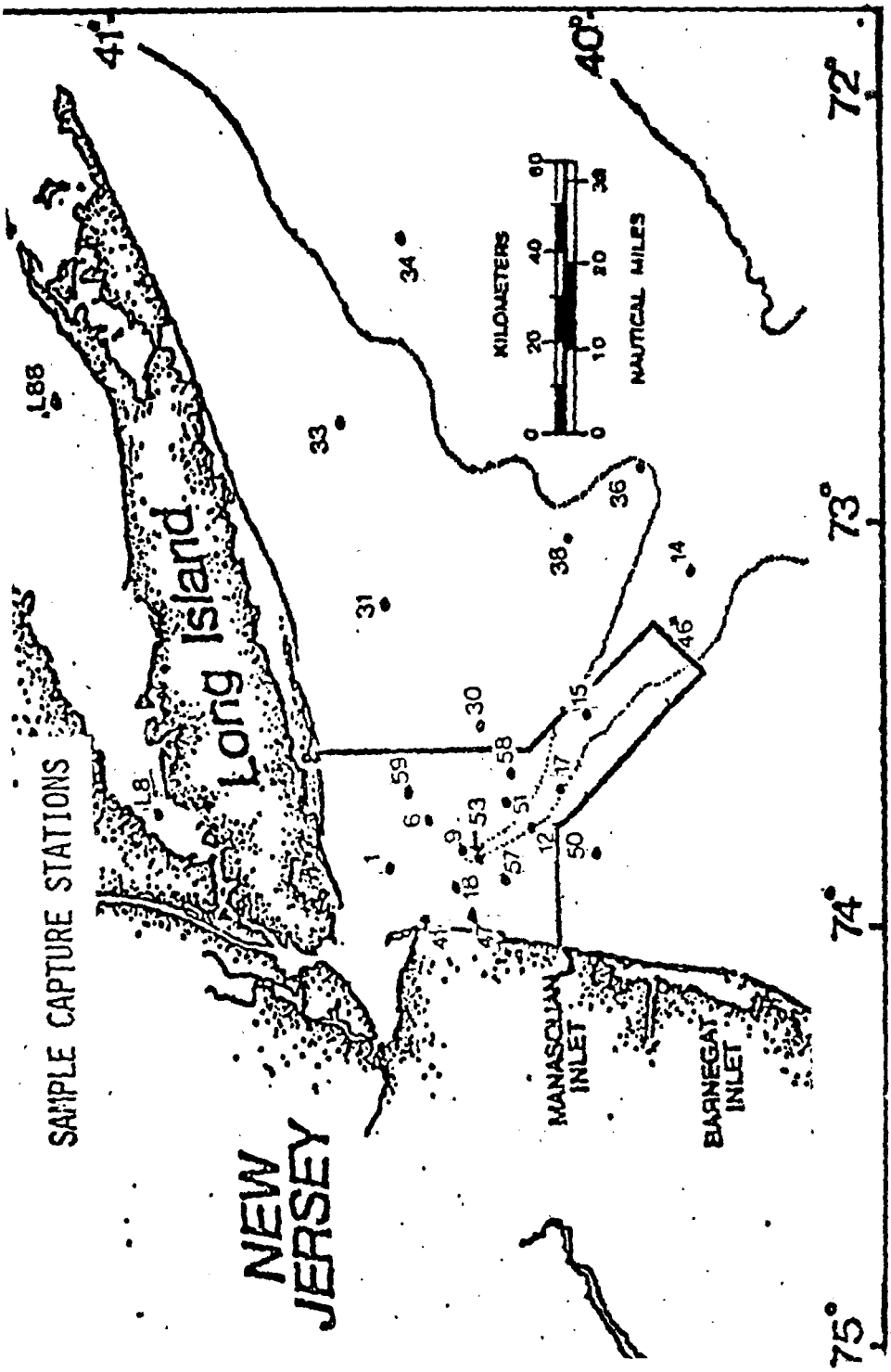

Fig. 2. Sample capture stations (see chart on following page).

Capture Stations	Shellfish					
	Rock Crab (Cancer irroratus)		Lobster (Homarus americanus)		Sea Scallop (Placopeskin magellianicus)	
New York Bight	BaP	Total PAH	BaP	Total PAH	BaP	Total PAH
1	ND	137				
6	ND	52	2	309		
9			25	352		
12	ND	518			3	127
14	ND	292			2	58
15	ND	157				
16	ND	163	ND	151		
18	ND	420	7	367		
30						
31					2	127
33	ND				ND	86
34	ND					
36	1	137			ND	83
38	ND	1600			ND	26
41						
46						
47			3	129		
50						
51						
53			12	208		
57						
58						
59						
Long Island Sound						
8	ND	437	15	328		
88	ND	1290	1	75		

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