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Identification of Hydrocarbons and Oxygen Compounds in Sediments from Niigata, Japan

K. Kawata,[1] A. Tanabe,[1] H. Mitobe,[1] A. Yasuhara[2]

[1] Niigata Prefectural Research Laboratory for Health and Environment, 314-1 Sowa, Niigata 950-2144, Japan
[2] The National Institute for Environmental Studies, 16-2 Onogawa, Tsukuba, Ibaraki 305-0053, Japan

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Since most organic compounds have low water solubility, most parts of them in the hydrosphere exist in sediment rather than water. A number of studies have been reported on their identification in sediment, e.g., the Mediterranean Sea (Tolosa et al. 1996), Dokai Bay (Hanada et al. 1995, Terashi et al. 1993) and Tokyo Bay (Hanada et al. 1995). These studies show that aliphatic hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) are ubiquitous organic compounds in sediment. Moreover, oxygen compounds, such as carboxylic acids and their esters, are also isolated from sediment as ones of predominant components (Hanada et al. 1995, Terashi et al. 1993).

The bulk of the riverine particulate organic contamination is trapped in an estuary and mouth of river, because reducing of river current velocity there results in extensive sedimentation of river-borne particulates (Latimer and Quinn 1996). We have already reported distribution of several PAHs in sediments from mouths of 29 rivers in Niigata Prefecture, Japan (Kawata et al. 1997). However, only a few reports have been performed on identification of the organic compounds in sediments from mouths of rivers in Japan. In this paper, we present identification of aliphatic and polycyclic hydrocarbons as well as oxygen compounds in sediments from mouths of three river estuaries and a port in Niigata, Japan.

MATERIALS AND METHODS

A gas chromatograph - mass spectrometer, Automass 50 (JEOL, Tokyo, Japan) was used for analysis. Reagents were obtained from Sigma-Aldrich, Wako Pure Chemical (Osaka, Japan), Kanto Chemical (Tokyo, Japan) and GL Science (Tokyo, Japan). A hexane solution containing 100 μg/ml of the six isotopes was prepared as a surrogate solution.

Surface sediments were collected from estuaries of three rivers and a port in Niigata Prefecture (Figure 1) on September 1995. The Hokura River flows 54.7 km including industrial area and agricultural area. The Shinano River flows 366.8 km via Nagano Prefecture and Niigata Prefecture to the Sea of Japan, draining 11,900 sq km including cultivated area and civilized area. The Niigata East Port locates in industrial area. The Tainai River flows in including industrial area and

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Correspondence to: K. Kawata

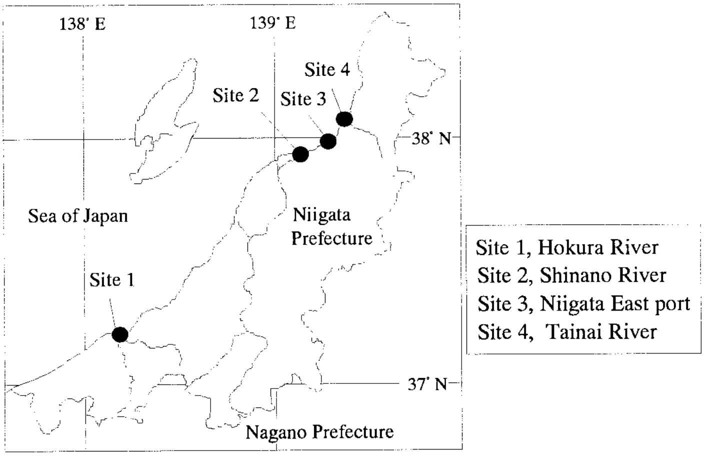

Figure 1. Sampling sites.

agricultural area draining 151 sq km. The sediment samples were stored in 200 ml glass bottles with ground stopper at -20℃ without headspace.

The sediment sample of 50 g was extracted ultrasonically with twice 40 ml each of acetone for 10 min followed by centrifugation at 3000 rpm (1700Xg) for 10 min. The sediment was then extracted with twice 30 ml each of hexane. The acetone and hexane extracts were combined and were added to 800 ml of 5 % sodium chloride solution. The result solution was extracted twice with 50 ml of hexane. The hexane layer combined was washed twice with 50 ml of 5 % sodium chloride solution. The hexane layer was dried over anhydrous sodium sulfate, and evaporated to about 5 ml. The resulting solution was passed through a column packed with 1 g of activated copper (40/80 mesh) followed by concentration to 1 ml under a pure nitrogen gas stream. The resulting extract was subjected to a column chromatography on a 1.0 X 30 cm glass column packed with 5 g of 5 % deactivated silica gel (Wakogel C-200). The following sequential elution scheme was used: 30 ml of hexane (Fraction 1), 50 ml of 5 % acetone in *n*-hexane (Fraction 2) and 50 % acetone in *n*-hexane (Fraction 3). Each fraction was concentrated to 1 ml. A 4-μL of the solution was analyzed by GC/MS in the scan monitoring mode (*m*/*z* 50 – 500). GC/MS conditions were as follows: column, a fused-silica column HP Ultra #2, 0.52 μm film thickness, 25 m long, 0.32 mm id (Hewlett-Packard); column temperature, programmed from 50℃ (held for 2 min) to 250℃ at a rate of 5℃/min, then to 310℃ (held for 8 min) at a rate of 10℃ /min; injector temperature, 250℃; injection mode, splitless; carrier gas pressure, programmed from 2 psi to 15 psi (held for 1 min) at a rate of 99 psi/min, then back to 2 psi at the same rate; ionization temperature, 230℃; ionization current, 350 μA; electron energy, 70 eV. The temperature-programmed retention indices (RIs) were calculated by the following equation:

$$RI_A = 100N + 100(t_A - t_N) / (t_{N+1} - t_N)$$

where RI_A is the RI of compound A, t_A is retention time of compound A, and t_N

and t_{N+1} are the retention times of the normal alkanes bracketing the compound A with carbon number N and N+1. Identification of compounds was based on coincidence of mass spectra and RIs with those of authentic standard compounds or published data (Hanada et al. 1995). Some compounds were identified by comparison of sample mass spectra with those of library spectra or published spectra.

RESULTS AND DISCUSSION

At sites 1 - 4, 183 compounds, including 31 alkanes (Fraction 1), 11 alkylbenzenes (Fraction 1), ten methyl esters (Fraction 2), 97 PAHs (Fractions 1 and 2), five phthalates (Fraction 3) and 24 carboxylic acids (Fraction 3), were identified; 144, 178, 160 and 123 compounds were identified from sites 1, 2, 3 and 4, respectively. The intensities of organic compounds were the highest in site 2, with a decreasing trend of site 3 > site 1 > site 4. The organic compounds identified from individual sampling sites are shown in Table 1. Although several compounds were found in only one or two sites, the vast majority of the compounds identified were common to all sites.

Normal alkanes ranged from C_{10} to C_{33}, pristane and phytane were the major alkanes in all the sites. Normal alkanes are reported as biological- or petroleum-derived product (Zeng and Vista 1997). Among the normal alkanes, C_{17}, C_{25}, C_{27} and C_{29} were predominant at all the sites. They have been reported to be derived from epicuticular waxes of higher plants (Tolosa et al 1996). Intensity of C_{29} was the highest at sites 1,3 and 4, whereas that of C_{27} was the highest at site 2. Regarding the compositions of C_{10} - C_{16}, the sediment from site 1 more abundant in C_{10} - C_{16} than all the other samples. At site 4, C_{17} was predominant among C_{10} - C_{20}. These differences in the compositions reflected the differences of the sources of the normal alkanes as well as degradation of the alkanes at each site (Zeng and Vista 1997).

Nine kinds of alkyl benzenes (C_{11}- to C_{13}-substituted benzenes) were identified at all sites. It was suggested that C_{10}- to C_{14}-substituted benzenes were unreacted residues of the industrial synthesis of linear alkylbenzenesulfonate detergents or degradative compounds of the detergents by desulfonation, and were provided by urban drainage (Takada et al. 1992). They were the most abundant at site 2 reflecting that the river flows through a civilized area in the basin. Ten methyl esters were identified at all the sites. Some of them have been also identified from sediments in Tokyo Bay and Dokai Bay (Hanada et al. 1995). They can be provided by the same sources as carboxylic acids described below. Phenol and a cresol were identified from all sites. Phenol and cresols are_identified from sediment in Tokyo Bay (Hanada et al. 1995). They are reported to exist in the exhaust from internal combustion engines (Larson and Weber 1994).

Forty-nine to 94 PAHs were identified from sites 1 - 4. Most of PAHs are derived from petrogenic and pyrogenic sources (Zeng and Vista 1997). In this study, most of the predominant PAHs identified were nonalkylated combustion-generated

Table 1. Organic compounds identified from sediments

#	Compound		Id [a]	RI	M [b]	*m/z* [c]	Site 1	Site 2	Site 3	Site 4
	Alkanes (Fraction 1)									
A1	Decane	(C_{10})	A	1000	142	57	+++	+++	+++	++
A2	Undecane	(C_{11})	A	1100	156	57	+++	+++	+++	++
A3	Dodecane	(C_{12})	A	1200	170	57	+++	+++	+++	++
A4	Tridecane	(C_{13})	A	1300	184	57	+++	+++	+++	++
A5	Tetradecane	(C_{14})	A	1400	198	57	+++	+++	+++	++
A6	Pentadecane	(C_{15})	A	1500	212	57	+++	+++	+++	++
A7	Hexadecane	(C_{16})	A	1600	226	57	+++	+++	+++	++
A8	Heptadecane	(C_{17})	A	1700	240	57	++++	++++	+++	+++
A9	Pristane	(C_{19})	A	1706	268	57	++++	+++	+++	++
A10	Octadecane	(C_{18})	A	1800	254	57	+++	+++	+++	++
A11	Phytane	(C_{20})	A	1810	282	57	+++	+++	+++	++
A12	Nonadecane	(C_{19})	A	1900	268	57	+++	+++	+++	++
A13	Eicosane	(C_{20})	A	2000	282	57	+++	++++	+++	++
A14	Heneicosane	(C_{21})	A	2100	296	57	+++	++++	+++	++
A15	Docosane	(C_{22})	A	2200	310	57	+++	++++	+++	++
A16	Tricosane	(C_{23})	A	2300	324	57	+++	++++	++++	++
A17	Tetracosane	(C_{24})	A	2400	338	57	+++	++++	+++	++
A18	Pentacosane	(C_{25})	A	2500	352	57	+++	++++	++++	+++
A19	Hexacosane	(C_{26})	A	2600	366	57	+++	++++	+++	++
A20	Heptacosane	(C_{27})	A	2700	380	57	+++	++++	++++	++++
A21	Octacosane	(C_{28})	A	2800	394	57	+++	++++	+++	+++
A22	Nonacosane	(C_{29})	C	2900	408	57	+++	++++	++++	++++
A23	Triacontane	(C_{30})	A	3000	422	57	+++	+++	+++	++
A24	Hentriacontane	(C_{31})	C	3100	436	57	+++	+++	++++	+++
A25	Dotriacontane	(C_{32})	A	3200	450	57	+++	+++	+++	++
A26	Tritriacontane	(C_{33})	C	3300	464	57	+++	+++	+++	+++
A27	Tetratriacontane	(C_{34})	C	3400	478	57	+++	+++	+++	++
A28	Pentatriacontane	(C_{35})	C	3500	492	57	++	+++	+++	+
A29	Hexatriacontane	(C_{36})	A	3600	506	57	+	+++	++	+
A30	Heptatriacontane	(C_{37})	C	3700	520	57	+	+++	++	-
A31	Octatriacontane	(C_{38})	C	3800	534	57	-	+++	++	-
	Alkyl benzenes (Fraction 1)									
B1	C_{10}-Benzene		B	1538	218	91	-	+	-	-
B2	C_{10}-Benzene		B	1546	218	91	-	+	-	-
B3	C_{11}-Benzene		B	1632	232	91	++	+++	++	++
B4	C_{11}-Benzene		B	1636	232	91	++	+++	++	++
B5	C_{11}-Benzene		B	1646	232	91	++	+++	++	++
B6	C_{12}-Benzene		B	1734	246	91	++	+++	+++	++
B7	C_{12}-Benzene		B	1739	246	91	++	+++	++	++
B8	C_{12}-Benzene		B	1749	246	91	++	+++	++	+
B9	C_{13}-Benzene		B	1830	260	91	++	+++	+++	++
B10	C_{13}-Benzene		B	1837	260	91	++	+++	++	++
B11	C_{13}-Benzene		B	1850	260	91	++	+++	++	+
	Methyl esters (Fraction 2)									
C1	Methyl tetradecanoate isomer		C	1689	242	74	++	++	++	+
C2	Methyl tetradecanoate		C	1727	242	74	++	++	++	+
C3	Methyl pentadecanoate isomer		C	1790	256	74	++	++	++	+
C4	Methyl pentadecanoate isomer		C	1798	256	74	++	++	++	+
C5	Methyl pentadecanoate		C	1827	256	74	++	++	++	+
C6	Methyl hexadecanoate isomer		C	1888	270	74	++	+++	++	+
C7	Methyl hexadecanoate		C	1925	270	74	+++	+++	+++	+++
C8	Methyl heptadecanoate isomer		C	1997	284	74	+	++	++	+
C9	Methyl heptadecanoate		C	2026	284	74	+	++	++	+
C10	Methyl octadecanoate		C	2129	298	74	++	++	++	++

Table 1. (continued)

#	Compound	Id [a]	RI	M [b]	*m/z* [c]	Site 1	Site 2	Site 3	Site 4
	Alcohols, phenols etc. (Fraction 3)								
D1	Phenol	A	978	94	94	++++	++++	++++	+++
D2	C_3-pentanol	C	1029	130	57	++	+++	++++	++
D3	Benzyl alcohol	B	1033	108	79	+++	+++	++++	+++
D4	C_4 acetate	C	1062	116	43	+	++	++	+
D5	Cresol	B	1076	108	108	++	+++	+++	+++
	PAH (Fraction 1)								
E1	Naphthalene	A	1182	128	128	++	+++	++	++
E2	2-Methylnaphthalene	A	1292	142	142	+++	+++	++	+
E3	1-Methylnaphthalene	A	1309	142	142	+++	+++	++	+
E4	2,6-Dimethylnaphthalene	A	1402	156	156	+++	+++	++	++
E5	1,3-Dimethylnaphthalene	A	1417	156	156	+++	+++	++	++
E6	1,6-Dimethylnaphthalene	A	1421	156	156	+++	+++	++	+
E7	2,3-Dimethylnaphthalene	A	1437	156	156	++	+++	++	+
E8	1,5-Dimethylnaphthalene	A	1440	156	156	++	+++	++	+
E9	Acenaphthylene	A	1447	151	151	++	++	+	+
E10	Acenaphthene	A	1483	154	154	++	++	++	+++
E11	Fluorene	A	1581	166	166	++	++	++	++
E12	Phenanthlene	A	1777	178	178	+++	++++	+++	+++
E13	Anthracene	A	1786	178	178	++	+++	++	++
E14	C_1-$C_{14}H_{10}$	C	1893	192	192	+++	+++	++	+
E15	C_1-$C_{14}H_{10}$	C	1899	192	192	+++	+++	++	+
E16	2-Methylanthracene	B	1908	192	192	++	+++	++	+
E17	1-Methylanthracene	B	1919	192	192	+++	+++	++	+
E18	C_1-$C_{14}H_{10}$	C	1924	192	192	+++	+++	++	+
	PAH (Fraction 2)								
E19	C_2-$C_{14}H_{10}$	C	2014	206	206	+	+	-	-
E20	C_2-$C_{14}H_{10}$	C	2020	206	206	+	-	-	-
E21	C_2-$C_{14}H_{10}$	C	2023	206	206	-	+	-	-
E22	C_2-$C_{14}H_{10}$	C	2033	206	206	+	-	-	-
E23	C_2-$C_{14}H_{10}$	C	2040	206	206	+	-	-	-
E24	C_2-$C_{14}H_{10}$	C	2027	206	206	-	+	+	-
E25	C_2-$C_{14}H_{10}$	C	2043	206	206	-	+	+	-
E26	C_2-$C_{14}H_{10}$	C	2050	206	206	+	+	+	-
E27	Fluoranthene	A	2056	202	202	+	+++	++	+
E28	Pyrene	A	2108	202	202	+	++	++	+
E29	C_1-$C_{16}H_{10}$	C	2178	216	216	-	++	+	+
E30	Benzo[*a*]fluorene	A	2206	216	216	++	+++	++	+
E31	C_1-$C_{16}H_{10}$	C	2215	216	216	-	+	+	-
E32	Retene	A	2217	234	234	+	+	+	+
E33	Benzo[*b*]fluorene	A	2225	216	216	++	++	++	+
E34	C_1-$C_{16}H_{10}$	C	2233	216	216	-	+	+	-
E35	C_1-$C_{16}H_{10}$	C	2241	216	216	-	+	-	-
E36	C_1-$C_{16}H_{10}$	C	2258	216	216	+	+	+	+
E37	C_1-$C_{16}H_{10}$	C	2265	216	216	+	+	+	+
E38	C_2-$C_{16}H_{10}$	C	2335	230	230	+	+	-	-
E39	C_2-$C_{16}H_{10}$	C	2346	230	230	+	++	-	-
E40	C_2-$C_{16}H_{10}$	C	2356	230	230	-	+	-	-
E41	Benzo[*a*]anthracene	A	2445	228	228	++	+++	++	+
E42	Chrysene /triphenylene	A	2457	228	228	++	+++	++	++
E43	C_1-$C_{18}H_{12}$	C	2556	242	242	-	++	-	-
E44	C_1-$C_{18}H_{12}$	C	2563	242	242	-	++	+	-
E45	C_1-$C_{18}H_{12}$	C	2574	242	242	++	+++	++	-
E46	C_1-$C_{18}H_{12}$	C	2584	242	242	++	++	+	+
E47	C_1-$C_{18}H_{12}$	C	2597	242	242	+	++	+	-

Table 1. (continued)

#	Compound	Id[a]	RI	M[b]	*m/z*[c]	Site 1	Site 2	Site 3	Site 4
E48	C_1-$C_{18}H_{12}$	C	2602	242	242	-	++	+	-
E49	C_2-$C_{18}H_{12}$	C	2692	256	256	+	++	++	+
E50	C_2-$C_{18}H_{12}$	C	2704	256	256	+	++	++	-
E51	C_2-$C_{18}H_{12}$	C	2713	256	256	+	++	+	+
E52	C_2-$C_{18}H_{12}$	C	2713	256	256	+	++	++	+
E53	C_2-$C_{18}H_{12}$	C	2724	256	256	+	++	+	-
E54	C_2-$C_{18}H_{12}$	C	2733	256	256	+	+	+	-
E55	C_2-$C_{18}H_{12}$	C	2738	256	256	+	+	+	-
E56	Benzo[*b*]fluoranthene	A	2756	252	252	++	+++	+++	++
E57	Benzo[*k*]fluoranthene / Benzo[*j*]fluoranthene	A	2763	252	252	++	+++	+++	++
E58	Benzo[*e*]pyrene	A	2827	252	252	++	+++	++	++
E59	Benzo[*a*]pyrene	A	2840	252	252	++	+++	++	++
E60	Perylene	A	2864	252	252	++++	++++	+++	++
E61	C_1-$C_{20}H_{12}$	C	2884	266	266	-	++	+	-
E62	C_1-$C_{20}H_{12}$	C	2891	266	266	-	+	+	-
E63	C_1-$C_{20}H_{12}$	C	2898	266	266	-	+	+	-
E64	C_1-$C_{20}H_{12}$	C	2915	266	266	-	++	+	-
E65	C_1-$C_{20}H_{12}$	C	2917	266	266	-	++	-	-
E66	C_1-$C_{20}H_{12}$	C	2921	266	266	-	++	-	-
E67	C_1-$C_{20}H_{12}$	C	2941	266	266	+	++	+	-
E68	C_1-$C_{20}H_{12}$	C	2948	266	266	+	++	+	-
E69	C_1-$C_{20}H_{12}$	C	2980	266	266	-	++	+	-
E70	C_1-$C_{20}H_{12}$	C	2988	266	266	-	++	+	-
E71	C_1-$C_{20}H_{12}$	C	3016	280	280	-	+	-	-
E72	C_1-$C_{20}H_{12}$	C	3022	266	266	+	++	-	-
E73	C_2-$C_{20}H_{12}$	C	3055	280	280	-	+	-	-
E74	C_1-$C_{20}H_{12}$	C	3062	280	280	-	+	-	-
E75	$C_{22}H_{14}$	C	3084	278	278	-	+	+	-
E76	C_1-$C_{20}H_{12}$	C	3094	280	280	-	+	-	-
E77	C_1-$C_{20}H_{12}$	C	3101	280	280	-	+	-	-
E78	$C_{22}H_{14}$	C	3115	276	276	++	++	++	+
E79	$C_{22}H_{14}$	C	3121	278	278	-	++	++	-
E80	Indino[1,2,3-*cd*]pyrene	A	3137	276	276	+	+++	+++	+
E81	Dibenzo[*a,h*]anthracene	A	3153	278	278	+	++	++	+
E82	$C_{22}H_{14}$	C	3158	278	278	-	+	-	-
E83	$C_{22}H_{14}$	C	3175	278	278	-	++	+	-
E84	Picene	A	3183	278	278	+	++	++	+
E85	Benzo[*ghi*]perylene	A	3196	276	276	++	+++	++	+
E86	$C_{24}H_{14}$	B	3458	302	302	-	+	+	-
E87	$C_{24}H_{14}$	B	3472	302	302	-	+	+	-
E88 E89	Naphtho[1,2-*b*]fluoranthene/ Naphtho[1,2-*k*]fluoranthene	B	3497	302	302	+	++	++	+
E90 E91	Naphtho[2,3-*b*]fluoranthene Dibenzo[*b,k*]fluoranthene	B	3511	302	302	+	++	++	+
E92	$C_{24}H_{14}$	B	3519	302	302	+	++	++	+
E93	Naphtho[2,3-*k*]fluoranthene	B	3532	302	302	-	+	+	-
E94	Naphtho[2,3-*e*]pyrene	B	3555	302	302	+	+	+	+
E95	Coronene	A	3563	300	300	++	++	++	+
E96	Dibenzo[*a,e*]pyrene	B	3574	302	302	+	++	++	+
E97	Naphtho[2,1-*a*]pyrene/ Dibenzo[*e,l*]pyrene	B	3579	302	302	+	++	++	+
E98	Naphtho[2,3-*a*]pyrene	B	3591	302	302	-	+	+	-
E99	Dibenzo[*a,i*]pyrene	B	3597	302	302	-	+	+	-

Table 1. (continued)

#	Compound	Id [a]	RI	M [b]	*m/z* [c]	Site 1	Site 2	Site 3	Site 4
	Phthalates (Fraction 3)								
F1	Diethyl phthalate	A	1720	222	149	-	+	+	-
F2	Dibutyl phthalate	A	1962	278	149	+++	+	++	++
F3	Benzyl butyl phthalate	A	2350	312	149	++	-	-	+
F4	Diheptyl phthalate	A	2452	312	149	-	-	-	+
F5	Di (2-ethylhexyl) phthalate		2554	390	149	++	+	+++	-
	Carboxylic acids (Fraction 3)								
G1	Hexanoic acid	C	985	116	60	++	+++	+++	-
G2	Heptanoic acid	C	1082	130	60	++	++	++	++
G3	Octanoic acid isomer	C	1133	144	73	+++	+++	+++	++
G4	Octanoic acid	C	1180	144	60	++	+++	+++	++
G5	Nonanoic acid	C	1278	158	60	+++	+++	++	+++
G6	Decanoic acid	C	1372	172	60	++	+++	++	++
G7	Undecanoic acid	C	1466	186	60	+	++	+	++
G8	Dodecanoic acid isomer	C	1528	200	60	+++	++	++	++
G9	Dodecanoic acid	C	1565	200	60	++	+++	+++	+++
G10	Tridecanoic acid isomer	C	1626	214	73	++	+++	++	-
G11	Tridecanoic acid	C	1665	214	73	++	+++	++	+
G12	Tetradecanoic acid isomer	C	1729	228	73	++	+++	+++	++
G13	Tetradecanoic acid	C	1769	228	73	+++	++++	++++	+++
G14	Pentadecanoic acid isomer	C	1830	242	73	+++	++++	+++	++
G15	Pentadecanoic acid	C	1865	242	73	++	+++	+++	++
G16	Hexadecanoic acid isomer	C	1927	256	43	+	++++	+++	-
G17	Hexadecanoic acid	C	1970	256	43	+	++++	++++	+++
G18	Heptadecanoic acid isomer	C	2027	270	43	-	+++	+++	-
G19	Heptadecanoic acid	C	2063	270	43	+	+++	+++	++
G20	Octadecanoic acid	C	2168	284	43	+++	++++	++++	++
G21	Nonadecanoic acid	C	2264	298	43	++	+++	+++	-
G22	Eicosanoic acid	C	2364	312	43	++	+++	++	++
G23	Heneicosanoic acid	C	2466	326	43	++	+++	++	-
G24	Docosanoic acid	C	2569	340	43	+++	++++	++++	++

[a] Identification method: comparison of sample mass spectra and RIs with those of authentic standard compounds (A) or published data (B); comparison of sample mass spectra with those of library spectra or published spectra (C). [b] Molecular weight. [c] Base ion.
+, identified with intensity of 10^3. ++, identified with intensity of 10^4. +++ identified with intensity of 10^5. ++++, identified with intensity of 10^6. –, not identified.

compounds, which are provided by urban runoff from civilized and industrial areas in the river basins (Pereira et al. 1996). Seven to eleven $C_{24}H_{14}$ PAHs were detected from the investigated sites. These compounds can be the same as the eleven $C_{24}H_{14}$ PAHs found by Allen et al. (1998) in urban aerosol in Boston, MA. Among the PAHs, perylene and retene are reported as to be mainly derived from natural sources (Cranwell and Koul 1998). Perylene was common in sediments from rivers in Niigata, Japan (Kawata et al. 1997).

Five phthalates were identified from the investigated sites. These phthalates except for diheptyl phthalate are suspected as endocrine disrupting compounds. They are reported as ubiquitous pollutants in the environment (Hanada et al. 1995, Tan 1995, Terashi et al. 1993) owing to their widespread use as plasticizers. Carboxylic acids with C_6 to C_{22} were identified at the investigated sites. They are emitted into the environment from anthropogenic and biogenic sources as well as photochemical transformations of several precursors (Larson and Weber 1994). Among the carboxylic acids, those with C_6 to C_{16} were reported as to be expected to have come from the combustion system including of lubricating oil constituents (Rogge et al. 1993). Hexadecanoic acid and Octadecanoic acid, which are reported as derivatives from seaweed (Hanada et al. 1995), were predominant in the identified acids at sites 2 and 3.

REFERENCES

Allen JO, Durant JL, Dookeran NM, Taghizadeh K, Plummer EF, Lafleur AL, Sarofim AF, Amith KA (1998) Measurment of $C_{24}H_{14}$ polycyclic aromatic hydrocarbons associated with a size-segregated urban aerosol. Environ Sci Technol 32: 1928-1932

Cranwell PA, Koul VK (1989) Sedimentary record of polycyclic aromatic and aliphatic hydrocarbons in the Windermere catchment. Wat Res 23: 275-283

Hanada Y, Kadokami K, Shiraishi H, Imamura K, Suzuki S, Hasegawa A (1995) Identification of chemical substances in environmental samples by gas chromatography/mass spectrometry. J Environ Chem 5: 47-64

Kawata K, Tanabe A, Mitobe H, Sakai M, Yasuhara A (1997) Distribution of perylene and five-ring polycyclic aromatic hydrocarbons in sediment and airborne particulate matter. Toxicol Environ Chem 63: 97-106

Larson RA, Weber EJ (1994) Reaction mechanisms in environmental organic chemistry. Lewis Boca, Raton Fl

Latimer JS, Quinn JG (1996) Historical trends and current inputs of hydrophobic organic compounds in an urban estuary: the sediment record. Environ Sci Technol 30: 623-633

Pereira WE, Domagalski JL, Hostettler FD, Brown LR, Rapp JB (1996) Occurrence and accumulation of pesticides and organic contaminants in river sediment, water and clam tissues from the San Joaquin River and tributaries, California. Environ Toxcol Chem 15: 172-180

Rogge WF, Hildemann LM, Mazurek MA, Cass GR, Simoneit BRT (1993) Sources of fine organic aerosol. 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks. Environ Sci Technol 27: 636-651

Tan GH (1995) Residue levels of phthalate esters in water and sediment samples from Klang River basin. Bull Environ Contam Toxicol 54:171-176

Takada H, Oguma N, Ishiwatari R (1992) Seasonal variations and modes of riverine input of organic pollutants to the coastal zone: 1. Flux of detergent-derived pollutants to Tokyo Bay. Environ Sci Technol 26: 2517-1523

Terashi A, Hanada Y, Kido A, Ishikawa S (1993) Organic compounds found in Dokai Bay, Japan. Bull Environ Contam Toxicol 50: 348-355

Tolosa I, Bayona JM, Albaiges J (1996) Aliphatic and polycyclic aromatic hydrocarbons and sulfur/oxygen derivatives in northwestern Mediterranean sediments: spatial and temporal variability, fluxes, and budgets. Environ Sci Technol 30: 2495-2503

Zeng EY, Vista CL (1997) Organic pollutants in the coastal environment off San Diego, California. 1. Source identification and assessment by compositional indices of polycyclic aromatic hydrocarbons. Environ Toxicol Chem 16: 179-188