Environmental
Contamination
and Toxicology

Distribution of Semivolatile Cyclic Compounds in Sediment from Niigata, Japan

K. Kawata,[1] A. Tanabe,[2] T. Asada,[1] K. Oikawa[1]

[1] Faculty of Applied Life Sciences, Niigata University of Pharmacy and Applied Life Sciences, 265-1 Higashijima, Niigata 956-8603, Japan
[2] Niigata Prefectural Research Laboratory for Health and Environment, 314-1 Sowa, Niigata 950-2144, Japan

Polycyclic aromatic hydrocarbons (PAHs) originate from the incomplete combustion of organic matter, the emissions of petrogenic products and the transformation of biogenic precursors. Although some PAHs, such as perylene, have biogenetic sources (Kawata et al. 1997), most PAHs have the anthropogenic sources and distribute in the environment as ubiquitous contaminants (Lopes et al. 2001). Their concentration levels act as an important indicator for evaluating the anthropogenic impact to the environment. PAHs enter surface waters mainly via atmospheric fallout, urban run-off, municipal effluents and oil spillage or leakage (Vrana et al. 2001). The PAHs migrate from the surface water to the sediment because of their extremely low solubility in water. Therefore, sediment is the best media for evaluation of the PAH's impact on the water environment.

A number of studies has been performed on their distributions in sediment (Kawata et al. 1992; Li et al. 2001; Lopes et al. 2001; Rao 2003; Su et al. 2000; Vrana et al. 2001). Most of the previous investigations dealt with the 16 PAHs, which have been listed as priority pollutants in Test Methods SW-846 by the U.S. Environmental Protection Agency. However, there are few investigations of the distribution of semivolatile cyclic compounds in sediment, such as tetrahydronaphthalene, biphenyl and dibenzyl ether. Tetrahydronaphthalene and biphenyl are included in petroleum. Dibenzyl ether is synthesized from benzyl chloride and is used as a dye, solvent, detergent, flavor and fragrance. Moreover, alkyl naphthalenes, such as methylnaphthalenes (Ou et al. 2004) and dimethylnaphthalenes, have been minor targets of investigation, although they are interesting components of petroleum.

We have previously reported the determination of 40 semivolatile cyclic compounds in sediment as well as in water and soil (Kawata et al. 2003). This paper describes the distribution of 29 semivolatile cyclic compounds in sediment from four rivers and a port in Niigata, Japan. The target compounds include tetrahydronaphthalene, biphenyl, terphenyls, diphenylmethane, triphenylmethane and dibenzyl ether as well as alkyl naphthalene including methylnaphthalenes and dimethylnaphthalenes. Eight typical PAHs with two to four rings, i.e.,

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Correspondence to: K. Kawata
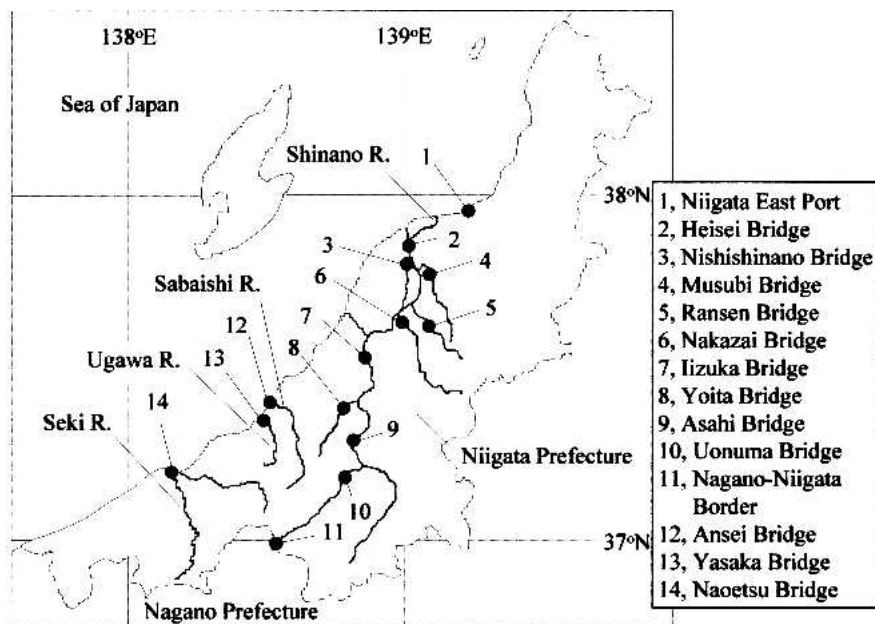
Figure 1. Sampling sites.

naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene and pyrene, were also determined in order to evaluate the contamination levels of the sediment by anthropogenic PAHs.

MATERIALS AND METHODS

A cyclic steam distillator was specially made by Sansho, Ltd. (Tokyo, Japan). A Hitachi M9000 gas chromatograph/mass spectrometer (GC/MS) equipped with a Hitachi AI-7000 auto-injector was used to determine the compounds in the samples. The GC was equipped with a fused-silica column J&W DB-5 (0.25 μm film thickness, 30 m long, 0.25 mm id). The oven temperature was held at 60°C for 1 min and then programmed to 300°C at 7.5°C/min and held for 7 min. The GC was operated at the injector temperature of 250°C; the helium carrier gas flow rate of 1.0 ml/min; and the interface temperature of 250°C. The MS was operated at the ion source temperature of 250°C; ionization current of 30 μA; multiplier voltage of 330 V; ionization time of 25 ms; and mass scan range of 40–350 at 45 ms/scan.

Hexane, acetone, and anhydrous sodium sulfate (pesticide grade) were purchased from Kanto Chemicals (Tokyo, Japan). Stable isotope-labeled compounds (surrogate compounds) and an internal standard compound were purchased from CDN Isotope (Quebec, Canada), Hayashi Pure Chemical Ind., Ltd. (Osaka, Japan), and Wako Pure Chemical Ind., Ltd. (Osaka, Japan). Copper powder (40–80 mesh, reduced-granular, elemental analysis grade) was purchased from Wako.

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Standard solutions of mixtures of the target compounds (100 and 20mg/ml) were prepared in hexane. A surrogate solution of a mixture of nine stable isotope-labeled compounds (1,2-diphenylethane-d14, *p*-terphenyl-d14, naphthalene-d8, acenaphthene-d10, fluorene-d10, phenanthrene-d10, anthracene-d10, fluoranthene-d10 and pyrene-d10) and an internal standard ($^{13}C_6$-hexachlorobenzene) solution was prepared in hexane. A Waters Sep-Pak Plus Silica (Milford, MA) was washed with 5 ml of hexane prior to use.

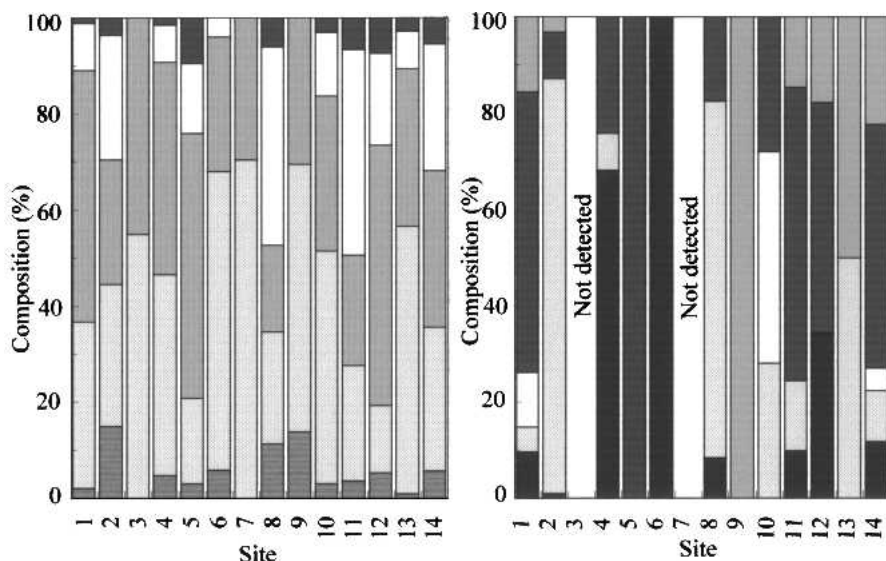**Table 1.** Summary of semivolatile cyclic compounds in sediments

Compound	Abbrev.	n*	Concentration (ng/g dry)			
			Min	Max	Average	MDL
Tetrahydronaphthalene	Thn	7	0.4	1.9	1.1	0.4
Biphenyl	Bp	9	0.7	6.7	3.0	0.4
Diphenylmethane	Dpm	1	0.4	0.4	0.4	0.4
Triphenylmethane	Tpm	2	1.1	1.3	1.2	0.4
Di-/triphenylmethane	Dpm/Tpm	3	0.4	1.3	0.9	
o-Terphenyl	*o*-Tp	1	0.7	0.7	0.7	0.4
m-Terphenyl	*m*-Tp	6	0.4	35	7.4	0.4
p-Terphenyl	*p*-Tp	1	0.7	0.7	0.7	0.4
Σ Terphenyls	Σ Tps	8	0.4	35	5.8	
Dibenzyl ether	DbE	8	0.4	6.2	1.7	0.4
Naphthalene	Np	10	2.4	11	6.0	0.8
1-Methylnaphthalene	1-Mn	10	0.9	10	4.9	0.4
2-Methylnaphthalene	2-Mn	10	1.2	14	7.0	0.4
Σ Methylnaphthalenes	Σ Mns	10	2.1	24	12	
2-Ethylnaphthalene	En	8	0.5	3.1	2.0	0.4
1,3-Dimethylnaphthalene	1,3-Dmn	9	0.8	10	4.9	0.4
1,4-/1,5-/1,6-Dimethylnaphthalene	1,4-Dmn	5	1.3	5.9	3.4	1.0
1,8-Dimethylnaphthalene	1,8-Dmn	4	0.5	0.8	0.6	0.5
2,3-Dimethylnaphthalene	2,3-Dmn	11	0.6	14	6.0	0.4
2,6/2,7-Dimethylnaphthalene	2,6-Dmn	8	1.1	14	5.9	0.8
Σ Dimethylnaphthalenes	Σ Dms	11	0.6	42	16	
2,3,5-Trimethylnaphthalene	Tmn	2	0.5	1.1	0.8	0.5
2,6-Diisopropylnaphthalene	Din	5	0.5	2.4	1.2	0.5
Σ Alkyl naphthalenes		11	0.6	71	29	
Acenaphthylene	Acy	7	0.6	14	4.0	0.5
Acenaphthene	Ac	10	0.5	9.3	2.6	0.5
Fluorene	Fl	10	1.5	29	7.9	0.5
Phenanthrene	Ph	14	1.1	240	40	0.5
Anthracene	An	9	0.9	8.7	3.2	0.5
Σ Tree-ring PAHs		14	1.1	300	51	
Fluoranthene	Flt	14	1.4	110	22	0.6
Pyrene	Py	14	0.6	90	20	0.6
Σ Four-ring PAHs		14	2.0	200	42	
Sum		14	3.6	570	130	
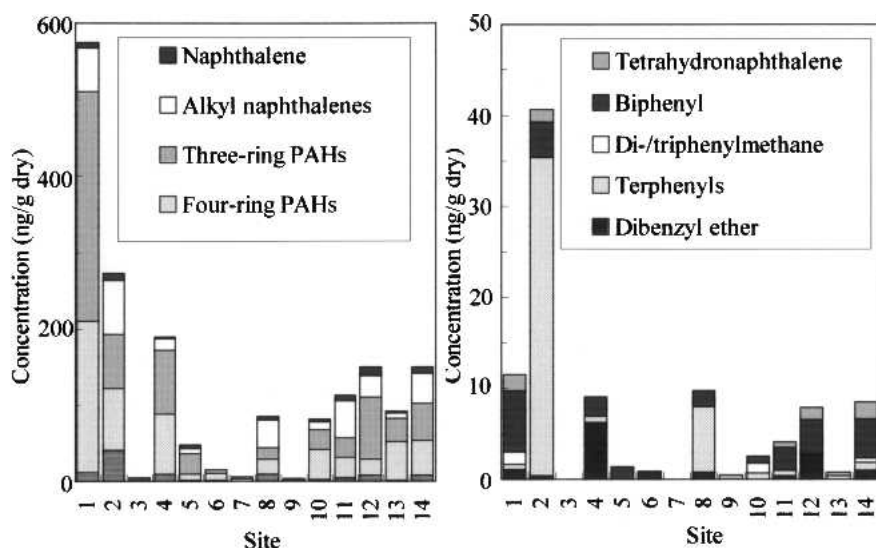
Figure 2. Concentrations of semivolatile cyclic compounds in sediment.

Sediment samples were collected at 14 sites from four rivers and a port in Niigata Prefecture, Japan (Figure 1) from November to December 1999. The Niigata East Port is located in an industrial area. The Shinano River flows 367 km via Nagano Prefecture and Niigata Prefecture to the Sea of Japan, draining 11,900 sq km including cultivated areas and civilized areas. The Sabaishi River and the Ugawa River flows 48 and 25 km, draining 277 and 109 sq km, respectively, including cultivated areas and civilized areas. The Seki River flows 64 km via Nagano Prefecture and Niigata Prefecture to the Sea of Japan, draining 1140 sq km including cultivated areas, industrial areas and civilized areas. The sediment samples were stored in 200 ml glass bottles equipped with ground glass stoppers at -20°C without any headspace.

Determination of the compounds was performed using a previously published isotope-internal standard method (Kawata et al. 2003). Briefly, a sediment sample (20 g) with surrogate compounds (0.2 µg each) was added to a 500 ml-round-bottom flask containing 350 ml of purified water. The flask was gradually heated until all the hexane was distilled out and then further distilled for 90 min. The hexane layer was dried over anhydrous sodium sulfate, and the sulfur was removed over 100–250 mg of copper powder. After the solution was condensed with a purified nitrogen stream to 1ml in volume, the obtained solution was placed in a silica gel cartridge. The cartridge was washed with 1 ml of hexane, and then subsequently eluted with 5 ml of acetone/hexane (20/80, v/v) solution. The eluate was condensed with a purified nitrogen stream to exactly 1 ml in volume. After 0.2 µg of the internal standard was added, the sample was store at 5°C until the GC/MS analysis. A sample (1 µl) was injected into the GC/MS. The compounds were determined using the internal standard method. All samples were corrected for the recovery efficiencies of the surrogate compounds.

Figure 3. Composition of semivolatile cyclic compounds in sediment. Patterns of bars correspond to those in Figure 2.

The correlation coefficient (r) of each calibration curve ranged from 0.998 to 1.000. The linear range of the standard curve was from 5 ng to 500 ng. The overall recoveries and relative standard deviation for the surrogate compounds were 80 and 16 % for 1,2-diphenylethane-d_{14}, 75 and 13 % for p-terphenyl-d_{14}, 89 and 11 % for naphthalene-d_8, 85 and 7.2 % for acenaphthene-d_{10}, 86 and 7.3 % for fluorene-d_{10}, 90 and 8.2 % for phenanthrene-d_{10}, 83 and 7.1 % for anthracene-d_{10}, 85 and 6.3 % for fluoranthene-d_{10}, and 85 and 9.2 % for pyrene-d_{10}, respectively.

RESULTS AND DISCUSSION

Out of the 40 semivolatile cyclic compounds (Kawata et al. 2003), 29 compounds were detected from the investigated sites. Table 1 summarized the detected semivolatile cyclic compounds in the sediments together with minimum detection limits (MDLs). Three to 25 compounds were found at sites 1 - 14. Among the compounds, diphenylmethane, triphenylmethane, o-terphenyl, p-terphenyl and 2,3,5-trimethylnaphthalene were found at only one site or two sites. While few reports have been published on the presence of diphenylmethane and triphenylmethane in sediments, terphenyls were reported to be detected from several sediment samples in Japan; m-terphenyl, which was detected at 6 sites in the present study, was the major contaminant in Japan (Ministry of Environment 2003).

Phenanthrene, fluoranthene and pyrene were detected at all the investigated sites. Phenanthrene was the most abundant compound of the target compounds. The

concentration range of phenanthrene was 1.1 - 240 ng/g dry base; it was lower than those of 283 - 600 ng/g at Fox River, Wisconsin (Su et al. 2000) and 546-2208 ng/g at in the Boese Sieben Creek, Saxony-Anhalt, Germany (Vrana et al. 2001). Fluoranthene and pyrene were detected at 1.4-110 ng/g and 0.69-90 ng/g, respectively. The concentration range of fluoranthene was lower than that of 0.2 - 936 ng/g in the sediments from 30 sites around Niigata, Japan, in 1984 to 1988 (Kawata et al. 1992) and that of 801 - 2393 ng/g in Germany (Vrana et al. 2001). The pyrene concentration in this study was almost comparable to that of 0.2 - 85 ng/g for Niigata (Kawata et al. 1992) and was lower than that of 659 - 1624 ng/g for Germany (Vrana et al. 2001).

Naphthalene, 1-methylnaphtalene, 2-methylnaphtalene, 2,3-dimethylnaphthalene, acenaphthene and fluorene were detected at 10 -11 sites (Table 1). The naphthalene concentration ranged from 2.4 to 11 ng/g. This value was lower than those of 32 ng/g at Ashtabula River (Li et al. 2001), 65 - 246 ng/g at Fox River (Su et al. 2000) and <5 - 205 ng/g at Boese Sieben Creek (Vrana et al. 2001). 1-Methylnaphtalene and 2-methylnaphtalene were detected at 0.9 - 10 ng/g and 1.2 - 14 ng/g, respectively. These values were rather lower than those of 1.5 - 30.6 ng/g and 0.3 - 57.8 ng/g from the Xiamen Harbour and Yuan Dan Lake, China (Ou et al. 2004), respectively. The concentrations of acenaphthene (0.5 - 9.3 ng/g) and fluorene (1.5 - 29 ng/g) were lower than those of 33 - 216 ng/g and 68 -113 ng/g at Fox River (Su et al. 2000), and 11 - 59 ng/g and 33 - 216 ng/g at Boese Sieben Creek (Vrana et al. 2001), respectively.

Biphenyl was found at nine sites. Biphenyl was detected from crude and used oils (Brandt et al. 2002; Stout et al. 2004) as well as deposit dust (Marynowski et al. 2004). However, only a few reports have been published on the presence of biphenyl in sediments. Stout et al. (2004) detected biphenyl in nine urban

Table 2. Correlations among semivolatile aromatic compounds in sediment

	Thn	Bp	Tps	DbE	Np	Mns	En	Dmns	Acy	Ac	Fl	Ph	An	Flt	Py
Thn		**		**	*			**	*	**	**	*	*	*	
Bp	0.85			**	**			**	**	**	**	**	**	**	**
Tps	0.25	0.27			*			*							
DbE	0.29	0.27	0.31		**			*							
Np	0.74	0.81	0.45	0.56		**	*	**		*				*	*
Mns	0.66	0.78	0.55	0.86	0.82		**	**		*	*			*	*
En	0.42	0.37	0.33	0.52	0.55	0.77		*							
Dmns	0.72	0.86	0.64	0.70	0.83	0.95	0.56			**	**	*	*	**	*
Acy	0.61	0.74	-0.13	0.20	0.41	0.35	-0.04	0.43		**	**	**	**	**	**
Ac	0.68	0.85	0.16	0.03	0.52	0.64	0.29	0.70	0.89		**	**	**	**	**
Fl	0.67	0.86	0.14	0.02	0.58	0.53	0.05	0.65	0.95	0.94		**	**	**	**
Ph	0.61	0.83	0.05	0.09	0.39	0.51	0.11	0.60	0.90	0.97	0.93		**	**	**
An	0.61	0.76	0.04	0.15	0.44	0.51	0.26	0.55	0.82	0.89	0.83	0.89		**	**
Flt	0.59	0.81	0.20	0.07	0.40	0.59	0.22	0.67	0.79	0.95	0.86	0.97	0.90		**
Py	0.50	0.71	0.21	0.09	0.33	0.57	0.31	0.61	0.73	0.93	0.79	0.92	0.89	0.97	

* $p < 0.05$, ** $p < 0.01$

waterways in the USA, and Thomas et al. (2002) identified biphenyl from sediments collected at four estuaries in the United Kingdom.

Figure 2 shows the concentrations of the target compounds in the sediment from each site. The total concentrations ranged from 3.6 ng/g at site 9 to 570 ng/g at site 1. Site 1 is located at an industrial port surrounded by manufacturing plants. Therefore, it was contaminated by emissions from ships as well as from manufacturing plants. Sites 2 - 11 are located on the mainstream or tributaries of the Shinano River. However, the detected compounds differed at each site in concentration and composition. The highest concentrations were found at site 2, whereas the lowest at site 9. While site 2 was located in an urban area, site 9 was located in a rural area. Moreover, sites 3, 6 and 7, where the total concentrations were as low as that at site 9, were also located in rural areas. Therefore, the sediments reflected the local contaminations only around the investigated sites.

The compositions of the target compounds are given in Figure 3. The PAHs were predominant at all the investigated sites; three-ring PAHs and/or four-ring PAHs were the major compounds. The target compounds except for the PAHs showed characteristic compositions at each site. Namely, tetrahydronaphthalene, biphenyl and dibenzyl ether were the main compounds at sites 9, 5, and 6, respectively. Biphenyl was the major component at sites 1, 11, 12 and 14; *m*-terphenyl was the major component at sites 2 and 8.

The coefficients of correlation among the main compounds are listed in Table 2. The concentrations of seven PAHs with three or four rings showed strong significant ($p < 0.01$) correlations of $r > 0.7$. These correlations were the same as for the urban dusts and airborne particulate matters near traffic roads (Kawata et al. 1992). Therefore, these compounds were mainly derived from combustion including gasoline burning by motor vehicles as the other sites in Japan, and were mainly attributable to runoff delivery as well as the atmospheric fallout of particulate (Kawata et al. 1992). The biphenyl concentration significantly correlated ($p < 0.01$) with those of the seven major PAHs. Moreover, tetrahydronaphthalene and dimethylnaphthalenes showed significant ($p < 0.05$) correlations among ten compounds including the seven PAHs and biphenyl. Therefore, these compounds appear to be derived from the same anthropogenic sources as the PAHs and biphenyl, and behaved similarly in the environment.

The concentrations of naphthalene and the methylnaphthalenes significantly correlated ($p < 0.05$) to those of tetrahydronaphthalene, biphenyl and the dimethylnaphthalenes. Therefore, naphthalene and the methylnaphthalenes appear to be derived from the same anthropogenic sources as those of tetrahydronaphthalene, biphenyl and the dimethylnaphthalenes, but behaved differently in the environment from these compounds. The concentration of dibenzyl ether significantly correlated to those of the methylnaphthalenes and dimethylnaphthalenes, nevertheless dibenzyl ether has different sources from the PAHs. On the other hand, ethylnaphthalene and the terphenyls did not show significant correlations except in a few cases (Table 2). Therefore, these

compounds appear to be derived from other sources and/or behaved differently in the environment from the other compounds mentioned above.

REFERENCES

Brandt C A, Becker, J M, Porta A (2002) Distribution of polycyclic aromatic hydrocarbons in soils and terrestrial biota after a spill of crude oil in Trecate, Italy. Environ Toxicol Chem 21: 1638–1643

Kawata K, Moriyama N, Fujieda Y (1992) Distribution of polynuclear aromatic hydrocarbons in environment at Niigata Area. Japanese J Toxicol Environ Health 38: 443-451

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

Kawata K, Tanabe A, Yagoh H, Ibaraki T, Yasuhara A and Shibamoto T (2003) Determination of Semivolatile Organic compounds in environmental samples by gas chromatography/mass spectrometry after extraction by cyclic steam distillation. J AOAC Int 86: 246-256

Li K, Christensen ER, Van Camp RP, Imamoglu I (2001) PAHs in dated sediments of Ashtabula River, Ohio, USA. Environ Sci Technol 35, 2896-2902

Lopes TJ, Edward T. Furlong ET (2001) Occurrence and potential adverse effects of semivolatile organic compounds in streambed sediment, United States, 1992–1995. Environ Toxicol Chem 20: 727–737

Marynowski L, Pieta M, Janeczek J (2004) Composition and source of polycyclic aromatic compounds in deposited dust from selected sites around the Upper Silesia, Poland. Geol Quart 48: 169–180

Ministry of Environment (2003) Chemicals in the environment. Ministry of Environment, Government of Japan, Tokyo, Japan.

Ou S, Zheng J, Zheng J, Richardson BJ, Lam PKS (2004) Petroleum hydrocarbons and polycyclic aromatic hydrocarbons in the surficial sediments of Xiamen Harbour and Yuan Dan Lake, China. Chemosphere 56: 107-112

Rao AS (2003) Polycyclic Aromatic Hydrocarbons in Sediments from Kolleru Wetland in India. Bull Environ Contam Toxicol 70: 964-971

Stout S A, Uhler A D, Emsbo-Mattingly S D (2004) Comparative evaluation of background anthropogenic hydrocarbons in surficial sediments from nine urban waterways. Environ Sci Technol 38: 2987-2994

Su M-C, Christensen E R, Karls J F, Kosuru S, Imamoglu I (2000) Apportionment of polycyclic aromatic hydrocarbon sources in lower Fox River, USA, sediments by a chemical mass balance model. Environ Toxicol Chem 19: 1481–1490

Thomas KV, Balaam J, Barnard N, Dyer R, Jones C, Lavender J, McHugh M (2002) Characterisation of potentially genotoxic compounds in sediments collected from United Kingdom estuaries. Chemosphere 49: 247–258

Vrana B, Paschke A, Popp P (2001) Polyaromatic hydrocarbon concentrations and patterns in sediments and surface water of the Mansfeld region, Saxony-Anhalt, Germany. J Environ Monit 3: 602–609