

The Levels and Distribution of Polycyclic Aromatic Hydrocarbons (PAH) Contamination in Bottom Sediments in Manila Bay

Evangeline C. Santiago
*Natural Sciences Research Institute
University of the Philippines
Diliman, Quezon City 1101
E-mail: ecs@nsri01.cs.upd.edu.ph*

ABSTRACT

The concentration levels of 18 PAH compounds extracted from 19 bottom sediments from the Limay Coast and 16 bottom sediments from the coast along Metro Manila and Cavite Province of Manila Bay were determined by Gas Chromatography/Mass Spectrometry.

The PAH contamination, the levels of other non-PAH petroleum hydrocarbon compounds, and total organic content in the sediments were assessed in relation to the location and depth of the sampling sites. The PAH concentrations and the levels of other petroleum hydrocarbons in the sediments showed that the spatial distribution of PAH and other hydrocarbon contamination in Manila Bay is largely dependent on the proximity of the sediment deposition site to known point sources of pollution. On the western side, the highest levels of PAH contamination normalized to % TOC (1.29×10^4 at L12, 1.28×10^4 at L16, 0.55 at L13, and 0.54 at L15) were obtained from sediments collected at deposition sites near the outfall of the Petron Oil Refinery. On the eastern side, sediments located at the effluent zones of the Paranaque and Malabon Rivers showed excessively higher levels of PAH normalized to % TOC (3.32×10^4 and 2.87×10^4 , respectively) compared to those obtained from other sites in the area.

The PAH contamination in the sediments from Manila Bay is dominated by alkylated naphthalenes and phenanthrenes which are associated with petrogenic sources. This indicates that the surface sediments in Manila Bay are exposed to chronic contamination of petroleum hydrocarbons introduced mainly by direct spillage on the western side and by urban run-off on the eastern side.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAH) are potentially toxic compounds released to the environment by spillage of petroleum (petrogenic sources), and by combustion of fossil fuels and other organic materials (pyrolytic sources). They are extremely hydrophobic compounds that tend to associate with natural particulates in the atmosphere, water, and soil (NAP 1985). They may eventually sink as components of sediments to the bottom of waterways, rivers, estuaries, and the open sea. The analysis of PAH in sediments has become

an important tool in determining the source of PAH contamination and in assessing the bioavailability of the PAH to benthic organisms.

In petrogenic sources, the PAH distribution is dominated by the alkylated homologs of naphthalene and phenanthrenes while in pyrolytic sources, the parental PAH are more predominant than their alkylated homologs (Giger and Blumer 1974; Youngblood and Blumer 1975; Wakeham et al. 1980). Low temperature combustion of fossil fuels like diesel fuel, generate alkylated PAH, as well as parental PAH like pyrene and flouranthene associated with combustion (Rogge et al. 1993). The combustion of gasoline and bunker fuel give PAH signatures with predominance of high molecular-weight PAH

Key words: hydrocarbon contamination, polycyclic aromatic hydrocarbons, coastal sediments, levels of hydrocarbon contamination.

likbenzo (ghi) perylene, indenopyrene, benzofluoranthenes, and benzopyrenes (Rogge et al. 1993). Unused crankcase oil gives molecular PAH signatures similar to the higher fractions of crude oil, but used crankcase oil can contribute pyrolytic PAH like benzopyrenes not normally found in crude oil (Pruell and Quinn 1988). It is shown that alkylated naphthalenes and phenanthrenes are more available to benthic organisms because of their relative ease of dissolution in water (NAP 1985). On the other hand, high molecular weight combustion PAH benzopyrenes and dibenzoanthracenes are more toxic than the alkylated homologs of naphthalenes and phenanthrenes, but are less available to the benthic organisms (NAP 1985). Since pyrolytic PAH are occluded in the sediments, the PAH distribution of marine sediments normally reflects a pyrolytic source. However, in environments where there is dumping of petroleum compounds, the PAH distribution shows contributions from petrogenic sources (Bayona et al. 1991).

This study is the first attempt to determine the PAH levels and to characterize the PAH contamination in sediments in Manila Bay. The molecular signatures of PAH in the sediments were determined by analysis of 18 PAH compounds. The PAH composition was assessed to determine possible sources of the contamination. The spatial distribution of the levels of contamination in the sediments was assessed in relation to known point sources of hydrocarbon contamination in the bay.

MATERIALS AND METHODS

Study Site Description and Sampling Locations

Two specific areas within Manila Bay were examined (Fig. 1a). The first area is located on the western side of Manila Bay, along the coast of Limay and Lamao towns in Bataan Province. Samples sites were selected in a gradient distribution around the Petron Refinery's marine outfall and the NPC Power Plant outfall (Fig. 1b).

The second area is located on the eastern side of Manila Bay along the coast of the heavily populated and industrialized Metro Manila and Cavite province. Four sample sites in this area, E1, E2, E9, and E14, were selected to coincide with the effluent zones of four major tributaries draining run off from the Metro Manila area (Fig. 1c). The rest of the samples were selected along offshore transects.

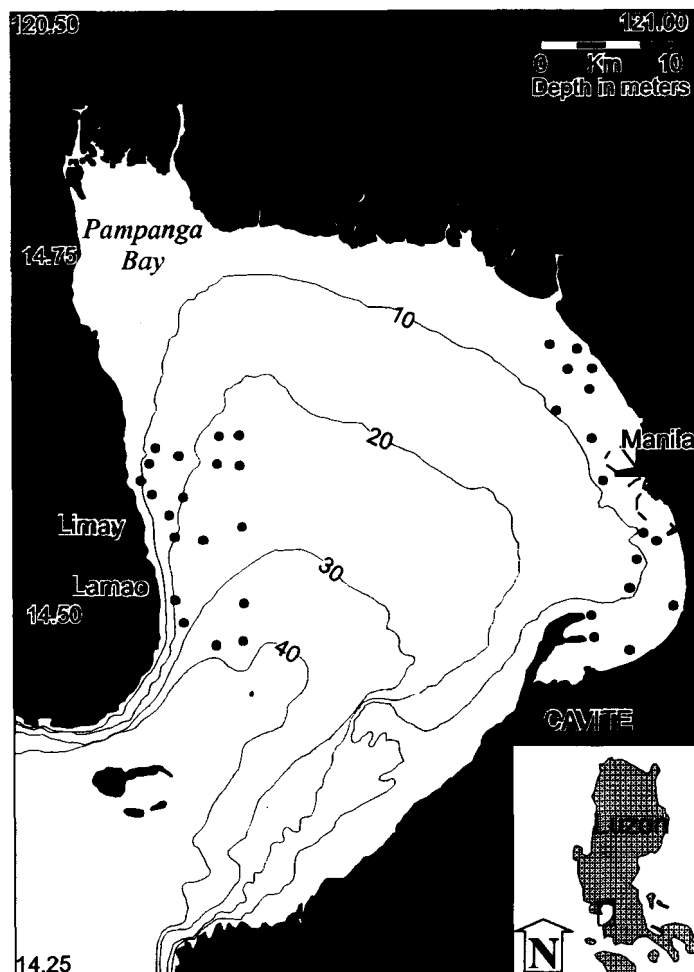


Fig. 1a. Map of Manila Bay showing the study sites and sampling locations.

Sampling and Analysis

Nineteen sediment samples from the western coast and sixteen sediment samples from the eastern coast were obtained using an Eckmann dredge sampler. The upper six-centimeter layer was air-dried. The fine-sized fractions were used for the analysis of moisture, %TOC, and PAH content of the sediment.

The %TOC in the sediment was determined using a LECO gas fusion furnace after removal of inorganic carbon.

The air-dried sediment was extracted with 90 ml of dichloromethane and 30 ml of methanol at room temperature under reflux with sonication for 6 hours. The crude extract was passed through a 2 x 50 cm glass column containing 5

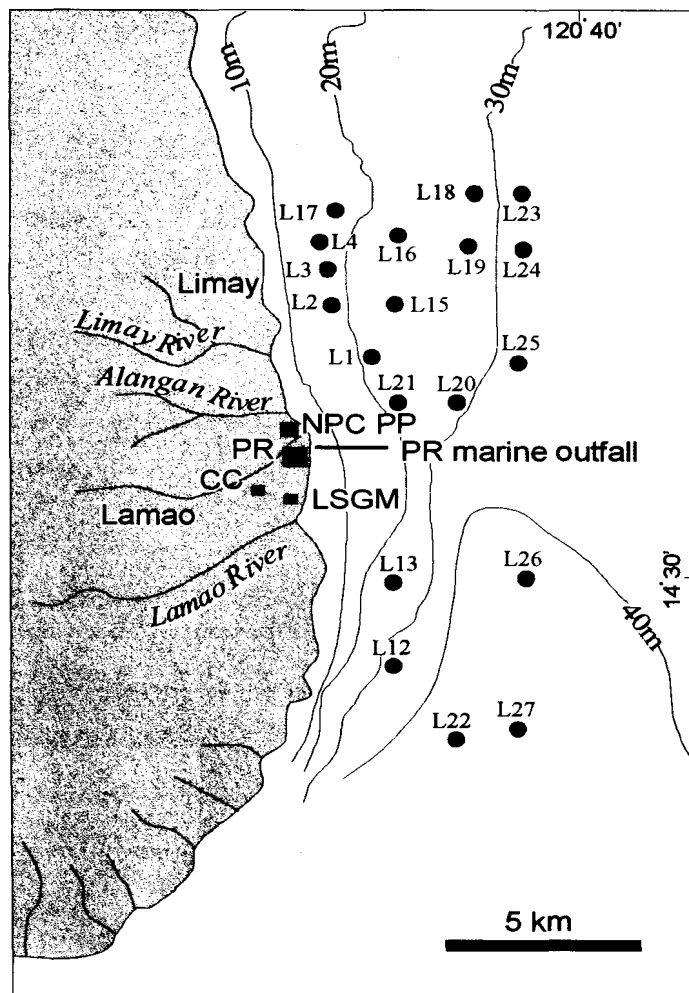


Fig. 1b. Western Manila Bay sites showing the sample sites and depth contours, river tributaries and possible point sources of PAH. The rectangles represent the industrial sites including Petron Refinery (PR) and its marine outfall, National Power Corporation Power Plant (NPC PP), the Columbian Carbon Plant (CC), and the Limay Slag Grinding Mill (LSGM). Sampling sites are represented as circles.

grams of deactivated alumina and the combined saturated and aromatic hydrocarbons was eluted with 30 ml of 25% dichloromethane in hexane. The saturated and aromatic fractions in the dried extract obtained from the alumina column were separated by column chromatography using 5 grams of fully activated silica gel; the saturated fraction was eluted with 30 ml hexane while the aromatic fraction was eluted with 25 ml of 10% dichloromethane in hexane. The neat residues of the fractions were weighed to obtain the amount in ug/g of the saturated and aromatic hydrocarbons in the sediment.

The PAH in the aromatic fraction were analyzed using Varian

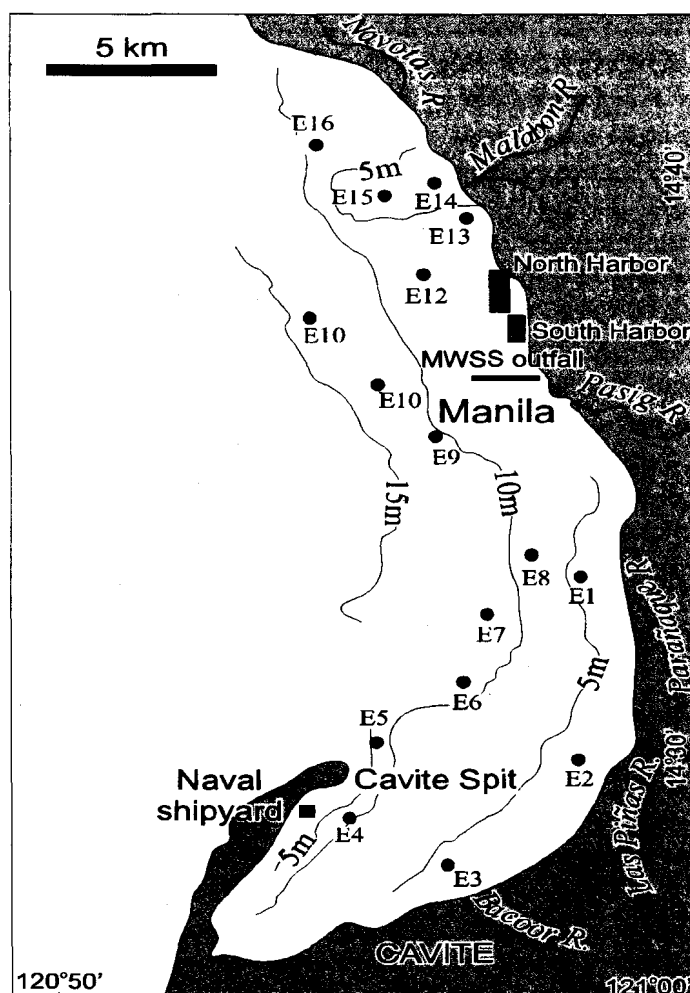


Fig. 1c. Eastern Manila Bay sites showing sample sites and depth contours, river tributaries, and possible point sources (rectangles) of PAH. Sampling sites are represented by circles.

Saturn IV GC/MS/MS with the gas chromatograph equipped with a 1093 SPI injector and the mass spectrometer with an ultra trace ion trap detector. The gas chromatograph was coupled to a 60 x 0.25 mm id fused silica column coated with 5% phenylmethylsilicone (DB-5. J and W Scientific). Using helium as carrier gas, the gas chromatograph was set to a temperature program, with initial temperature of 40°C, temperature rise of 4°C/min up to 290°C and a hold for 25min at 290°C. The mass spectrometer was set up in the electron impact mode with a mass range from 60 to 290 m/z and scantime of 1 sec.

The extracted ion chromatogram for the target ion for each

PAH was obtained from the total ion chromatograms. The PAH were identified by a comparison of the retention time and the mass spectra obtained for the target ions with those of authentic standards. The mass spectra were also compared with those derived from the INCO_S library of mass spectra. Where no standards were available, the relative retention times published in the literature and the mass spectra from the library were used to identify the peaks.

Quantification was done by integrating the extracted ion chromatograms. The integrated peaks of the extracted ion chromatograms of the authentic standards were used in an external calibration to obtain the response factors for the PAH. The response factors for methyl phenanthrene and trimethylphenanthrene were assumed to be similar with dimethylphenanthrene for lack of standards.

The method was validated using NIST reference material 1941a. Recovery values for most PAH range between 70 to 98 % except for chrysene and indenopyrene, which gave below 60% recovery. The procedural blank did not give any PAH; a minimum quantification limit of 1ng/gram was estimated for the method. Reported concentration values were not corrected for recovery.

Analysis of PAH Data

For the determination of the molecular distribution profiles, the PAH concentrations were normalized to the obtained total of PAH concentration. The normalized concentrations were used to plot the distribution of PAH in the sediment. The molecular distributions of PAH in the sediments were compared with profiles from primary sources of PAH.

RESULTS

%Total Organic Carbon (%TOC), Total Saturated Hydrocarbons (TSH), Total Aromatic Hydrocarbons (TAH) and Total Polycyclic Aromatic Hydrocarbons (TPAH)

Table 1 lists the depth of sampling sites, grain size distribution of sediments, total organic carbon, and hydrocarbon content of the surface sediments.

The percentage of TOC (%TOC) in the sediments includes

all anthropogenic organic pollutants, as well as biogenic substances from marine and terrestrial sources. The %TOC values of the sediments from the western side are more homogeneous, ranging from 0.98 to 1.93. On the eastern side, %TOC values are more varied ranging from 0.4 to 2.84.

The Total Saturated Hydrocarbons (TSH) include all non-polar hydrocarbons that are eluted by hexane from the silica/alumina column. Examples are straight chain hydrocarbon n-alkanes, the branched hydrocarbons, possible alkylated cyclic and acyclic alkenes and some alkylated benzenes and chlorinated hydrocarbons. The fraction called Total Aromatic Hydrocarbons (TAH) includes the polycyclic aromatic hydrocarbons, alkylated polycyclic hydrocarbons, acyclic and cyclic unsaturated compounds, as well as slightly polar substituted aromatic compounds that can be eluted with 25% dichloromethane in hexane from the silica/alumina column.

Normalization of the hydrocarbon concentrations of the sediments to its %TOC would correct the variability of the hydrocarbon concentrations in the sediments, which is caused by the difference of the surface area of organic coatings of the sediments. Thus, normalization of the concentrations to %TOC would allow a more standardized comparison of the hydrocarbon concentrations of the sediments.

On the western side (Table 1), the sites that gave the highest values for the saturated hydrocarbons are L1, L2, L3, L4, which are located around the outfall of the Petron refinery and the NPC power plant, and L13, which is found near the outlet of the Lamao River. Among all the sites on the western side, only L12 gave higher aromatic hydrocarbons than saturated hydrocarbons.

On the eastern side (Table 1), the highest levels of saturated and aromatic fractions are found in the sediments of the E1 and E14, sites near the outlet of Pasay and Malabon-Navotas rivers, respectively. The sites that gave the next highest values are E4, a site near the dockyard of navy vessels at Sangley Point in Cavite City; E9, a site near the Metropolitan Waterworks and Sewerage System (MWSS) sewage outfall and about 7 kilometers offshore from the outlet of the Pasig River; and E10, just within the North Harbor. It is likely that these sites have high values of saturated and aromatic hydrocarbons because of their proximity to the known point sources of hydrocarbon contamination.

The TPAH levels on the western side (Table 1) are highest at

Table 1. Depth of sampling site, grain size distribution of sediments, total organic carbon and hydrocarbon content of the surface sediments from Manila Bay

Sample Site	Depth m	Grain Size % silt-clay	%TOC*	TSH** g/g, dried wt	TSH%TOC x 10000	TAH*** ug/g, dried wt	TAH%TOC x 10000	TPAH**** ug/g, dried wt	TPAH%TOC
L1	19.0	92	0.98	149	152	56	57	0.64	0.66
L2	12.0	85	1.31	184	140	56	43	0.73	0.56
L3	15.0	99	0.98	262	267	94	96	0.13	0.13
L4	15.0	99	1.24	261	210	59	48	0.29	0.23
L12	30.0	90	1.35	176	131	190	141	1.74	1.29
L13	28.0	95	1.35	217	160	134	99	0.34	0.25
L14	26.0	60	1.35	115	85	23	17	0.74	0.55
L15	23.0	86	1.36	86	63	6	5	0.73	0.54
L16	27.0	99	1.25	92	73	13	10	1.61	1.28
L17	27.0	9	1.33	104	78	0	0	0.40	0.30
L18	28.0	90	1.13	88	77	6	6	0.32	0.29
L19	28.0	94	1.13	131	116	11	10	0.22	0.19
L20	28.0	93	1.33	88	66	16	12	0.47	0.35
L22	45.0	96	1.64	92	56	17	11	1.46	0.89
L23	30.0	86	1.68	171	102	29	18	0.52	0.31
L24	32.0	98	1.89	174	92	43	23	0.85	0.45
L25	37.0	97	1.93	175	91	32	17	0.57	0.30
L26	42.0	96	1.79	180	101	42	23	0.99	0.55
L27	42.0	96	1.58	125	79	31	20	0.57	0.36
E1	2.7	9	0.40	665	1661	100	250	0.65	1.61
E2	1.8	27	2.84	3822	346	649	228	9.42	3.32
E3	2.7	80	0.96	222	231	27	28	0.60	0.62
E4	6.4	86	1.11	792	714	161	145	1.30	1.17
E5	7.0	67	1.01	364	361	36	36	0.73	0.73
E6	9.5	75	1.60	466	292	70	44	0.51	0.32
E7	11.2	80	1.42	466	328	97	69	1.06	0.75
E8	4.3	58	0.65	120	185	26	41	0.21	0.32
E9	12.0	93	1.55	1048	676	125	81	1.50	0.97
E10	11.5	83	1.48	861	582	140	95	1.18	0.79
E11	13.0	78	1.34	609	454	117	88	1.05	0.78
E12	9.4	74	1.60	640	400	126	79	0.46	0.29
E13	5.6	62	1.23	488	397	146	119	1.15	0.94
E14	3.7	70	2.51	3010	1199	755	301	7.21	2.87
E15	2.5	16	0.44	193	440	32	72	0.19	0.43
E16	9.0	75	1.14	307	269	60	53	0.48	0.42

*Total organic carbon, **Total saturated hydrocarbons, ***Total aromatic hydrocarbons, ****Total polycyclic aromatic hydrocarbons-sum of 18 PAH reported

L12, followed by L16 and L22. High values were observed in sampling sites L1, L2, L14, L15, L20, L24, L26, and L27, which are close to the outfall of the refinery. L24, L20, L26, and L27 could be deposition sites for fine sediments because of their depth, proximity to the source, and position along the

predicted current flow.

The TPAH levels on the eastern side (Table 1) are highest at E2 and E14, consistent with the results for the total saturated and aromatic hydrocarbons. High TPAH levels at sites E1,

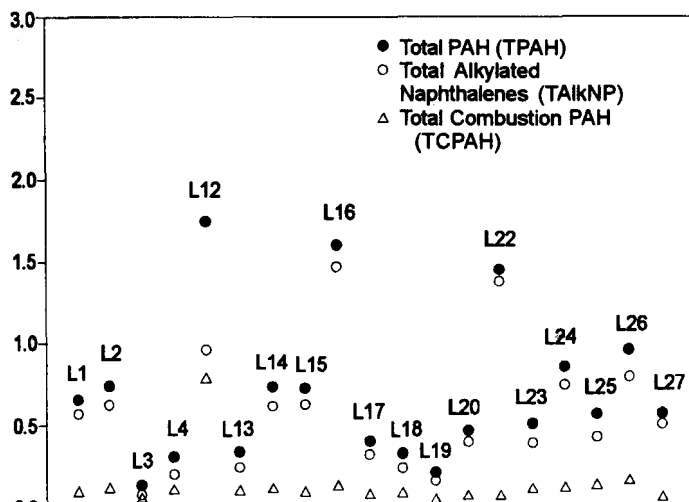


Fig. 2a. Plot of Total PAH, Total Alkylated Naphthalenes and Phenanthrenes (TAlkNP), and Total Combustion PAH (TCPAH) in surface sediments on western Manila Bay.

E4, and E9 are consistent with similarly high levels of total saturated and total aromatic hydrocarbons at these sites.

Alkylated PAH and Parental PAH

Concentration levels in the sediments

Table 2 shows the concentration of the individual PAH in the surface sediments together with values of the total PAH (TPAH), total alkylated naphthalenes and phenanthrenes (TAlkNP), and total parental PAH (TCPAH). The Apparent Effects Threshold (AET) for some of the PAH are also indicated. Fig. 2a shows that, in almost all the samples on the western side, the TAlkNP constitutes most of the TPAH, while much lower values of TCPAH in the range of 0.05 to 0.21 $\mu\text{g/g}$ were obtained. A notable exception is L12, which shows an almost equal distribution of TAlkNP and TCPAH (0.96 and 0.78 $\mu\text{g/g}$, respectively), and which gives the highest TPAH on the western side when combined. The two other sites, which gave relatively high values of TPAH and TAlkNP, are L16 and L22, the latter being the deepest sampling site on the western side. The least contaminated site is L3, where TAlkNP and TCPAH are lowest, at 0.08 and 0.05 $\mu\text{g/g}$, respectively. Fig. 2b indicates a similar pattern on the eastern side, where all sediment samples have higher concentration

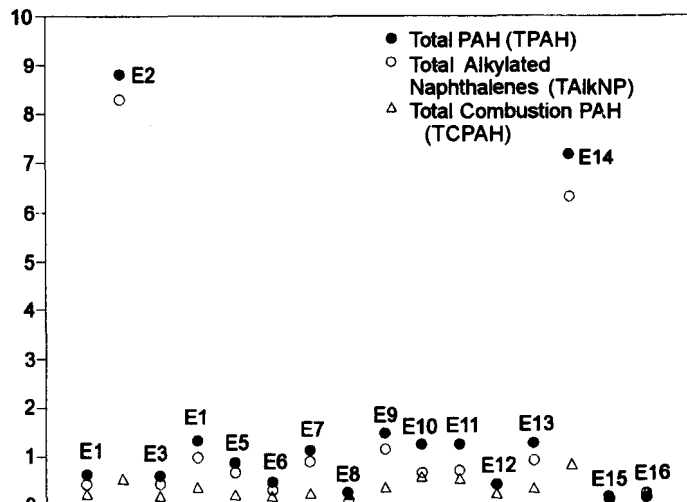


Fig. 2b. Plot of total PAH (TPAH), total alkylated naphthalenes and phenanthrenes (TAlkNP), and total combustion parental PAH (TCPAH) in surface sediments in Eastern Manila Bay.

values for the TAlkNP compared to the parental PAH. Sediments from two sites, E2 and E14, yielded exceptionally high values of TPAH, of which almost 90% were TAlkNP. Although the parental PAH is generally lower than the alkylated PAH, the range of concentration (0.06 to 1.02 $\mu\text{g/g}$) in the samples from the eastern side is higher compared to those from the western side. With the exception of E2 and E4, the ratio of the TAlkNP to TCPAH in the eastern samples is lower than in the western samples. The lowest values for the TAlkNP and TCPAH on the eastern side were obtained at E15, which is the shallowest of the sampling sites.

Concentration profiles of PAH in sediments

Table 3 lists the normalized concentrations of PAH in the surface sediment samples. The profiles of the PAH from the western side are almost uniform, indicating predominance of the alkylated homologs of naphthalenes. Exceptions are the profiles at L3, L12, and L13 where the alkylated phenanthrene homolog P3 is dominant. On the eastern side, the profiles are more varied, with the alkylated naphthalenes predominating in E3, E4, E5, E6, E7, E11, E13, and E16 and the alkylated phenanthrenes predominating at E1, E2, E9, E12, E14, and E15. Figs. 3a-f compare the profiles of selected samples with the profiles of selected primary sources of PAH.

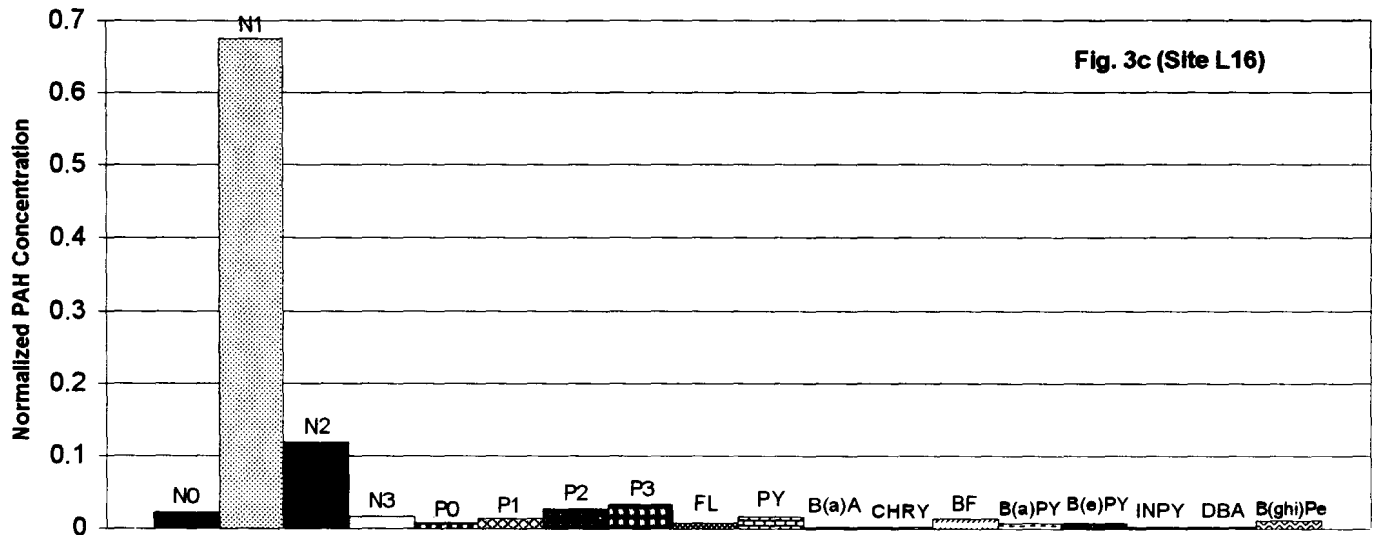
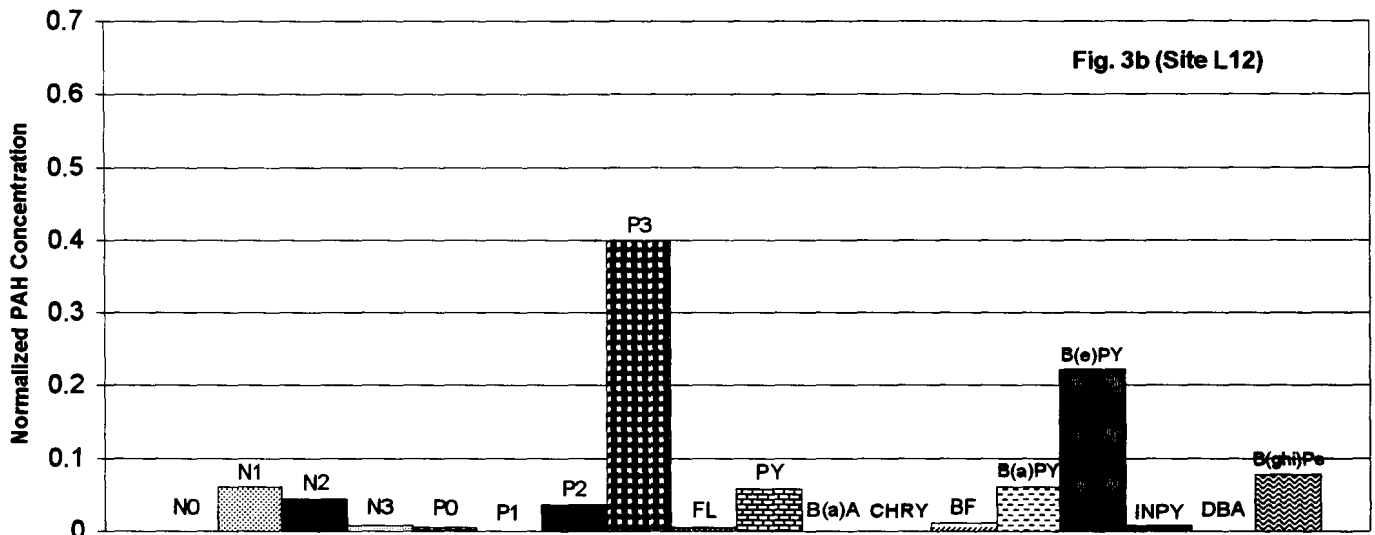
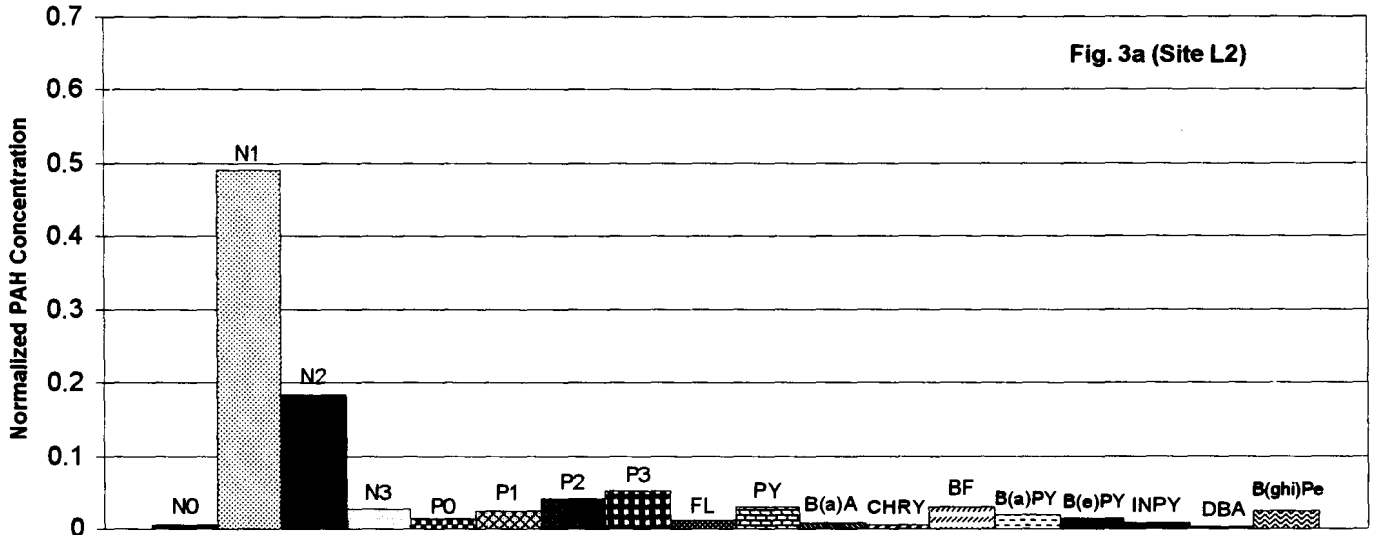
Table 2. Concentrations of individual PAH (ug/g, dried wt.), TPAH*, TALKNP**, TCPAH*** Manila Bay surface sediments and Apparent Effects Threshold (AET)**** for individual PAH.

SAMPLE	NO	N1	N2	N3	PO	P1	P2	P3	FL	PY	B(a)A	CHR(Y)	BF	B(e)P(Y)	B(e)P(Y)	INPY	DBA	B(ghi)Pe	TPAH	TALKNP	TCPAH
L1	0.006	0.371	0.115	0.017	0.008	0.012	0.020	0.014	0.007	0.014	0.003	0.004	0.016	0.006	0.006	0.006	0.002	0.017	0.647	0.564	0.081
L2	0.004	0.361	0.135	0.020	0.011	0.019	0.031	0.038	0.009	0.021	0.006	0.004	0.021	0.014	0.011	0.006	0.002	0.020	0.736	0.620	0.114
L3	LDL#	LDL	0.010	0.005	0.005	0.012	0.020	0.024	0.004	0.004	0.002	0.002	0.009	0.008	0.006	0.005	0.003	0.010	0.131	0.076	0.052
L4	LDL	0.030	0.046	0.018	0.002	0.020	0.039	0.038	0.011	0.019	0.007	0.003	0.014	0.007	0.007	0.007	0.001	0.025	0.296	0.193	0.101
L12	LDL	0.105	0.077	0.015	0.009	LDL	0.062	0.695	0.011	0.103	0.000	0.000	0.020	0.106	0.387	0.015	0.002	0.135	1.744	0.963	0.779
L13	LDL	0.041	0.038	0.011	0.008	0.012	0.020	0.113	0.005	0.009	0.002	0.001	0.023	0.016	0.012	0.006	0.001	0.021	0.339	0.242	0.085
L14	LDL	0.247	0.174	0.032	0.012	0.051	0.015	0.064	0.016	0.022	0.005	0.005	0.018	0.009	0.009	0.009	0.001	0.041	0.736	0.596	0.134
L15	0.004	0.403	0.116	0.019	0.010	0.018	0.031	0.026	0.006	0.011	0.005	0.005	0.020	0.013	0.013	0.010	0.000	0.014	0.729	0.628	0.097
L16	0.038	1.084	0.190	0.028	0.014	0.020	0.046	0.055	0.013	0.027	0.005	0.005	0.023	0.012	0.013	0.006	0.003	0.019	1.603	1.475	0.126
L17	LDL	0.157	0.060	0.013	0.009	0.013	0.029	0.030	0.007	0.016	0.003	0.002	0.014	0.008	0.009	0.006	0.001	0.014	0.403	0.321	0.080
L18	LDL	0.085	0.072	0.016	0.010	0.014	0.024	0.018	0.007	0.013	0.003	0.005	0.020	0.009	0.010	0.005	0.001	0.012	0.328	0.241	0.085
L19	LDL	0.083	0.031	0.007	0.009	0.009	0.016	0.015	0.004	0.008	0.002	0.002	0.007	0.004	0.005	0.003	0.001	0.011	0.218	0.169	0.048
L20	LDL	0.187	0.113	0.022	0.011	0.019	0.025	0.024	0.008	0.015	0.002	0.003	0.011	0.007	0.006	0.005	0.001	0.007	0.469	0.401	0.065
L22	LDL	0.964	0.248	0.036	0.011	0.031	0.045	0.036	0.012	0.006	0.002	0.003	0.015	0.006	0.006	0.005	0.001	0.024	1.456	1.371	0.081
L23	LDL	0.141	0.101	0.031	0.017	0.031	0.041	0.038	0.013	0.014	0.003	0.005	0.023	0.013	0.006	0.011	0.002	0.022	0.517	0.400	0.113
L24	LDL	0.411	0.158	0.031	0.019	0.034	0.048	0.047	0.013	0.010	0.003	0.004	0.019	0.011	0.013	0.006	0.002	0.010	0.843	0.748	0.090
L25	LDL	0.094	0.104	0.030	0.023	0.043	0.069	0.069	0.014	0.017	0.004	0.005	0.029	0.017	0.010	0.015	0.003	0.022	0.570	0.431	0.135
L26	LDL	0.399	0.168	0.033	0.007	0.043	0.067	0.067	0.027	0.048	0.007	0.010	0.024	0.011	0.017	0.013	0.002	0.046	0.993	0.783	0.207
L27	LDL	0.282	0.104	0.020	0.011	0.032	0.031	0.031	0.004	0.009	0.003	0.003	0.012	0.005	0.009	0.005	0.001	0.007	0.573	0.511	0.060
E1	0.001	0.080	0.055	0.028	0.009	0.040	0.015	0.199	0.017	0.044	0.011	0.006	0.026	0.021	0.013	0.015	0.003	0.058	0.643	0.428	0.213
E2	0.019	0.664	0.486	0.464	0.135	LDL	1.960	4.616	0.088	0.334	0.051	0.117	0.075	0.031	0.022	0.047	0.009	0.250	9.436	8.354	1.024
E3	0.001	0.152	0.117	0.025	0.018	0.034	0.049	0.047	0.021	0.014	0.012	0.011	0.026	0.011	0.009	0.011	0.002	0.045	0.605	0.444	0.160
E4	0.015	0.538	0.301	0.058	0.024	0.005	0.024	0.014	0.017	0.028	0.014	0.009	0.056	0.062	0.025	0.032	0.010	0.081	1.318	0.978	0.334
E5	0.028	0.372	0.097	0.016	0.009	0.037	0.065	0.044	0.011	0.010	0.006	0.008	0.015	0.006	0.005	0.005	0.001	0.020	0.758	0.667	0.088
E6	LDL	0.068	0.064	0.013	0.018	0.038	0.061	0.049	0.021	0.037	0.008	0.008	0.035	0.013	0.010	0.014	0.002	0.052	0.513	0.311	0.199
E7	0.001	0.359	0.247	0.084	0.018	0.054	0.074	0.060	0.017	0.019	0.012	0.008	0.029	0.011	0.008	0.013	0.002	0.041	1.062	0.897	0.160
E8	LDL	LDL	0.005	0.007	0.011	0.015	0.016	0.012	0.013	0.017	0.012	0.012	0.032	0.014	0.005	0.008	0.003	0.032	0.215	0.066	0.147
E9	0.001	0.100	0.059	0.022	0.031	0.129	0.231	0.564	0.024	0.068	0.024	0.013	0.056	0.052	0.027	0.027	0.007	0.053	1.469	1.138	0.352
E10	0.001	0.130	0.088	0.020	0.042	0.105	0.173	0.112	0.043	0.075	0.032	0.038	0.079	0.036	0.022	0.027	0.010	0.133	1.181	0.672	0.466
E11	0.001	0.182	0.185	0.044	0.025	0.084	0.125	0.058	0.025	0.041	0.029	0.026	0.060	0.022	0.012	0.022	0.003	0.092	1.056	0.714	0.333
E12	LDL	LDL	0.027	0.012	0.024	0.025	0.062	0.045	0.022	0.044	0.014	0.024	0.038	0.022	0.018	0.017	0.003	0.051	0.456	0.195	0.254
E13	0.004	0.418	0.209	0.042	0.017	0.026	0.113	0.102	0.015	0.037	0.018	0.015	0.035	0.016	0.010	0.014	0.002	0.067	1.161	0.933	0.220
E14	0.006	1.237	0.969	0.731	0.071	0.257	1.072	2.014	0.067	0.269	0.039	0.063	0.071	0.027	0.019	0.051	0.010	0.156	7.176	6.357	0.771
E15	LDL	LDL	0.011	0.005	0.008	0.022	0.036	0.048	0.007	0.010	0.003	0.003	0.013	0.007	0.005	0.004	0.001	0.003	0.188	0.130	0.056
E16	LDL	0.056	0.086	0.023	0.015	LDL	0.045	0.025	0.015	0.025	0.007	0.009	0.043	0.023	0.004	0.020	0.005	0.074	0.479	0.250	0.225
AET****	0.50	0.30			0.26			1.00	1.00	0.55	0.90		0.70			0.10					

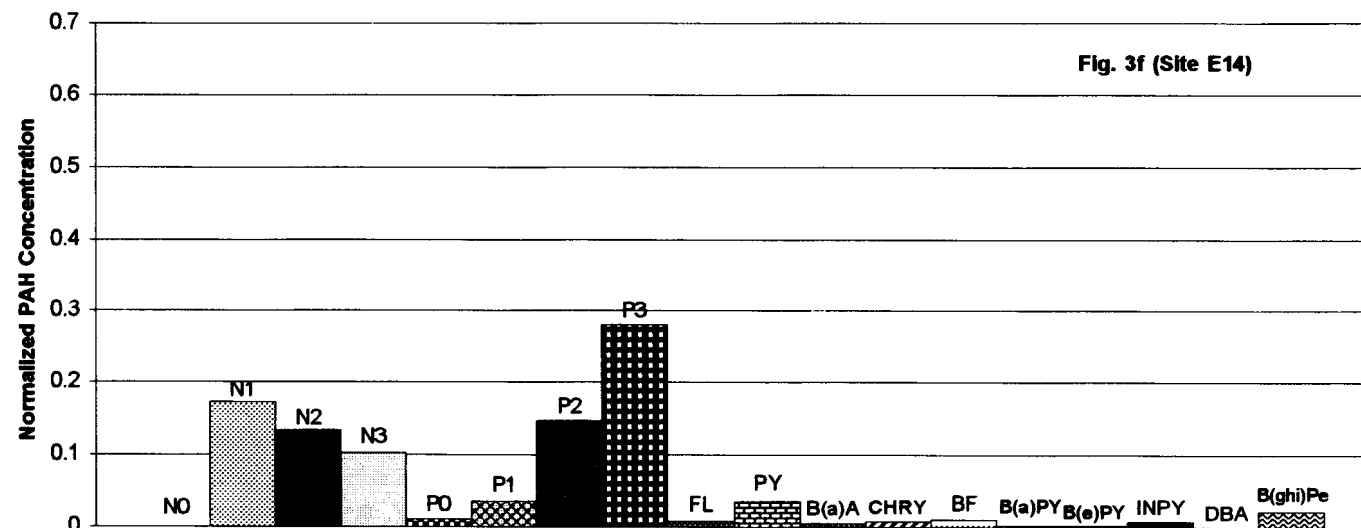
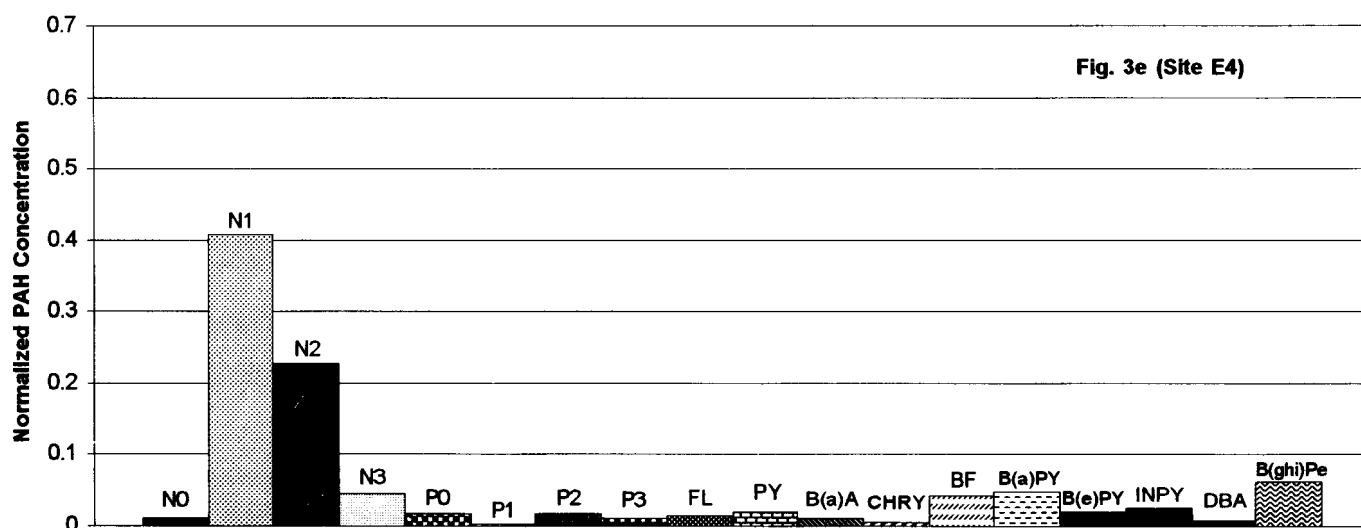
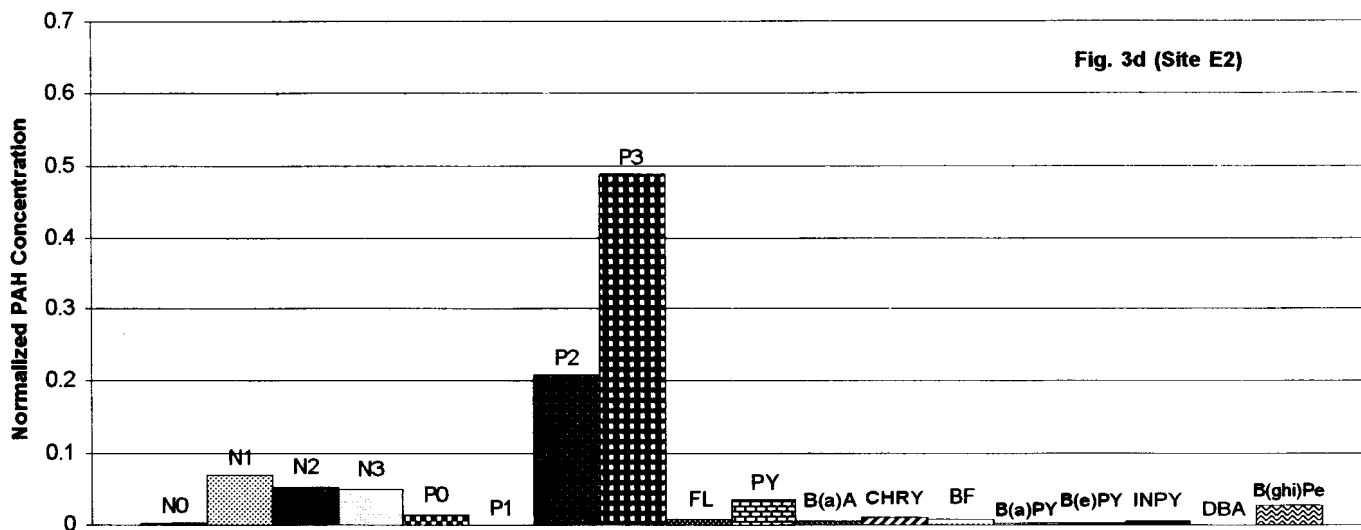
Less than the quantification, assigned 0.001 ug/g
 *** sum of Fl, Py, B(a)Py, B(e)Py, IndPy, DBA and B(ghi)Pe
 **** sum of 18 PAH reported
 ***** apparent effects threshold (Long and Morgan, 1990)
 ** sum of NO, N1, N3, PO, P1, P2, P3

Table 3. Normalized concentrations of PAH in the surface sediment samples in Manila Bay.

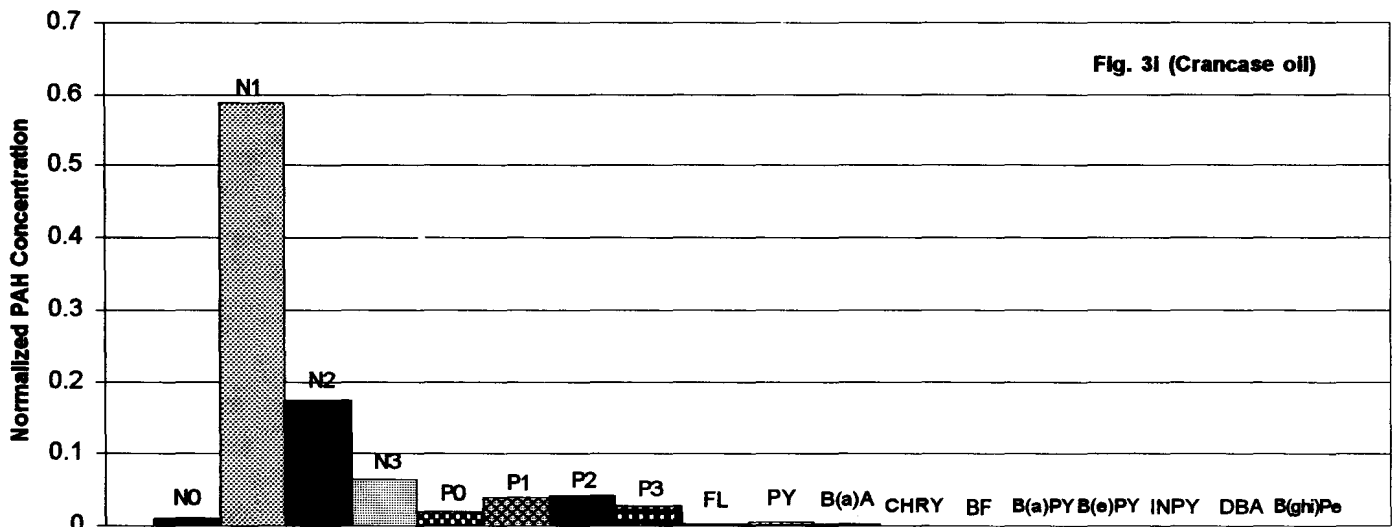
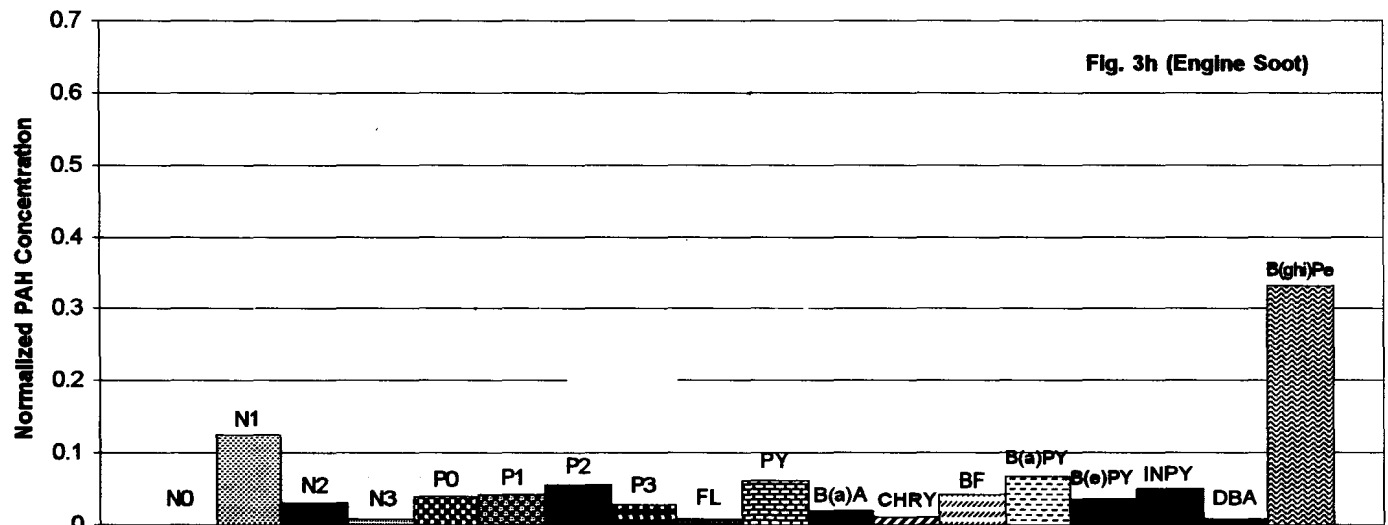
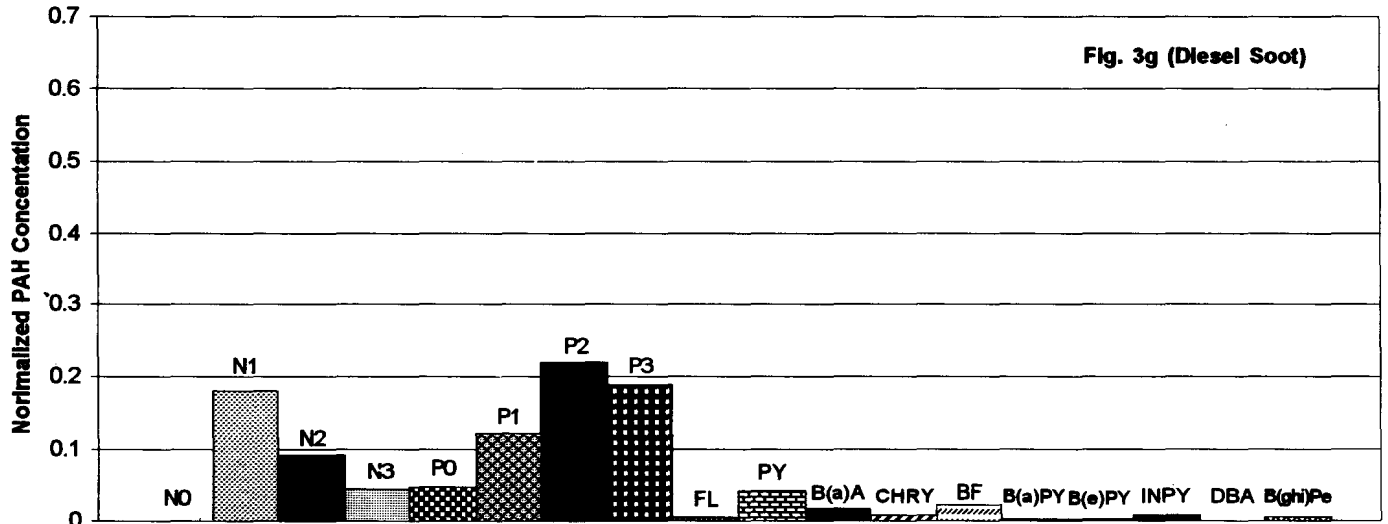
SAMPLE	NO	N1	N2	N3	PO	P1	P2	P3	F	ANT	FL	PY	BaA	CHRY	BF	BaPY	BePY	INPY	DBA	B(ghi)Pe
L1	0.010	0.579	0.179	0.027	0.013	0.018	0.032	0.022	0.002	0.002	0.010	0.022	0.005	0.006	0.026	0.010	0.009	0.010	0.003	0.026
L2	0.006	0.493	0.185	0.028	0.015	0.026	0.043	0.051	0.001	0.002	0.012	0.029	0.008	0.005	0.029	0.019	0.014	0.009	0.003	0.027
L3	0.000	0.000	0.080	0.035	0.037	0.089	0.151	0.186	0.018	0.006	0.027	0.028	0.016	0.017	0.071	0.060	0.049	0.035	0.020	0.077
L4	0.000	0.102	0.154	0.060	0.008	0.068	0.132	0.128	0.004	0.004	0.038	0.064	0.022	0.011	0.049	0.023	0.025	0.023	0.004	0.083
L12	0.000	0.060	0.044	0.009	0.005	0.000	0.035	0.399	0.000	0.001	0.006	0.059	0.000	0.000	0.042	0.061	0.222	0.008	0.001	0.077
L13	0.000	0.120	0.111	0.033	0.024	0.036	0.059	0.332	0.003	0.004	0.014	0.025	0.005	0.003	0.068	0.048	0.035	0.018	0.003	0.060
L14	0.000	0.336	0.237	0.043	0.016	0.069	0.021	0.087	0.004	0.003	0.022	0.030	0.007	0.007	0.024	0.012	0.012	0.012	0.002	0.055
L15	0.006	0.556	0.161	0.027	0.014	0.025	0.043	0.036	0.001	0.002	0.009	0.015	0.006	0.007	0.028	0.018	0.018	0.014	0.000	0.020
L16	0.024	0.693	0.122	0.018	0.009	0.013	0.030	0.035	0.000	0.001	0.009	0.017	0.003	0.003	0.015	0.007	0.008	0.004	0.002	0.012
L17	0.000	0.413	0.149	0.033	0.022	0.033	0.072	0.074	0.003	0.003	0.018	0.040	0.007	0.005	0.035	0.020	0.022	0.014	0.003	0.034
L18	0.000	0.260	0.220	0.049	0.032	0.043	0.072	0.056	0.003	0.004	0.022	0.040	0.011	0.015	0.060	0.027	0.030	0.016	0.002	0.038
L19	0.000	0.381	0.141	0.031	0.042	0.042	0.073	0.068	0.000	0.003	0.017	0.038	0.011	0.010	0.034	0.016	0.022	0.016	0.004	0.052
L20	0.000	0.400	0.242	0.046	0.024	0.040	0.053	0.051	0.002	0.003	0.018	0.032	0.005	0.006	0.024	0.015	0.012	0.010	0.002	0.016
L22	0.000	0.662	0.170	0.025	0.007	0.022	0.031	0.025	0.001	0.001	0.008	0.004	0.002	0.002	0.010	0.004	0.004	0.003	0.001	0.016
L23	0.000	0.272	0.195	0.061	0.032	0.061	0.080	0.074	0.002	0.005	0.025	0.027	0.006	0.011	0.045	0.024	0.012	0.022	0.005	0.042
L24	0.000	0.488	0.187	0.037	0.023	0.041	0.057	0.056	0.001	0.003	0.015	0.012	0.003	0.005	0.022	0.013	0.016	0.007	0.003	0.012
L25	0.000	0.164	0.183	0.052	0.040	0.076	0.120	0.120	0.002	0.005	0.024	0.029	0.008	0.009	0.051	0.029	0.017	0.026	0.005	0.039
L26	0.000	0.402	0.169	0.034	0.007	0.043	0.067	0.067	0.001	0.001	0.028	0.049	0.007	0.010	0.024	0.011	0.017	0.014	0.002	0.047
L27	0.000	0.492	0.181	0.035	0.020	0.056	0.054	0.054	0.002	0.003	0.007	0.016	0.005	0.005	0.021	0.009	0.017	0.010	0.002	0.013
E1	0.002	0.125	0.086	0.044	0.014	0.062	0.023	0.311	0.002	0.002	0.027	0.068	0.017	0.009	0.041	0.033	0.020	0.023	0.005	0.090
E2	0.002	0.071	0.053	0.049	0.014	0.000	0.208	0.490	0.001	0.005	0.009	0.036	0.005	0.012	0.008	0.003	0.002	0.005	0.001	0.027
E3	0.002	0.252	0.193	0.041	0.030	0.057	0.082	0.078	0.000	0.002	0.035	0.023	0.020	0.018	0.043	0.018	0.014	0.018	0.003	0.075
E4	0.012	0.413	0.231	0.045	0.018	0.004	0.018	0.011	0.000	0.004	0.013	0.021	0.011	0.007	0.043	0.048	0.019	0.025	0.008	0.062
E5	0.038	0.510	0.132	0.022	0.012	0.051	0.089	0.060	0.003	0.001	0.015	0.013	0.009	0.011	0.020	0.009	0.008	0.007	0.001	0.028
E6	0.000	0.133	0.125	0.025	0.036	0.074	0.118	0.095	0.000	0.006	0.040	0.072	0.015	0.015	0.068	0.025	0.020	0.027	0.005	0.101
E7	0.001	0.339	0.233	0.080	0.017	0.051	0.069	0.056	0.002	0.002	0.016	0.018	0.011	0.007	0.028	0.010	0.007	0.012	0.002	0.039
E8	0.000	0.000	0.025	0.034	0.049	0.069	0.074	0.054	0.000	0.012	0.060	0.079	0.054	0.054	0.148	0.064	0.022	0.039	0.015	0.148
E9	0.001	0.067	0.040	0.015	0.021	0.086	0.154	0.377	0.001	0.005	0.016	0.046	0.016	0.009	0.037	0.035	0.018	0.018	0.005	0.035
E10	0.001	0.110	0.075	0.017	0.035	0.089	0.147	0.095	0.002	0.009	0.036	0.063	0.027	0.033	0.067	0.031	0.018	0.023	0.009	0.113
E11	0.001	0.173	0.175	0.041	0.023	0.079	0.119	0.065	0.003	0.006	0.023	0.039	0.027	0.024	0.057	0.021	0.012	0.021	0.003	0.087
E12	0.000	0.000	0.059	0.027	0.052	0.054	0.136	0.099	0.002	0.015	0.049	0.096	0.032	0.052	0.084	0.049	0.038	0.037	0.008	0.111
E13	0.004	0.361	0.181	0.037	0.015	0.023	0.098	0.088	0.003	0.005	0.013	0.032	0.016	0.013	0.030	0.014	0.008	0.012	0.002	0.049
E14	0.001	0.172	0.135	0.102	0.010	0.036	0.150	0.281	0.002	0.005	0.009	0.037	0.005	0.009	0.010	0.004	0.003	0.007	0.001	0.022
E15	0.000	0.000	0.056	0.028	0.044	0.117	0.190	0.257	0.006	0.008	0.035	0.054	0.017	0.018	0.068	0.036	0.025	0.022	0.006	0.015
E16	0.000	0.116	0.180	0.048	0.032	0.000	0.094	0.052	0.000	0.007	0.032	0.052	0.014	0.018	0.089	0.049	0.009	0.043	0.010	0.155



Figs. 3a-3c. PAH profiles of selected sediments from Western Manila Bay.



Figs. 3d-3f. PAH profiles of selected sediments from Eastern Manila Bay.



Figs. 3g-3i. PAH profiles of selected sediments from Eastern Manila Bay.

DISCUSSION

TSH, TAH, and TPAH and %TOC of the Surface Sediments

High levels of TSH, TAH, and TPAH correlate with high % TOC values in both the western and eastern sediments. High levels of petroleum hydrocarbons including PAH also correlate positively with proximity to the point source and to possible deposition areas (deeper areas near the point source with high distribution of silt-clay fraction). This is consistent with the observation of Boehm and Farrington (1984) in their study of the PAH geochemistry of recent sediments in the Georges Bank Region. With increasing water depth and hence increasing silt-clay content of the sediment, higher PAH concentrations were found. The relationship of PAH levels to silt-clay content and to %TOC suggests that sedimentological processes are the dominant determinants of the PAH levels in surface sediments.

On the eastern side of Manila Bay, high levels of PAH were observed at sites very close to the river outlets and known point sources of petroleum hydrocarbons at the naval shipyard, the North and South Harbors. Much lower levels observed at sites adjacent to these deposition sites within a distance of less than 2.5 kilometers suggest limited movement of sediments due to bottom currents.

On the western side, there are two areas where high PAH levels in the sediments were observed. Near the marine outfall of the refinery, relatively higher values were found on deeper sites within the area bounded 8 kilometers up north and 3 kilometers down south from the outfall of the refinery and about 10 kilometers eastward offshore from the outfall. This suggests that compared to the eastern side, fine sediments may be transported in wider areas. High values of PAH at sites L12, L22, L26, and L27 were observed at the lower part of the western coast. Two possibilities as to the source of contamination of these sediments may be considered. One possibility is that the source could also be the refinery and the finer sediments are transported to this far side of the bay because of the influence of tidal flow near the mouth of the bay, causing greater flushing of sediments from the upper part of the coast. The other possibility is that the same influence could force in more polluted sediments from the mouth of the bay to this part of the coast.

Concentration Profiles of PAH

The predominance of N1 and N2 homologs in sixteen out of the nineteen western sediments (except L3, L12, and L13) suggests that a petrogenic source is the major contributor of PAH in the sediments. It is possible that the refinery effluents and the spillage of crude oil from the oil terminal activities are major sources of the petrogenic N1 and N2, since higher concentrations of these compounds were observed in sediments close to the refinery outfall and the piers. On the eastern side, the predominance of N1 and N2 at E3 and E4 could be attributed to the motor boat activities in the fishing areas in Bacoor Bay and to the terminal activities at the naval shipyard near Cavite City. The proximity of L3 to the outlet of the Limay River and of L13 and L12 to the outlet of the Lamao River suggests that the diesel soot contamination could have been contributed by runoff from the rivers. The composition of the parental PAH in the majority of the sediments in both study sites is more or less uniform and is characterized by the predominance of B(ghi)Pe, BF, Py, and Fl while B(a)A, Chry, IndPy, and DBA are present in smaller amounts. This parental PAH profile may be regarded as the contamination largely representing input from combustion sources.

Using the AET values (Long and Morgan 1990) for evaluating the sedimentary contamination in Manila Bay (Table 2), the acceptable AET value of 0.3 ug/g for N1 is exceeded at L1, L2, L15, L16, L22, L24, and L26 on the western side and at E2, E4, E5, E7, E13, and E14 on the eastern side. The parental PAH in all the sediments are below the AET values. Again, this indicates that certain areas in Manila Bay are exposed to chronic contamination of weathered petroleum compounds that may already be harmful to the aquatic organisms in the bay. On the other hand, the parental PAH observed is generally low in the sediments.

Statistical Analysis of PAH Data from Surface Sediments

The t-test for the TPAH, TAlkNP and TCPAH values reported in Table 2 for the surface sediments showed that the mean concentration of TPAH and TAlkNP for the sediments in the western side and eastern side are not significantly different although the variances in the values of TPAH and TAlkNP in the sediments on both sides of the bay are different. TPAH and TAlkNP are more homogeneous in the western side

compared to the variability of the values for the sediments in the eastern side. On the other hand the t-test on the TCPAH of the sediments indicated that the variances in the TCPAH in the sediments on the western and eastern side are not significantly different although the means are significantly different. The mean of TCPAH values in the western side is much smaller than that of the eastern side.

CONCLUSION

The range of the concentration levels of PAH contamination of the sediments from the eastern side is higher (0.29- 3.32 x10000 normalized to %TOC) than the sediments from the western side (0.13-1.29 x 10000 normalized to %TOC). In both sides, the alkylated homologues of naphthalene and phenanthrene dominate the PAH distribution in almost all the sediments, indicating that the major input of PAH contamination in Manila Bay is petrogenic. The combined concentrations of the parental PAH associated with combustion namely, Fluoranthene (Fl), Pyrene (Py), Benzoanthracene (B(a)A), Chrysene (Chry), Benzofluoranthene (BF), Benzo(a)pyrene (B(a)Py), Benzo(e)pyrene (B(e)Py), Indenopyrene (IndPy), and Benzo(ghi)perylene (B(ghi)Pe) constitute a much smaller contribution to the PAH in the sediments.

The levels of TPAH and TALKNP among the sediments on the western side are more homogeneous than the corresponding levels of hydrocarbons among the sediments on the eastern side; however, the mean (absolute) concentration for TPAH and TALKNP in the sediments for both sides of the bay are not significantly different. The levels of TCPAH, which are associated with combustion, are lower in the sediments on the western side compared to the levels in the sediments on the eastern side.

The distribution of the PAH contamination in the surface sediments within the areas investigated indicated that proximity to the point source of pollution and depth of deposition of sediments are the primary factors that influence the levels of PAH contamination in the sediments.

ACKNOWLEDGMENTS

The author is sincerely grateful to the Department of Science and Technology, the UP Natural Sciences Research Institute, the UP Office of the Research Coordination, and to the UP-Ateneo DMU-de la Salle Ph. D. Consortium for providing

financial support to the project. The author is thankful to Elma C.Llaguno of the UP Institute of Chemistry and to Teofilo Abrajano of Memorial University of Newfoundland (MUN), Canada for their invaluable support as advisers for this project. The assistance of Fernando Siringan and Joselito Duyanen of UP National Institute of Geological Sciences, and Linda Winsor and Jiggs Diegor of MUN are greatly appreciated. The author likewise acknowledges the assistance of Cherry L. Ringor in preparing the figures.

REFERENCES

- Bayona, J. M., P. Fernandez, C. Porte, M. Valls, & J. Albaiges, 1991. Partitioning of U wastewater organic microcontaminants among coastal compartments. *Chemospher.* 23(3): 313-326.
- Boehm, P. D. & J. W. Farrington, 1984. Aspects of polycyclic aromatic hydrocarbons geochemistry of recent sediments in the Georges Bank Region. *Enviro. Sci. and Tech.* 18: 840-845.
- Giger, W. & M. Blumer, 1974. Polycyclic aromatic hydrocarbons in the environment: Isolation and characterization by chromatography, visible, ultraviolet and mass spectrometry. *Anal. Chem.* 46: 1663-1671.
- Long, E. R. & L. G. Morgan, 1990. The potential for biological effects of sediment-sorbed contaminants tested in the National Status and Trends Program. NOAA Technical Memorandum NOS OMA 52, NOAA Ocean Assessment Division, Seattle, Washington. National Academy Press. 1985. Oil in the sea, inputs, fates, effects. Washington DC.
- Pruell, R. & J. Quinn, 1988. Accumulation of PAH in crankcase oil. *Environmental Pollution* 49: 89-97.
- Rogge, W. F., L. M. Hildemann, M. A. Maruzek, & G.R. Cass, 1993. Sources of fine organic aerosol. 2. Non-catalyst and catalyst-equipped automobiles and heavy duty diesel trucks. *Enviro. Sci. and Tech.* 27: 636-651.
- Wakeham, S. G., C. Schaffner, & W. Giger, 1980. Polycyclic aromatic hydrocarbons in recent lake sediments. Compounds Having Anthropogenic Origins. *Geochim. Cosmochim. Acta* 44: 403-413.
- Youngblood, W. W. & M. Blumer, 1975. Polycyclic aromatic hydrocarbons in the environment: homologous series in soils and recent marine sediments. *Geochim. Cosmochim. Acta* 39: 1303-1314.