Correlation of Polynuclear Aromatic Hydrocarbons with Environmental Components in Sediment from Hirakata Bay, Japan

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Polynuclear aromatic hydrocarbons (PAH) including fluoranthene, pyrene, 1,2-benzanthracene, chrysene, 3,4-benzpyrene (1,2-benzpyrene) and 1,12-benzperylene, were identified in sediments from Hirakata Bay. Their concentrations were proved to be in the range from several hundred $\mu\text{g/kg}$ to several mg/kg of dry samples.

Significant positive correlations were statistically found between total amount of PAH and Pb, Hg, Cd, Cu, Zn and ignition loss in bay sediment. In addition, significant positive correlations were statistically found between ignition loss and the content of clay as well as the sum of (clay+silt) contents for both river and bay sediments. Based on the fact, it is presumed that organic substances in sediments are present in an adsorbed form to clay and silt.

Polynuclear aromatic hydrocarbons (PAH), mainly formed by incomplete combustion or pyrolysis of organic substances such as petroleum, coal and wood, are distributed not only in urban and industrial areas but also widely in the natural environment. Since municipal and industrial effluents, atmospheric precipitation and fall-out are supply sources of PAH to the aquatic environment, a marked pollution has been noted in the river water running through the urban and industrial districts, and sea shore water. Since PAH are fat-soluble, it is presumed that PAH are transported with suspended solids or seston in water, and finally, a large proportion of the PAH is removed from water by sedimentation, while a part is concentrated in fish and shellfish *via* aquatic food chains. Information on the correlation of PAH with environmental components in sediment is important to explain the behavior of PAH in the aquatic environment.

Giger *et al.*¹⁾ have determined the concentrations of PAH in sediments from Buzzards Bay, USA. Greffard *et al.*²⁾ have found the presence of 1 to 1710 $\mu\text{g/kg}$ of dry samples of 3,4-benzpyrene in sediments from Toulon Bay, France. Mallet *et al.*³⁾ have found 5

$\mu\text{g/kg}$ of dry samples of 3,4-benzpyrene in sediments at the west coast of Greenland, where ships navigate scarcely and is practically an uninhabited area. They presumed that not only surface water, ship waste, atmospheric precipitation or fall-out, but also biosynthesis by aquatic plants might be the sources of PAH. In our country, Tomita *et al.*⁴⁾ have reported the presence of 2.9 to 255.2 $\mu\text{g/kg}$ of dry samples of 3,4-benzpyrene in sediments from the Lake Hamana. Tatsu-kawa *et al.*⁵⁾ have determined the concentrations of anthracene and phenanthrene in sediments from Seto Inland Sea, and showed the concentrations to be 20~430 and 20~81 $\mu\text{g/kg}$ of dry samples, respectively. Kawakami *et al.*⁶⁾ have suggested that the main source of 3,4-benzpyrene in sediments from Osaka Bay and Keihin Canal might be coke industrial effluent, based on the distribution of 3,4-benzpyrene.

For the purpose of obtaining the data which may serve to explain the behavior of PAH in Hirakata Bay, Yokohama, the authors have determined the concentrations of PAH, heavy metals, ignition loss, and particle-size composition in sediments of Hirakata Bay. In this paper, the distribution of PAH and the statistical correlation of PAH with environmental components in sediments are reported.

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SAMPLING AND ANALYSES

Sediments in Hirakata Bay, Tokyo Bay and rivers which flow into Hirakata Bay, were collected four times in a period from August, 1973 to May, 1974, at sampling stations shown in Fig. 1. Hirakata Bay is situated in

FIG. 1. Sampling Stations in Hirakata Bay, Tokyo Bay and Rivers Which Flow into Hirakata Bay. ● Sampling station.

Kanazawa-ku, Yokohama, and four rivers, namely the Miya, the Mutsura, the Jiju and the Takatori Rivers, enter into Hirakata Bay. Because Kanazawa-ku has a population of about 137,000 (census taken in October, 1976) and no sewer system including a final sewage disposal is set up, almost all domestic and indus-

trial effluents directly flow through the river into Hirakata Bay. Since factories around Hirakata Bay are mainly manufacturing automobile parts, it is characteristic that the effluents from metal surface treating and plating factories discharge into the rivers. The four river waters and sediments are contaminated by the organic substances in the effluents, especially in domestic effluent, a marked pollution of organic substances has been detected in water and sediment of Hirakata Bay.

PAH in sediments were identified and determined according to the procedure already reported (Matsushima *et al.*⁷⁾), which consists of solvent extraction, clean up and fractionation by column chromatography, identification and determination by mass fragmentography. Heavy metals in sediments were determined using atomic absorption spectrophotometry by Nakagawa *et al.*⁸⁾ and ignition loss was measured gravimetrically by use of a reducing flame. The content of gravel was measured by use of a 2 mm sieve. Contents of coarse sand + fine sand, silt and clay were measured gravimetrically by a dispersion procedure.

RESULTS AND DISCUSSION

Results of analyses of PAH, heavy metals and ignition loss as well as those of a dispersion procedure in sediments from Hirakata Bay, Tokyo Bay and the rivers which flow into Hirakata Bay are shown in Table I. As for PAH, anthracene + phenanthrene, fluoranthene, pyrene, 1,2-benzfluorene, 1,2-benzanthracene, pyrene, 1,2-benzfluorene, 1,2-benzanthracene,

TABLE Ia. PAH AND ENVIRONMENTAL COMPONENTS IN SEDIMENT OF HIRAKATA BAY ON A DRY WEIGHT BASIS

PAH (ppm)	Aug. 28, 1973										
	St. 1	St. 2	St. 3	St. 4	St. 5	St. 6	St. 7	St. 8	St. 9	St. 10	St. 11
Anthracene+Phenanthrene	0.42	1.44	1.47	4.12	0.23	0.40	0.25	0.20	0.41	0.34	0.11
Fluoranthene	0.48	1.04	0.93	3.64	0.38	0.51	0.52	0.39	0.72	0.63	0.16
Pyrene	0.43	0.91	0.65	3.52	0.42	0.73	0.63	0.39	0.77	0.51	0.13
1,2-Benzfluorene	0.10	0.16	0.27	0.70	0.13	0.28	0.28	0.17	0.22	0.17	0.065
1,2-Benzanthracene	0.15	0.32	0.24	2.09	0.18	0.26	0.37	0.22	0.42	0.33	0.12
Chrysene	0.18	0.37	0.29	1.82	0.26	0.37	0.44	0.27	0.40	0.31	0.087
3,4-Benzpyrene											
(+1,2-Benzpyrene)	0.21	0.43	0.33	4.05	0.60	1.00	1.14	0.83	1.14	0.73	0.18
Perylene	0.054	0.12	0.12	0.76	0.16	0.32	0.37	0.23	0.26	0.23	0.058
3-Methylcholanthrene	nd*	nd*	nd*	nd*	nd*	nd*	nd*	nd*	nd*	nd*	nd*
1,2,5,6-Dibenzanthracene	0.067	0.099	0.068	0.97	0.20	0.31	0.43	0.29	0.31	0.21	nd*
1,12-Benzperylene	0.075	0.53	0.34	3.47	0.30	0.97	1.21	0.87	1.09	0.67	0.15
Ignition loss (%)	5.5	6.5	7.4	17.3	9.3	10.9	7.3	11.6	10.0	13.0	5.0
Conglomerate (%)	0.9	8.3	1.3	—	14.8	—	—	—	—	—	5.1
Coarse sand(%) + Fine sand (%)	89.9	65.9	82.0	72.0	70.4	56.6	77.2	73.5	67.5	78.4	92.4
Silt (%)	5.5	19.9	14.1	24.7	11.7	38.6	20.6	21.8	28.7	18.1	1.1

Clay (%)	3.8	5.9	2.5	3.3	3.1	4.7	2.2	4.7	3.8	3.5	1.5
Hg (ppm)	0.16	0.19	0.24	0.66	0.24	0.41	0.52	0.32	0.38	0.41	0.26
Zn (ppm)	191	318	454	728	317	789	547	325	416	395	124
Pb (ppm)	23	191	66	147	70	86	74	45	76	53	18
Cd (ppm)	0.8	1.5	1.7	2.8	1.6	2.7	1.9	1.9	2.6	1.3	1.0
Cu (ppm)	39	67	66	138	77	267	130	79	95	88	16
Mn (ppm)	226	270	248	299	190	246	266	207	211	251	184
Cr (ppm)	29	31	44	37	57	441	180	113	63	69	24

 $\text{nd}^* < 0.040 \text{ ppm}$

TABLE 1b. PAH AND ENVIRONMENTAL COMPONENTS IN SEDIMENT OF HIRAKATA BAY ON A DRY WEIGHT BASIS

PAH (ppm)	Nov. 28, 1973											
	St. 1	St. 2	St. 3	St. 4	St. 5	St. 6	St. 7	St. 8	St. 9	St. 13	St. 10	St. 11
Anthracene + Phenanthrene	0.087	0.59	0.39	1.65	0.40	0.21	0.19	1.97	0.93	0.67	0.24	0.17
Fluoranthene	0.11	0.92	0.43	1.33	0.64	0.31	0.31	1.37	1.28	1.33	0.64	0.34
Pyrene	0.11	0.91	0.38	1.33	0.63	0.30	0.30	1.32	1.19	1.34	0.60	0.27
1,2-Benzfluorene	0.040	0.27	0.12	0.23	0.18	0.089	0.091	0.42	0.25	0.69	0.17	0.081
1,2-Benzanthracene	0.048	0.43	0.19	0.45	0.27	0.12	0.13	0.52	0.45	0.65	0.24	0.14
Chrysene	0.051	0.46	0.20	0.47	0.31	0.14	0.16	0.56	0.55	0.86	0.27	0.14
3,4-Benzpyrene												
(+1,2-Benzpyrene)	0.095	1.16	0.32	0.91	0.52	0.22	0.24	0.83	0.81	1.64	0.38	0.21
Perylene	0.075	0.44	0.099	0.24	0.14	0.072	0.076	0.22	0.19	0.45	0.12	0.078
3-Methylcholanthrene	nd*	nd*	nd*	nd*	nd*	nd*	nd*	nd*	nd*	nd*	nd*	nd*
1,2,5,6-Dibenzanthracene	nd*	nd*	0.10	nd*	0.11	0.047	0.056	0.18	0.15	0.54	0.077	0.048
1,12-Benzperylene	0.090	1.15	0.38	0.78	0.64	0.12	0.32	0.91	1.09	1.74	0.43	0.11
Ignition loss (%)	5.4	10.1	8.3	4.4	12.4	9.7	12.5	12.3	9.8	17.0	8.2	—
Conglomerate (%)	1.7	—	—	1.4	—	—	—	—	—	—	—	—
Coarse sand (%)												
+Fine sand (%)	84.0	64.2	77.3	96.5	49.0	44.9	52.2	60.4	64.6	74.6	87.1	—
Silt (%)	11.8	32.0	22.2	1.1	46.6	51.0	43.8	34.7	33.1	20.5	10.7	—
Clay (%)	2.5	3.8	0.5	1.1	4.3	4.1	3.9	4.9	2.2	4.9	2.1	—
Hg (ppm)	0.08	1.06	0.14	0.10	0.49	0.32	0.29	0.31	0.37	1.17	0.22	—
Zn (ppm)	190	507	503	167	698	654	341	474	466	1762	369	—
Pb (ppm)	42	191	75	45	132	93	52	89	108	861	44	—
Cd (ppm)	1.7	2.6	1.7	1.4	2.8	2.5	2.2	2.3	2.2	6.8	1.4	—
Cu (ppm)	42	162	75	45	151	136	90	114	115	462	55	—
Mn (ppm)	345	385	321	250	342	410	325	308	312	305	277	—
Cr (ppm)	48	45	77	18	101	164	94	100	56	455	53	—

$$\text{nd}^* < 0.040 \text{ ppm}$$

TABLE 1c. PAH AND ENVIRONMENTAL COMPONENTS IN SEDIMENT OF HIRAKATA BAY ON A DRY WEIGHT BASIS

[illegible]

(+1,2-Benzpyrene)	0.40	1.62	0.26	0.80	1.00	0.52	0.44	6.07	1.64	0.77	0.090
Perylene	0.10	0.41	0.078	0.15	0.20	0.13	0.14	1.32	0.29	0.16	0.035
3-Methylcholanthrene	nd*	nd*	nd*	nd*	nd*	nd*	nd*	nd*	nd*	nd*	nd*
1,2,5,6-Dibenzanthracene	0.13	0.44	0.081	0.17	0.21	0.13	0.13	1.30	0.30	0.14	0.024
1,12-Benzperylene	0.51	2.06	0.34	0.78	1.09	0.55	0.54	4.37	1.56	0.69	0.11
Ignition loss (%)	33.4	6.9	6.5	7.2	12.0	11.3	10.2	9.4	13.1	9.1	5.1
Conglomerate (%)	—	—	—	—	—	—	—	—	—	—	—
Coarses and (%)											
+Fine sand (%)	55.8	75.4	83.7	92.4	37.2	46.6	45.1	54.8	41.9	82.8	92.1
Silt (%)	34.8	23.0	15.2	5.4	57.9	46.9	48.6	41.3	53.2	15.1	4.9
Clay (%)	9.4	1.6	1.1	2.2	5.0	6.5	6.3	3.9	4.9	2.1	2.9
Hg (ppm)	0.92	0.68	0.20	0.25	0.67	0.45	0.41	0.44	0.86	0.30	0.19
Zn (ppm)	1169	687	421	191	590	744	380	512	683	270	148
Pb (ppm)	100	241	56	38	118	103	52	83	158	40	19
Cd (ppm)	2.9	2.9	1.1	1.2	2.3	1.8	1.7	2.3	2.8	1.1	0.7
Cu (ppm)	186	116	61	44	136	136	92	112	147	53	22
Mn (ppm)	320	344	289	225	284	373	276	263	301	304	336
Cr (ppm)	511	39	70	20	91	178	124	110	65	47	35

nd* < 0.020 ppm

TABLE Id. PAH AND ENVIRONMENTAL COMPONENTS IN SEDIMENT
OF HIRAKATA BAY ON A DRY WEIGHT BASIS

PAH (ppm)	May 28, 1974											
	St. 1	St. 2	St. 3	St. 4	St. 5	St. 6	St. 7	St. 8	St. 9	St. 13	St. 10	St. 11
Anthracene+Phenanthrene	0.82	0.46	2.57	0.21	0.34	0.11	0.11	1.06	0.82	0.99	0.075	0.004
Fluoranthene	0.86	0.73	2.06	0.62	0.74	0.18	0.34	1.48	0.86	1.86	0.18	0.007
Pyrene	0.78	0.69	1.73	0.71	0.74	0.16	0.33	1.42	0.86	1.87	0.16	0.007
1,2-Benzfluorene	0.19	0.17	0.37	0.14	0.16	0.036	0.072	0.54	0.28	0.49	0.052	0.002
1,2-Benzanthracene	0.39	0.29	0.65	0.31	0.56	0.11	0.18	1.02	0.62	0.76	0.11	0.005
Chrysene	0.45	0.42	1.03	0.42	0.66	0.12	0.22	0.96	0.87	1.06	0.12	0.005
3,4-Benzpyrene												
(+1,2-Benzpyrene)	0.70	0.61	1.43	0.64	1.12	0.36	0.60	1.94	1.46	2.06	0.12	0.008
Perylene	0.14	nd*	0.21	0.091	0.20	nd*	nd*	0.33	0.20	0.44	nd*	0.002
3-Methylcholanthrene	nd*	nd*	nd*	nd*	nd*	nd*	nd*	nd*	nd*	nd*	nd*	nd**
1,2,5,6-Dibenzanthracene	0.21	0.16	0.32	0.13	0.40	0.13	0.18	0.50	0.29	0.49	0.034	0.005
1,12-Benzperylene	0.41	0.38	0.69	0.28	1.54	0.46	0.63	1.36	1.33	1.23	0.11	0.010
Ignition loss (%)	7.7	7.3	13.7	4.8	12.4	7.3	12.1	11.1	11.3	14.8	3.8	2.6
Conglomerate (%)	—	—	—	0.6	—	—	—	—	—	—	2.0	—
Coarse sand (%)												
+Fine sand (%)	87.6	61.2	81.6	94.4	47.9	67.5	47.7	48.7	53.8	57.4	91.3	98.6
Silt (%)	9.6	33.2	17.0	5.0	46.0	30.2	45.0	47.6	42.9	40.3	6.7	0.9
Clay (%)	2.7	5.5	1.4	—	6.2	2.4	7.3	3.7	3.3	2.3	—	0.5
Hg (ppm)	0.18	1.02	0.28	0.20	0.65	0.36	0.77	0.44	0.49	1.13	0.17	0.12
Zn (ppm)	261	590	525	185	518	470	611	501	542	1282	128	102
Pb (ppm)	42	129	79	83	106	64	87	80	127	620	20	17
Cd (ppm)	0.8	1.8	1.6	1.1	2.8	1.7	2.4	1.8	2.2	5.9	0.5	0.7
Cu (ppm)	50	117	70	56	128	107	147	100	116	315	20	12
Mn (ppm)	292	307	243	254	276	260	317	307	262	263	260	428
Cr (ppm)	42	42	61	28	71	146	183	98	47	284	31	31

nd* < 0.020 ppm

nd** < 0.002 ppm

chrysene, 3,4-benzpyrene (1,2-benzpyrene), 1,2,5,6-dibenzanthracene and 1,12-benzperylene were identified and determined. Concentrations of PAH in sediments from the rivers and Hirakata Bay were within the range of several hundred $\mu\text{g/kg}$ to several mg/kg of dry samples, about an order higher than those in sediment from Tokyo Bay adjacent to Hirakata Bay, and those of several to several hundred $\mu\text{g/kg}$ of dry samples in sediments from Buzzards Bay, USA (Giger *et al.*¹¹⁾).

The ratios of the sum of (anthracene+phenanthrene+fluoranthene+pyrene) concentrations to total amount of individual PAH concentration at a same sampling station, were amounted to 70~80% for the river and bay waters, while those for the river sediments and the bay sediments were as low as 50~60% and 30~50%, respectively. These data coincides well with those obtained for the samples from Tokyo Bay (Matsushima, in preparation). Namely, the ratios were amounted to more than 60% for the Tama River water which flows into Tokyo Bay, while those for estuary sediments and sediments of Tokyo Bay were as low as about 50% and 30~40%, respectively. The difference in the ratios between water and sediment may be due to the different rates of decomposition, volatilization and/or precipitation of PAH from water to sediment. Experiments on the mode of disappearance of PAH in Hirakata Bay sediments, which indicated that the smaller the molecular weight of PAH was, the greater was its rate of disappearance (Matsushima, in preparation). Further, studies on core samples

of Tokyo Bay sediments showed that the concentrations of PAH tend to be maximum at the surface layer of the sediment and decrease toward lower direction, and the smaller the molecular weight of PAH is, the greater is its rate of decrease (Matsushima, in preparation). Based on these facts, it is presumed that the difference in the ratios between water and sediment is mainly due to the different decomposition rate of PAH.

Applying statistical techniques, correlations between PAH and environmental components were examined. The author assumed that the correlation with the level of risk below 5% is statistically significant. The sample collected from St. 8 on Feb. 15, 1974, was excluded from the statistical analysis according to the rejection test, because the PAH concentrations in this station are remarkably high compared with those in sediments sampled at other stations, probably due to direct dumping from fishing boats. Results of the correlations of PAH and heavy metals in sediments are shown in Table II. Significant positive correlations were statistically found between total amount of PAH and Pb, Hg in sediments of Hirakata Bay, between total amount of PAH and Cd, and between total amount of PAH and Cu, Zn, with the level of risk below 1, 2 and 5% respectively. Similar correlations were also found between individual PAH, namely 3,4-benzpyrene (1,2-benzpyrene), 1,12-benzperylene, pyrene, chrysene, and heavy metals such as Pb, Hg, Cd, Cu, Zn. On the contrary, in river sediments, such correlations were only partly ob-

TABLE II. CORRELATION COEFFICIENTS BETWEEN PAH AND METAL CONCENTRATIONS IN SEDIMENT

	Total PAH		3,4-Benzpyrene (1,2-Benzpyrene)		1,12-Benzperylene	
	River	Bay	River	Bay	River	Bay
Pb	0.46	0.59 ^a	0.42	0.56 ^a	0.57 ^c	0.49 ^c
Hg	0.30	0.61 ^a	0.34	0.64 ^a	0.41	0.65 ^a
Cd	0.49	0.51 ^b	0.53 ^c	0.50 ^c	0.66 ^a	0.50 ^c
Cu	0.37	0.44 ^c	0.32	0.48 ^c	0.48	0.47 ^c
Zn	0.35	0.50 ^c	0.33	0.51 ^b	0.40	0.48 ^c
Mn	0.04	-0.04	0.11	-0.33	0.23	-0.18
Cr	-0.13	0.13	-0.15	0.23	-0.10	0.19

^a $p < 0.01$

^b $p < 0.02$

^c $p < 0.05$.

served. In sediments from Osaka Bay, significant positive correlations were statistically found between 3,4-benzpyrene and Cd, Cu, Pb (Kawakami *et al.*⁹⁾). While, correlations between 3,4-benzpyrene and heavy metals in dust in the atmosphere have been studied by Tomita⁹⁾ and Matsushita *et al.*¹⁰⁾ According to Tomita, significant positive correlations were statistically observed between 3,4-benzpyrene and Cd, Fe, Pb, Cr, Ni in dust from air of Osaka City. Matsushita *et al.* have reported that in dust from air of Kawasaki City, Kanagawa Pref., heavy metals which correlated significantly with 3,4-benzpyrene, were Pb, Cd and V. Therefore, by use of correlations of PAH and other environmental pollutants such as heavy metals, the dynamics of PAH in air-water interface is explained.

The correlations between PAH, ignition loss and clay, silt contents were investigated. The correlation between total amount of PAH and ignition loss is shown in Fig. 2. For bay sedi-

FIG. 2. Correlation between Total Amount of PAH and Ignition Loss in Sediment of Hirakata Bay.

$r=0.55$, $p<0.02$.

ments, a significant positive correlation was statistically found with the level of risk below 2%, while in the river sediments no such correlation could be observed. For bay sediments, similar correlations were found between 3,4-benzpyrene (1,2-benzpyrene), 1,12-benzperylene and ignition loss with correlation coefficients of 0.50 and 0.45, respectively, with the level of risk below 5%. These facts that

positive correlations can not be found for river sediments may be explained by that, in river sediments, so many kinds of organic substances come from a variety of sources and their decomposition rates are remarkably different from each other. On the other hand, in bay sediments, the most part of unstable compounds are easily decomposed and the residue may be in relatively stable states. However, between total amount of PAH and clay content, the sum of (clay+silt) contents, no clear correlations could be found for both river and bay sediments.

The correlation between ignition loss and the sum of (clay+silt) contents is shown in Fig. 3. For both river and bay sediments

FIG. 3. Correlation between Ignition Loss and the Sum of (Clay+Silt) Contents in Sediment of Hirakata Bay.

$r=0.37$; $r=0.67$, $p<0.01$ (except St. 13).

(except St. 13) a significant positive correlation with the level of risk below 1% was statistically found between the above two factors. Also, between ignition loss and clay content, the author found statistically a significant positive correlation with the correlation coefficient of 0.68 and the level of risk below 1% for river sediments, while a correlation coefficient was 0.77 and the level of risk below 0.1% for bay sediments (except St. 13). Based on these facts, it is presumed that organic substances in sediments are present in an adsorbed form to clay and silt.

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