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Brominated Phenols and Anisoles in River and Marine Sediments in Japan

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Halogenated anisoles in oysters collected at Tokyo Bay, Japan, were identified by Miyazaki et al. (1981). We also found brominated and chlorinated anisoles in most of the fish and shellfish samples analyzed from Japan (Watanabe et al. 1983a). Recently, Giam et al. (1984) reported the presence of these compounds in the marine atmosphere from New Zealand. It has become clear that these anisoles are ubiquitous environmental pollutants, though these levels are low.

Brominated anisoles may possibly result from the decomposition of the corresponding brominated phenols through microbiological methylation, as in the case of pentachlorophenol (Rott et al. 1979; Neilson et al. 1983). Thus, brominated phenols may be a source of environmental pollution. Little data are available on the levels of these compounds but chlorinated phenol levels have been monitored in the environmental samples considerably (Ernst and Weber 1978; Weber and Ernst 1978; Paasivirta et al. 1980; Wegman and Broek 1983). In the present work, an attempt has been made to determine the environmental levels of brominated phenols along with chlorinated phenols in river and marine sediments collected from Osaka, Japan. The brominated and chlorinated anisole levels in the samples were also examined.

MATERIALS AND METHODS

Most of the halogenated phenols for references were obtained commercially. The other halogenated phenols were prepared according to methods described in our previous report (Watanabe et al. 1984). Halogenated anisoles were prepared from the corresponding halogenated phenols by methylation with dimethyl sulfate.

Sediment materials were collected with a dredger from upper river and marine sediment layers in Osaka Prefecture, Japan, from 1981 through 1983. Sampling sites are shown in Figure 1.

A JEOL JMS DX-300 mass spectrometer connected to a Hewlett Packard 5710A gas chromatograph and a JEOL JMS 3500 data system were used for determination of halogenated phenols by mass fragmentographic analysis under the following conditions: separation column, a capillary column (0.31 mm x 25 m) of cross-linked 5% phenyl methyl silicon; column temperature, 100 to 210 °C (8 °C/min.); carrier gas (He) flow rate, 1 ml/min.; electron impact ionization voltage, 70 eV; ion source temperature, 220 °C.

A Varian 2100 gas chromatograph connected to an electron capture detector (^{63}Ni) was used to determine the halogenated anisole levels. The conditions were as follows: separation column, 2% OV-17 column (2 mm x 1.8 m); column temperature, 150 °C; carrier gas (N_2) flow rate, 30 ml/min.

Extraction and clean-up of halogenated phenols and anisoles in the sediment samples were carried out according to the same method described previously in the analysis of flame retardant Tetrabromobisphenol-A in sediment (Watanabe et al. 1983b). Both halogenated phenols and anisoles were extracted with acetone in the sediment. The acetone extracted was added to 2% NaCl solution. This combined solution was then extracted with hexane after adjusting the pH to about 10. Halogenated phenols remained in the basic solution though the anisoles could be extracted with hexane. The halogenated phenols were extracted with a mixture of hexane and diethyl ether (2:1) after adjusting the pH to about 2. The extract halogenated phenols were then converted to ethyl ether derivatives by ethylation with ethyl bromide. These derivatives following treatment with conc. sulfuric acid were determined by mass fragmentography using a GC/MS.

The hexane extract containing halogenated anisoles was cleaned with a Florisil column. This column was eluted with 20% diethyl ether/hexane after being washed with hexane. The halogenated anisoles eluted in this fraction were determined by gas chromatography. Further confirmation was also made by mass fragmentography using a capillary column described above.

Recovery tests were made by adding known amounts of halogenated phenols and anisoles (each 0.1 mg/kg dry weight) to the sediment. Each recovery determination was carried out 5 times. The mean recoveries in the sediment were as follows: 2,4-dibromophenol, 68 ± 6%; 2,4,6-tribromophenol, 93 ± 6%; 2,4,6-trichlorophenol, 93 ± 6%; 2,3,4,6-tetrachlorophenol, 94 ± 7%; pentachlorophenol, 89 ± 9%; 2,4-dibromoanisole, 92 ± 4%, 2,4,6-tribromoanisole, 90 ± 5%; 2,4,6-trichloroanisole, 73 ± 3%; 2,3,4,6-tetrachloroanisole, 89 ± 5% and pentachloroanisole, 92 ± 6%.

RESULTS AND DISCUSSION

Figure 2 shows the mass fragmentograms of halogenated phenol standards and the sediment extract collected at sampling site

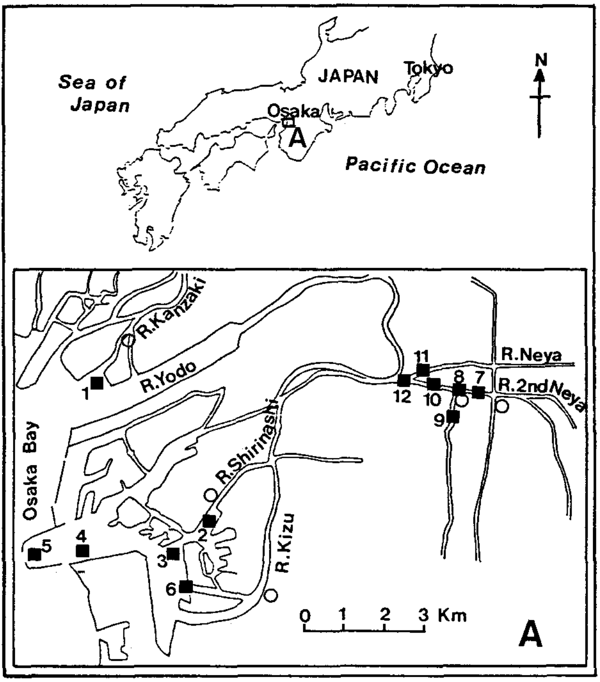

Figure 1. Location map of sediment samples.
(■--sampling site, ○--sewage treatment plant)

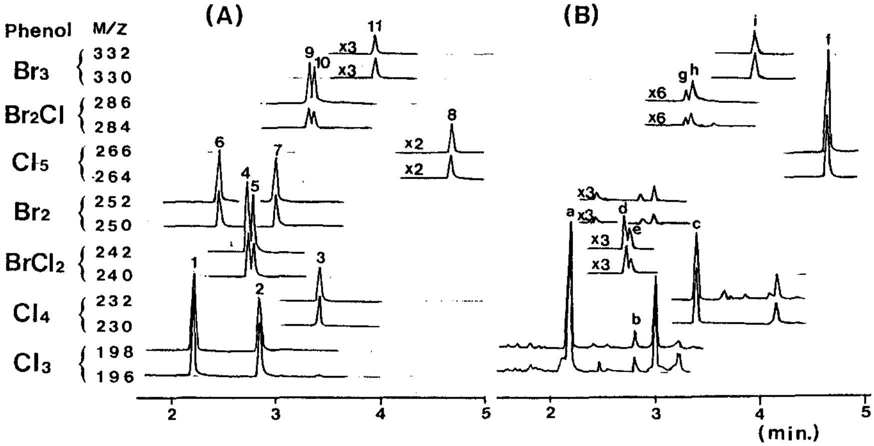

Figure 2. Mass fragmentograms of (A). halogenated phenol standards and (B). an extract of the sediment from sampling site #7, after ethylation. (1: 2,4,6-trichloro-, 2: 2,4,5-trichloro-, 3: 2,3,4,6-tetrachloro-, 4: 2-bromo-4,6-dichloro-, 5: 4-bromo-2,6-dichloro-, 6: 2,6-dibromo-, 7: 2,4-dibromo-, 8: pentachloro-, 9: 2,6-dibromo-4-chloro-, 10: 2,4-dibromo-6-chloro-, 11: 2,4,6-tribromophenetole). G.C. conditions are described in the text.

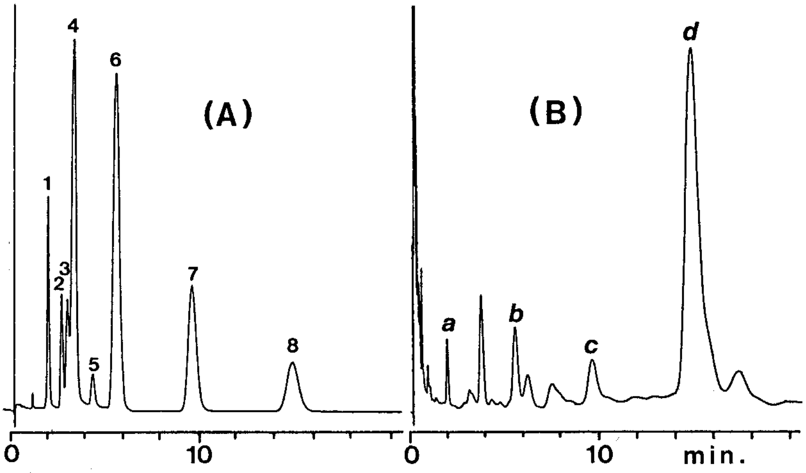

Figure 3. Gas chromatograms of (A). halogenated anisole standards and (B). an extract of the sediment from sampling site #7. (1: 2,4,6-trichloro-, 2: 2,3,6-trichloro-, 3: 2-bromo-4-chloro- + 4-bromo-2-chloro- + 2,6-dibromo-, 4: 2-bromo-4,6-dichloro- + 4-bromo-2,6-dichloro-, 5: 2,4,5-trichloro-, 6: 2,4-dibromo- + 2,6-dibromo-4-chloro- + 2,4-dibromo-6-chloro- + 2,3,4,6-tetrachloro-, 7: 2,4,6-tribromo-, 8: pentachloroanisole). G.C. conditions are described in the text.

#7 after ethylation. Brominated phenols, i.e., bromodichlorophenol (peak d and e), dibromochlorophenol (peak g and h) and tribromophenol (peak i), were found in the samples, along with chlorinated phenols (peak a, b, c and f). No dibromophenol was found since dibromophenols were detected in the control sample.

As shown in Figure 3, 2,4,6-tribromoanisole (peak *c*) was also present in the sediment samples along with chlorinated anisoles (peak *a*, *b* and *d*).

The residue levels of halogenated phenols and anisoles in the sediment samples are given in Table 1, as determined on a dry weight basis. The brominated phenol levels were lower than those of the chlorinated phenols being about one-tenth the chlorinated phenols content. Tribromophenol was found in nearly all the samples analyzed (occurrence; 10/12) and was thus considered an ubiquitous environmental contaminant, just as organochlorinated pesticides such as hexachlorocyclohexane and DDT compounds, though its residue level is generally low. However, higher residue levels of this compound were found in the two sediment samples collected at sampling sites #7 and 8, and were nealy the same as those of the organochlorinated pesticides.

2,4,6-Tribromoanisole was found in only two of the 12 samples analyzed and had a very low residue level. Other brominated

Table 1. Halogenated phenol, anisole and organochlorine pesticide levels in the sediment samples (µg/kg, on dry weight basis)

	Compound	Samplig site[1]											
		1	2	3	4	5	6	7	8	9	10	11	12
Brominated phenol	2,4-dibromo-	nd^2	nd^2	nd^2	nd^2	nd^2	nd^2	nd^2	nd^2	nd^2	nd^2	nd^2	nd^2
	2,6-dibromo-	"	"	"	"	"	"	"	"	"	"	"	"
	2-bromo-4,6-dichloro-	nd^3	nd^3	0.2	nd^3	nd^3	nd^3	2.4	4.4	nd^3	nd^3	0.4	nd^3
	4-bromo-2,6-dichloro-	"	"	0.2	"	"	"	0.9	2.1	"	"	nd^3	"
	2,6-dibromo-4-chloro-	"	"	0.2	"	"	"	1.1	2.3	"	"	"	"
	2,4-dibromo-6-chloro-	"	"	0.3	0.2	"	"	0.6	1.2	"	"	"	"
	2,4,6-tribromo-	1.0	"	1.2	0.8	0.9	1.3	16	36	2.3	2.4	0.9	"
	Total	1.0	nd^2	2.1	1.0	0.9	1.3	21	46	2.3	2.4	0.9	nd^2
Chlorinated phenol	2,4,6-trichloro-	0.4	0.6	2.2	1.5	1.1	2.3	26	51	1.4	2.2	6.5	nd^3
	2,4,5-trichloro-	0.4	0.9	1.8	0.8	0.6	1.4	4.4	9.0	1.9	1.6	2.0	"
	2,3,4,6-tetrachloro-	0.7	1.2	3.6	1.5	1.7	1.7	31	65	5.3	3.3	5.2	0.6
	pentachloro-	0.3	12	13	6.3	6.9	3.7	42	105	18	12	7.9	1.9
	Total	1.8	15	21	10	10	9.1	103	230	27	19	22	2.5
Halogenated anisole	2,4,6-tribromo-	nd^4	nd^4	nd^4	nd^4	nd^4	nd^4	0.7	0.7	nd^4	nd^4	nd^4	nd^4
	2,4,6-trichloro-	nd^4	nd^4	nd^4	nd^4	nd^4	nd^4	0.5	0.5	nd^4	nd^4	nd^4	nd^4
	2,3,4,6-tetrachloro-	"	"	"	"	"	"	1.8	2.0	"	"	0.5	"
	pentachloro-	"	3.5	1.0	0.7	"	0.7	29	30	3.5	5.8	3.3	"
	hexachlorobenzene	2.6	7.4	14	2.1	0.8	350	3.5	5.8	8.1	8.1	1.8	3.7
	Total HCH[5]	7.2	39	28	17	7.1	290	22	41	20	110	15	42
	Total DDT[6]	52	270	190	20	20	150	29	36	66	180	22	130

[1] See Figure 1. [2] nd: < 2.0 ppb. [3] nd: < 0.2 ppb [4] nd: < 0.5 ppb.
[5] Total HCH (hexachlorocyclohexane): α-HCH + β-HCH + γ-HCH. [6] Total DDT: p,p'-DDE + p,p'-DDD + p,p'-DDT.

anisoles were absent from the samples. Thus, sediment pollution by brominated anisoles may be not serious, but that of pentachloroanisole may be.

Chlorinated phenols in the environment have been found to arise from such sources as pentachlorophenol as a wood fungicide, degradation products of pesticides having a chlorophenolic structure such as CNP (2,4,6-trichlorophenyl-4'-nitrophenyl ether) and by-broducts from the chlorination of water such as wastewater. However, sources of brominated phenols still remain unclear. A very probable source may be by-products from chlorinated wastewater. The chlorination of water containing bromide ions and phenol results in the formation tribromophenol (Sweetman and Simmons 1980). The production of brominated phenols such as bromodichloro-, dibromochloro-, dibromo- and tribromophenol was found to occur through the chlorination of both natural (Bean et al. 1980) and wastewater (Watanabe et al. 1984).

Brominated phenol residure levels in sediment samples collected at sampling sites #7 and 8 were considerably higher than those collected at other sites as indicated above. Sewage treatment plants were located in the vicinity of sampling sites #7 and 8. Thus, the brominated phenols in the two sediment samples may have been the by-products from chlorinated wastewater. However, there were also sewage treatment plants in the upper reaches of the stream of sampling sites #1, 2 and 6 situated in estuaries of Osaka Bay. The low brominated phenol residue levels at these sites may be due to dilution of brominated phenols produced by chlorination of wastewater by sea water.

Tetrachloro- and pentachlorophenol are not produced by the chlorination of water containing phenol but di- and trichlorophenol are produced. These chlorinated phenol residue levels in sediments collected at sampling sites #7 and 8 were also higher than those in the other sampling sites. However, organochlorine pesticides residues at these sites were found to occur in essentially the same quantities, as can be seen from Table 1. The reason of the greater amounts of tetrachloro- and pentachlorophenols in sediments from sampling sites #7 and 8 is not known.

Halogenated anisoles may possibly arise from microbiological methylation products of halogenated phenols in the sediment, as described above.

River and marine sediment pollution by brominated and chlorinated phenols has been confirmed. The residue level of tribromophenol is generally low. However, a local high residue level was observed. The residue level of tribromoanisole in the sediment was negligible, though that of tribromoanisole in fish and shellfish was recognizable, as described in our previous paper (Watanabe et al. 1983a). Consequently, brominated phenol and anisole levels in the environment should be monitored.

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