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Characterization and determination of organic compounds in the mutagenic XAD-2 extracts of drinking water

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ABSTRACT

Amberlite XAD-2 extracts, which exhibit mutagenicity in the Ames assays, of drinking water sampled each month during the period from April 1988 to March 1989 were studied in order to characterize and determine the organic pollutants. The major organic pollutants were phthalate ester plasticizers such as dibutyl and di(2-ethylhexyl) phthalate. Several polynuclear aromatic hydrocarbons (PAHs) and the organochlorine pesticide oxadiazon were also identified to be present at low concentrations. The XAD-extractable and chromatographable organic pollutants were found to be composed of PAHs with a mean concentration of 0.136 μg/l (*ca.* 10% of the total amount of organic compounds detected), phthalates with a mean value of 0.405 μg/l (*ca.* 30%) and other compounds with a mean value of 0.845 μg/l (*ca.* 60%). The concentrations and compositions of these organic pollutants were correlated with the effective rainfall content of the river and with the water temperature.

INTRODUCTION

Mutagenic and carcinogenic organic compounds found in source water [1] and drinking water [2] have recently caused concern as to their potential effects on human health. Mutagenicity in source water has generally been attributed to contamination by industrial waste or agricultural run-off, and to a lesser extent to naturally occurring substances. In comparison studies of raw water *vs.* finished water, Glatz *et al.* [3] and Maruoka and Yamanaka [4] suggested that chlorination may play a major role in the production of organic mutagens in potable water. Subsequent laboratory studies by Cheh *et al.* [5], in which a drinking water treatment process was simulated, clearly demonstrated that non-volatile mutagens were produced by chlorine disinfection. Several volatile compounds such as chloroacetones and 2-chloropropenal, and chlorinated hydroxyfuranone (MX), exhibiting mutagenicity have been identified to be present in chlorinated water [6–12], but many of the non-volatile mutagenic substances have not been fully characterized.

The potential health effects of organic contaminants in drinking water can be studied only after they have been isolated from the water and identified. However, because most of these compounds are present at micrograms per litre (ppb) levels or less in drinking water, a concentration step is necessary prior to the analytical identifi-

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cation of individual contaminants. Conventional techniques used for isolating organic compounds from the water for analytical purposes include liquid–liquid extraction [13–17], carbon adsorption [18–22] and resin adsorption [23–28]. These methods, like other concentration procedures, failed to provide a totally representative concentrate as one or more groups of organic components are not recovered effectively. Consequently, determining the variation in the types and amounts of organic substances present in drinking water is important in developing on effective concentration procedure.

This work was designed to characterize and determine the organic substances present in the mutagenic XAD-2 extract of drinking water collected each month during a 1-year period. These findings would provide background information that will be useful in assessing the health implications and trends of organic contaminant behaviour in water treatment process and drinking water distribution systems.

EXPERIMENTAL

Chemicals

Organic solvents (acetone, *n*-hexane, and methanol) were of analytical-reagent grade for pesticide residue analysis (Wako, Osaka, Japan). They were checked for purity by evaporating 100 ml to 100 μl and gas chromatographic (GC) analysis. The acetonitrile used for high-performance liquid chromatography (HPLC) was a Cica–Merck HPLC-grade solvent (Kantoh Chemicals, Tokyo, Japan). Water for HPLC was obtained from Nacalai Tesque (Kyoto,Japan). *n*-Alkane, phthalate ester plasticizer and polynuclear aromatic hydrocarbon (PAH) standards were commercially available. Standard solutions of these compounds both alone and as mixtures were prepared by dissolving the compounds in methanol or *n*-hexane, with subsequent serial dilutions.

Collection and preparation of XAD-2 resin extract

A 200-ml volume of Amberlite XAD-2 resin (Rohm and Hass, Philadelphia, PA, USA) was cleaned in a Soxhlet extractor with acetone–*n*-hexane (50:50, v/v) for 24 h, in order to remove interferences from the resin. During the cleaning, a portion of the solvent was evaporated and checked for interferences by GC. If necessary, the solvent washing in the Soxhlet extractor was repeated. When the blank chromatogram showed no interferences, the resin was removed from the extractor. The solvent remaining on the adsorbent was then evaporated completely in a vacuum desiccator for 24 h. The cleaned XAD-2 resin was placed in a glass column (16 cm × 4 cm I.D.) and washed with 10 l of purified water (distilled and filtered through a 0.45-μm membrane filter) before sample collection.

Drinking water was introduced bottom-to-top into the XAD-2 resin column, which was connected directly to the water tap in the laboratory. Water samples were continuously passed through the resin column at room temperature, at a flow-rate of 400 ml/min, during each sampling period (Table I) in order to collect XAD-2-extractable organic substances. The column was then washed with 2 l of distilled water and residual water was blown from the column with dry nitrogen.

The XAD-2 resin adsorbent was removed from the column and the organic substances on the resin were then extracted by sonication with 200 ml of acetone–*n*-

hexane (50:50, v/v). The sonication extractions were repeated twice more with a fresh 200-ml volume of the mixed solvent. These extracts were dried over anhydrous sodium sulphate and evaporated to dryness by means of a rotary evaporator at 40°C.The dry concentrate was dissolved, as rapidly as possible, in 5 ml of diethyl ether or methanol, producing a concentration factor of 10^6, and stored in a refrigerator at 4°C until the subsequent chromatographic analyses were performed.

The XAD-2 resin extracts of drinking water were fractionated into several fractions by thin-layer chromatography (TLC) on Polyamid 11 F_{254} (20 × 20 cm, thickness 0.15 mm) precoated TLC plates (Merck, Darmstadt, Germany) using chloroform as developing solvent [29]. The detection of the spots on the plates was performed by UV irradiation. The separated zones were scraped off by using special recovery tubes (Wako) and the adsorbed substances were then eluted with diethyl ether. The percentage recovery of individual fractions was determined by using GC and Ames assays [29].

Analysis of XAD-2-extractable organic pollutants

The XAD-2 resin extracts were analysed using a Shimadzu GC-6A gas chromatograph with flame ionization detection (FID). A glass column (2 m × 0.3 cm I.D.) packed with 2% silicone OV-1 on Uniport HP (60–80 mesh) was employed. The temperature of the column oven was increased from 80 to 260°C at 5°C/min. The injector and detector temperatures were 260°C. The carrier gas (nitrogen) flow-rate was 50 ml/min. A Shimadzu Model Chromatopac 1A data system was used to determine the retention times and the peak areas on the chromatograms. *n*-Alkanes, phthalate esters and PAHs were identified by comparison of their retention times with those of authentic standards injected under the same GC conditions (Table II).

PAHs in the XAD-2 resin extracts were analysed using a Shimadzu LC-9A liquid chromatograph with UV detection (Senshu Scientific, Tokyo Japan). The column (150 cm × 4.6 mm I.D.) packed with LiChrosorb RP-18 (Gasukuro Kogyo, Tokyo, Japan), grain size 5 μm. The following conditions were employed: column temperature, ambient; mobile phase, acetonitrile–water (60:40, v/v); flow-rate, 0.8 ml/min. A Shimadzu Chromatopac C-R6A data system was used to determine the retention times and the peak areas on the chromatograms. Individual PAHs were identified by comparison of their retention times with those of authentic samples (Table II).

A Hitachi M-80 combined gas chromatograph–mass spectrometer equipped with a Hitachi M-003 data-processing system was used for characterization of samples with the ion source operated at 250°C at a trap current of 70 μA and an electron energy of 70 eV. A Hewlett-Packard fused-silica capillary column (25 m × 0.25 mm I.D.) coated with OV-1 was used for the GC separations of the XAD-2-extractable organic compounds from drinking water. The oven temperature of the gas chromatograph was increased from 120 to 250°C at 5°C/min. Compounds were identified by comparison of their retention times and mass spectra with those of authentic standards.

Recovery tests were performed by spiking water with phthalate esters and PAHs at the 0.1 μg/l level and carrying out the entire procedure, in order to evaluate the total analytical precision for individual hydrocarbons. A small-scale column (20 cm × 2 cm I.D.) packed with clean XAD-2 resin (50 ml) was used for the recovery

tests. After processing with 100 l of the above spiking water at a flow-rate of 100 ml/min, the residual water was blown from the column with dry nitrogen. The hydrocarbons adsorbed on the XAD-2 resin were then extracted by sonication with acetone–*n*-hexane (50:50, v/v) (3 × 50 ml). The resulting extracts were concentrated to 100 μl using a Kuderuna–Danish concentrator for GC and HPLC analyses. Although drastic precautions were taken during the evaporation steps, loss of the more volatile compounds such as naphthalenes and biphenyl occurred (Table II).

The corresponding detection limits were 1 ng/l for phthalate esters by GC and 1 ng/l for PAHs by HPLC.

RESULTS AND DISCUSSION

Chemical characteristics of organic contaminants

The XAD-2 resin extracts were prepared from the laboratory tap water each month during spring (April, May and June 1988), summer (July, August and September), fall (October, November and December) and winter (January, February and March 1989). The drinking water in this area is distributed from Asaka water treatment plants (Saitama prefecture), which draw their water from midstream region of the Tone River. The flow-rate is generally low in the winter and high in the summer. There were heavy rainfalls in September and October 1988 in this river basin, before collecting samples. Data on mutagenicity, biochemical oxygen demand (BOD) and water temperature levels in the Tone River as source water are summarized in Table I.

The XAD-2 resin extracts of drinking water showed mutagenic levels ranging from 43 to 385 induced TA100 revertants per litre equivalent of the water, with a

TABLE I

DATA ON MUTAGENICITY, BIOCHEMICAL OXYGEN DEMAND (BOD) AND WATER TEMPERATURE LEVELS

Water sample	Sampling period	Volume of sample (l)	Mutagenicity[a] (revertants/l)	Water temperature (°C)	BOD (mg/l)
Spring					
a	16–20/04/88	4000	93	17.0	2.8
b	16–21/05/88	5000	53	15.0	2.5
c	20 and 25/06/88	3600	134	22.6	2.5
Summer					
a	12–18/07/88	4000	385	20.3	1.2
b	22–29/08/88	5000	97	23.0	1.3
c	17–24/09/88	4500	43	20.6	1.1
Fall					
a	15–21/10/88	5000	178	15.8	2.4
b	18–24/11/88	4500	233	13.8	3.7
c	13–19/12/88	4100	154	7.5	4.0
Winter					
a	17–23/01/89	5300	152	8.3	4.9
b	15–22/02/89	3600	177	9.9	4.0
c	10–16/03/89	4800	71	11.8	3.5

[a] Mutagenicity assays for each drinking water concentrate (XAD-2 extract) were conducted using Salmonella typhimurium TA100 strain in the absence of rat liver homogenate (S9).

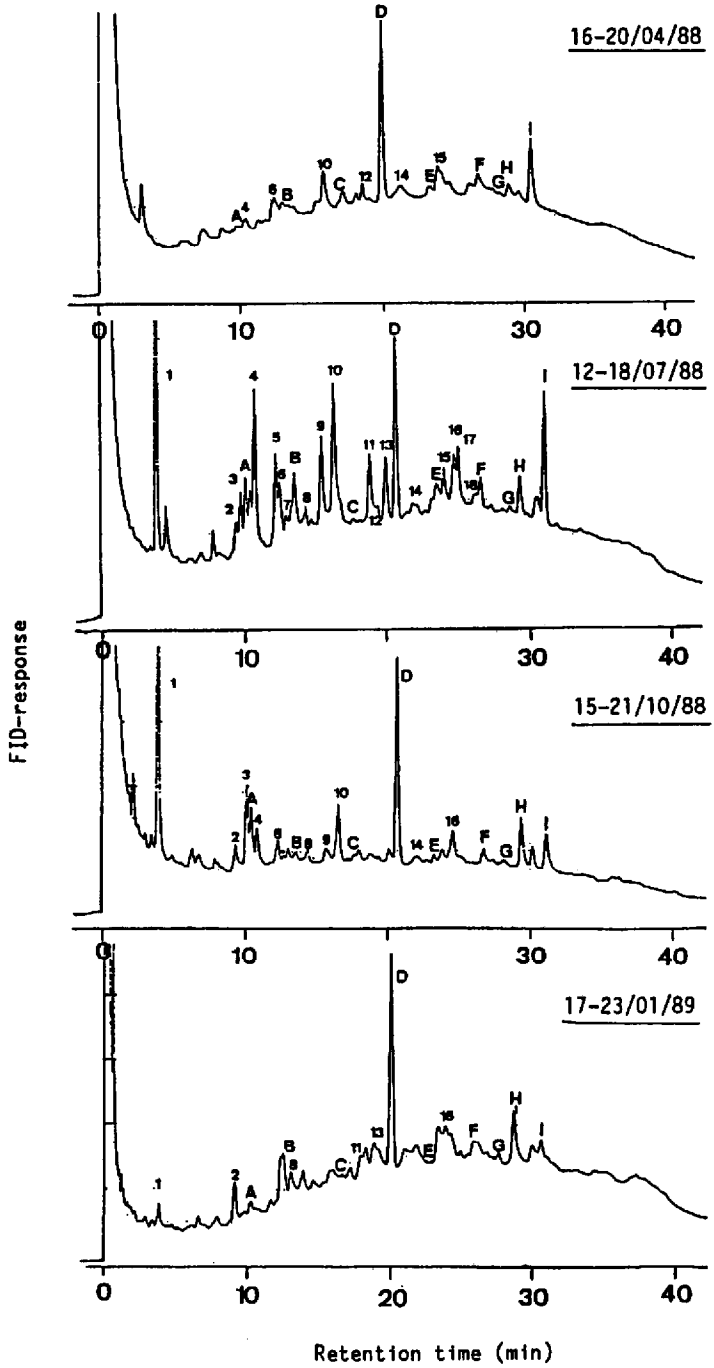

Fig. 1. Typical gas chromatograms (with FID) of XAD-2 extract of drinking water collected during spring, summer, fall and winter. The temperature of GC column (packed with 2% OV-1–Uniport HP) was raised from 80 to 260°C at 5°C/min. A 5-μl volume of the extract, equivalent to 5 l of drinking water, was injected into the column. Peaks: A = DMP; B = DEP; C = DDP; D = DBP; E = DAP; F = BBP; G = DHP; H = DCHP; I = DEHP. The numbered peaks were used for evaluation of seasonal variations in the concentrations of organic pollutants in water.

mean value of 134.8 revertants/l. Although the mutagenic levels in the extracts showed some seasonal scatter, it seems that the high levels were detected in the summer a and fall (a and b) water and low levels were observed in the spring (a and b), summer (b and c), and winter c samples. In general, it is assumed that an increase in water temperature during the warmer season would increase the formation of mutagenic substances on chlorination in water treatment processes. However, the reasons for the low levels of mutagenic activity in the summer (b and c) samples are still not clear.

Preliminary characterization of the mutagenic XAD-2 extracts of drinking water was performed by GC using a packed column and FID. Fig. 1 shows the gas

TABLE II

CHROMATOGRAPHIC BEHAVIOUR AND RECOVERY DATA FOR HYDROCARBONS WHICH MAY BE FOUND IN DRINKING WATER

Compound tested	Retention time (min)				Recovery (%)[b]
	GC[a]			HPLC[a]: 5 ng[c]	
	5 μg[c]	0.5 μg[c]	0.05 μg[c]		
PAHs					
Naphthalene	4.41	4.56	4.88	9.61	52
2-Methylnaphthalene	7.28	7.35	7.70	13.96	63
Biphenyl	8.80	8.94	9.20	13.00	65
2,3-Dimethylnaphthalene	10.42	10.67	10.89	17.05	74
Dibenzofuran	12.20	12.50	12.82	13.76	80
Fluorene	13.15	13.55	13.81	15.56	83
Benzophenone	14.70	15.13	15.50	7.55	82
9-Fluorenone	17.01	17.68	17.81	8.31	81
Anthracene	18.00	18.67	18.95	20.88	83
Phenanthrene	18.10	18.39	18.89	18.59	98
Carbazole	20.40	20.67	20.95	8.05	88
9,10-Anthraquinone	22.20	22.48	22.83	9.05	79
Fluoranthene	23.23	23.60	23.94	26.58	97
Pyrene	24.23	24.55	24.93	30.62	77
Chrysene	30.46	30.80	31.20	38.47	90
9,10-Phenanthraquinone	35.00	36.00	36.78	5.16	78
Phthalates					
Dimethyl phthalate (DMP)	10.63	11.00	11.29	–[d]	69
Diethyl phthalate (DEP)	13.80	14.20	14.53	–	78
Di-*n*-propyl phthalate (DPP)	17.95	18.20	18.42	–	83
Di.*n*-butyl phthalate (DBP)	20.95	21.40	21.63	–	88
Di-*n*-amyl phthalate (DAP)	25.23	25.41	25.95	–	90
Benzyl butyl phthalate (BBP)	28.36	28.56	28.77	–	88
Di-*n*-heptyl phthalate (DHP)	30.46	30.80	31.20	–	91
Dicyclohexyl phthalate (DCHP)	30.90	31.06	31.63	–	90
Di(2-ethylhexyl) phthalate (DEHP)	31.60	32.12	32.48	–	98

[a] For GC and HPLC operating conditions, see Experimental.
[b] Average of three recovery tests.
[c] Amount of compound chromatographed.
[d] Not determined.

chromatograms of the extracts, each of which is representative of four seasons. Over 50 compounds that respond to FID were detected in one extract collected during summer (summer a sample), whereas smaller numbers of compounds were found in the summer b and c samples. Some of the large peaks on the chromatograms could be identified tentatively as phthalate ester plastizers by comparison of their retention times with those of authentic compounds. However, the nature of the small peaks could not be determined because the GC retention times vary with the amounts of compounds injected under the given GC conditions (Table II).

Because of the complexity and the very low concentrations of individual compounds, the XAD-2 extracts of drinking water were further separated into several fractions on Polyamid 11 F_{254} precoated TLC plates, using chloroform as the developing solvent. Fig. 2 shows the typical thin-layer chromatograms of the extracts and several standard compounds of interest; the results of GC determinations and mutation tests for each separated component are summarized in Table III. The recovery of compounds in the fractions was *ca.* 80% (from comparison of GC peak areas) of the amount of sample applied, while the mutagenicity recovered of the amount of sample applied, while the mutagenicity recovered from the plates was about 80% of the overall acitivity applied.

As Table III shows, over 90% of compounds in the fractions recovered from the TLC plates were non-polar (R_F = 0.6–1.0), although compounds with a wide range of polarities can be seen on the chromatograms (Fig. 2). The mutagenicity detected in the original extracts was concentrated into the non-polar fractions, with a few exceptions (Table III). These results indicate that XAD-2 resin extracts of drinking water may be composed of mainly phthalate ester plasticizers and PAHs. Semipolar (R_F = 0.3–0.6) and polar fractions (R_F = 0.0–0.3), which may also include chlorophenols or chlorinated organic acids, exhibited no or weak mutagenicity.

Fig. 3 shows the reconstructed ion chromatogram of the non-polar fraction

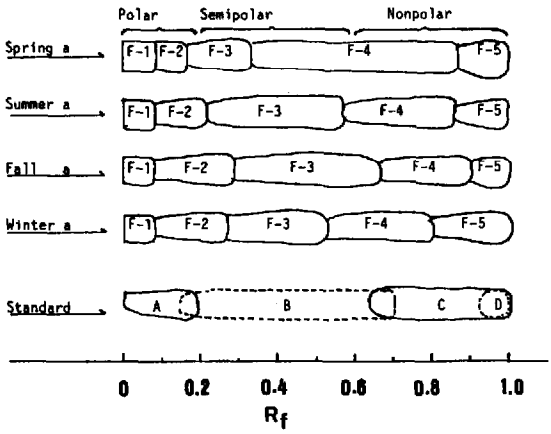

Fig. 2. Typical thin-layer chromatograms of XAD-2 extracts of drinking water and a mixture of chlorinated organic compounds of interest on a Polyamid TLC plate with chloroform as the developing solvent. A = Chlorinated organic acids; B = chlorophenols; C = phthalate ester plasticizers and PAHs; D = organochlorine pesticides and PCBs. For GC determinations and mutation tests for each fraction, see Table III.

TABLE III

DISTRIBUTION OF XAD-2-EXTRACTABLE ORGANIC CONTAMINANTS AND MUTAGENICITY OF DRINKING WATER ON POLYAMID 11 F_{254} TLC PLATE WITH CHLOROFORM

Water Sample	Distribution (%)									
	Organic contaminants[a]					Mutagenicity[b]				
	F-1[c]	F-2	F-3	F-4	F-5	F-1	F-2	F-3	F-4	F-5
Spring										
a	2.63	2.77	0.37	43.65	50.58	13.92	12.58	18.88	37.06	17.50
b	2.30	1.05	2.72	28.57	65.36	3.92	15.81	19.26	38.76	22.22
c	1.10	0.70	0.60	71.10	26.53	0	0	0	86.26	13.74
Summer										
a	14.50	0.91	0.92	61.74	21.84	0	0	1.85	94.46	3.69
b	0.86	2.48	1.18	56.74	38.74	4.10	5.45	5.53	77.35	7.57
c	1.52	7.08	3.87	70.59	16.93	7.50	7.92	9.68	65.20	9.70
Fall										
a	6.83	2.32	2.19	74.23	14.43	3.53	2.80	11.65	76.28	5.73
b	0.88	0.80	1.32	45.60	51.40	4.82	7.49	5.52	57.58	24.59
c	0.97	0.95	0.93	47.92	49.23	1.62	0	5.52	52.60	40.26
Winter										
a	2.10	1.05	0.99	47.56	48.30	3.21	13.20	7.50	47.50	28.53
b	2.50	1.88	1.53	43.21	52.88	5.00	6.93	13.25	45.31	29.51
c	3.83	2.14	0.68	39.36	55.00	3.83	12.20	11.50	37.00	35.47

[a] Amount of organic contaminants derived from the GC peak areas for each fraction, relative to the total peak areas for these fractionated components.

[b] Mutagenicity derived from the initial and linear portion of the dose–response curve for each fraction, relative to the total mutagenicity for these fractionated component.

[c] See Fig. 2.

obtained by the Polyamid TLC fractionations of the XAD-2 extract (summer a) and Table IV lists the compounds identified.

Phthalate ester plasticizers such as dibutyl and di(2-ethylhexyl) phthalate were the main organic contaminants detected by GC-FID of the extracts. As these phthalate esters are frequently encountered in the laboratory as artifacts, it should be pointed out that they were not found in the procedural blank; these widely used plasticizers do seem to be present in the water samples. Several PAH compounds such as naphthalenes, dibenzofuran, fluorene, anthracene, phenanthrene and fluoranthene and their oxygenated derivatives such as fluorenone, anthraquinone, chloromethylanthraquinone and phenanthraquinone (see Fig. 4) were also detected as minor components present in the extract. These compounds are generally introduced into the aquatic environment by petroleum activity and combustion processes [30,31]. Furthermore, several fatty acid esters such as palmitate and stearate, its chlorohydroxylated derivative and the organochlorine pesticide oxadiazon were found. These compounds may originate from domestic wastewater treatment plants and agricultural run-offs. A number of organic compounds, similar to those reported here, have been identified previously in drinking water [16,24,25,32,33].

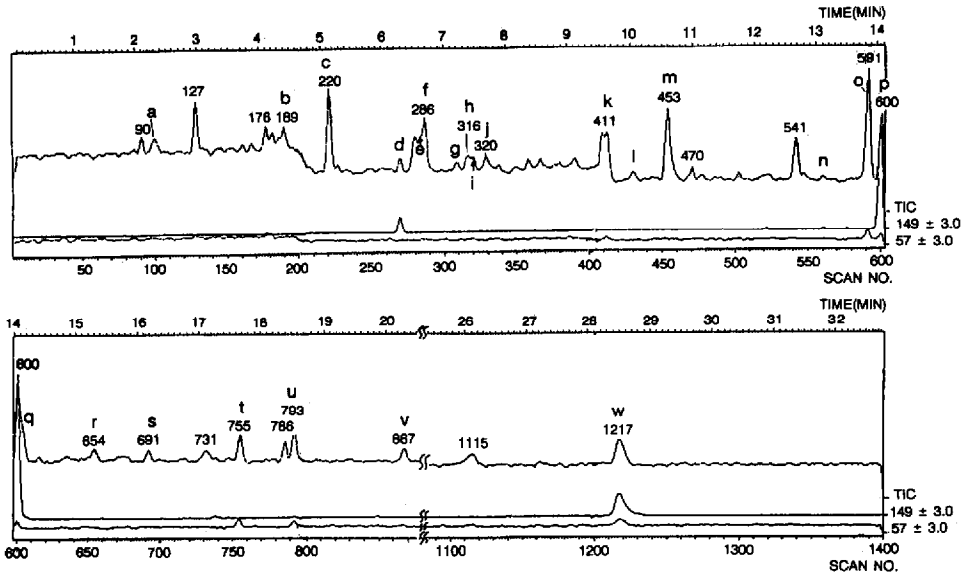

Fig. 3. Reconstructed ion chromatogram of the TLC-fractionated component (non-polar fraction in Fig. 2) of XAD-2 extracted collected during summer (summer a sample; 12–18 July 1988). The temperature of the GC column (fused-silica capillary coated with OV-1) was raised from 120 tot 240°C at 5°C/min. The letters above the peaks correspond to those in Table IV.

TABLE IV

COMPOUNDS INDENTIFIED IN THE XAD-2 EXTRACTS OF DRINKING WATER

Peak	Scan no.	M^+	Name	Formula	Identification[a]
a	100	154	Biphenyl	$C_{12}H_{10}$	a
b	189	168	Methylbiphenyl	$C_{13}H_{13}$	b
c	220	168	Dibenzofuran	$C_{12}H_8O$	a
d	269	220	Diethyl phthalate	$C_{12}H_{14}O_4$	a
e	280	166	Fluorene	$C_{13}H_{10}$	a
f	286	150	Methyl 3-methylbenzoate	$C_9H_{10}O_2$	b
g	308	182	Benzophenone	$C_{13}H_{10}O$	a
h	316	182	Methyldibenzofuran	$C_{13}H_9O$	b
i	320	156	Dimethylnaphthalene	$C_{12}H_{12}$	a
j	328	182	Methyldibenzofuran isomer	$C_{13}H_9O$	b
k	409	180	Fluorenone	$C_{13}H_8O$	a
l	430	170	Diphenyl ether	$C_{12}H_{10}O$	a
m	453	178	Anthracene/phenanthrene	$C_{14}H_{12}$	a
n	560	192	Methylanthracene	$C_{15}H_{14}$	a
o	591	270	Methyl palmitate	$C_{17}H_{34}O_2$	b
p	600	278	di-*n*-Butyl phthalate	$C_{16}H_{22}O_4$	a
q	605	208	Anthraquinone	$C_{14}H_{10}O_2$	a
r	654	256	Chloromethylanthraquinone	$C_{15}H_{11}ClO$	b
s	691	202	Fluoranthene	$C_{16}H_{10}$	a
t	755	298	Methyl stearate	$C_{19}H_{38}O_2$	a
u	792	344	Oxadiazon	$C_{15}H_{17}N_2Cl_2O$	a
v	867	348	Chlorohydroxymethyl stearate	$C_{19}H_{37}ClO_3$	b
w	1217	390	di(2-Ethylhexyl) phthalate	$C_{24}H_{34}O_2$	a

[a] Identification: a = comparison with authentic standard; b = tentative, based on interpretation of mass spectrum.

Organic pollutant levels in drinking water

On the basis of the qualitative information given above (Figs. 1–4 and Table IV), quantitative analyses of the XAD-2 extracts and their TLC-fractionated components of drinking water were performed by means of GC–FID and HPLC with UV

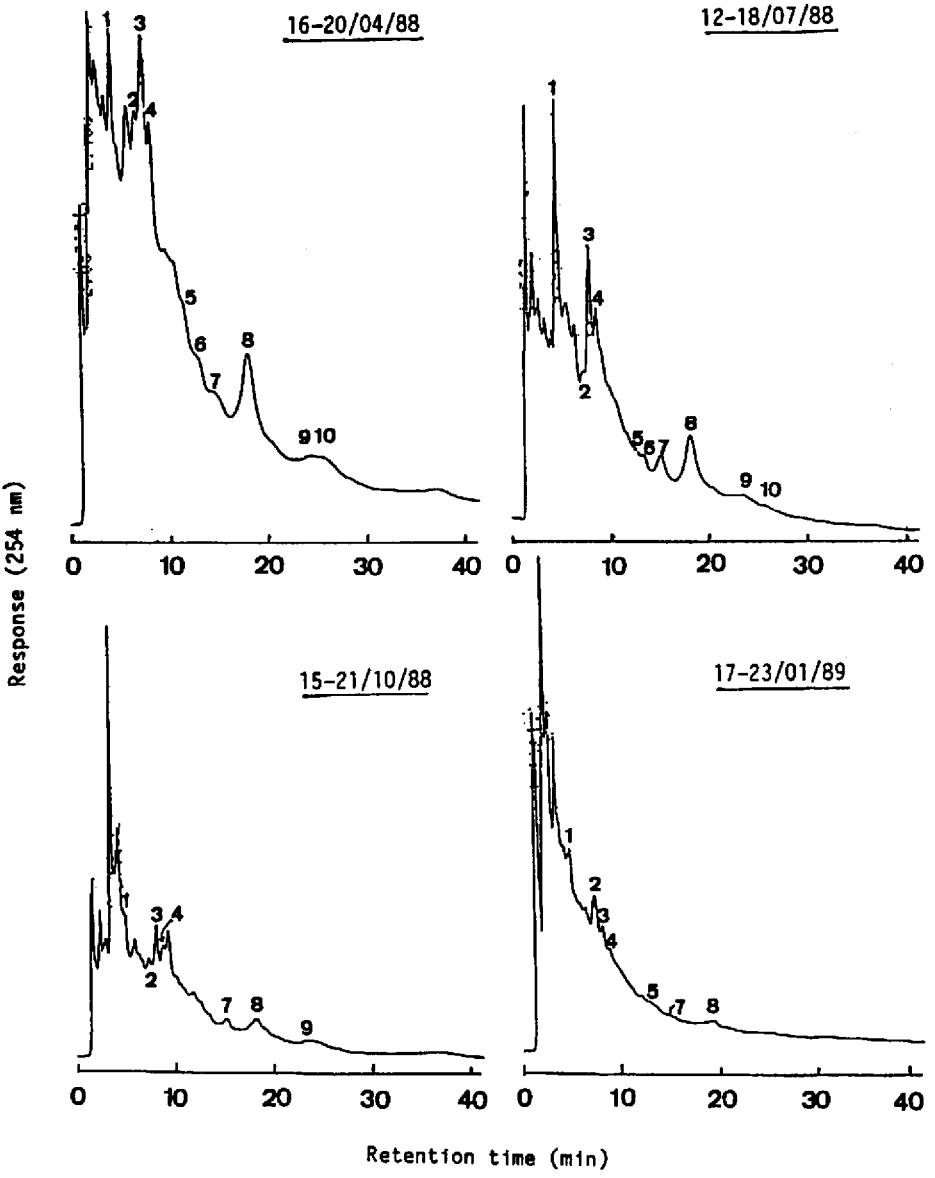

Fig. 4. Typical high-performance liquid chromatograms of the TLC-fractionated components (non-polar fractions in Fig. 2) of XAD-2 extracts. 1 = 9,10-Phenanthraquinone; 2 = benzophenone; 3 = fluorenone; 4 = anthraquinone; 5 = biphenyl; 6 = dibenzofuran; 7 = fluorene; 8 = phenanthrene; 9 = anthracene; 10 = fluoranthene.

detection. The results for these samples are listed in Table V as the concentrations of phthalate ester plasticizers, PAHs and other components. The concentrations of phthalate esters and other unknown components in drinking water were directly evaluated on the basis of the GC analyses of the XAD-2 extracts (Fig. 1), whereas the PAH levels were determined by HPLC analyses of their TLC-fractionated components (Fig. 4). Seasonal variations in the concentrations of these hydrocarbons in drinking water are also presented graphically in Figs. 5 and 6.

The range of total XAD-2-extractable organic pollutants in drinking water susceptible to chromatographic analysis was from 0.624 to 2.642 μg/l with a mean concentration of 1.389 μg/l, depending on the sampling periods (Table V and Fig. 5). As a general trend, high concentrations of these compounds were detected in the waters collected in summer and fall, whereas low values were observed for winter and spring samples, with the exception of three samples (summer c, fall and winter b). As already mentioned, there were heavy rainfalls in September and October 1988 in the Tone River basin, before sample collection [34]. Therefore, the low levels of these organic pollutants in the water samples collected in September and October can be explained by the heavy rains during the sampling periods.

Water samples taken from the laboratory tap showed phthalate ester levels ranging from 0.132 to 0.952 μg/l with a mean concentration of 0.409 μg/l, depending on the sampling period (Table IV and Fig. 5). High concentrations of these compounds were detected in the summer and fall samples, whereas low values were observed for the spring and late winter samples, with a few exceptions. The seasonal

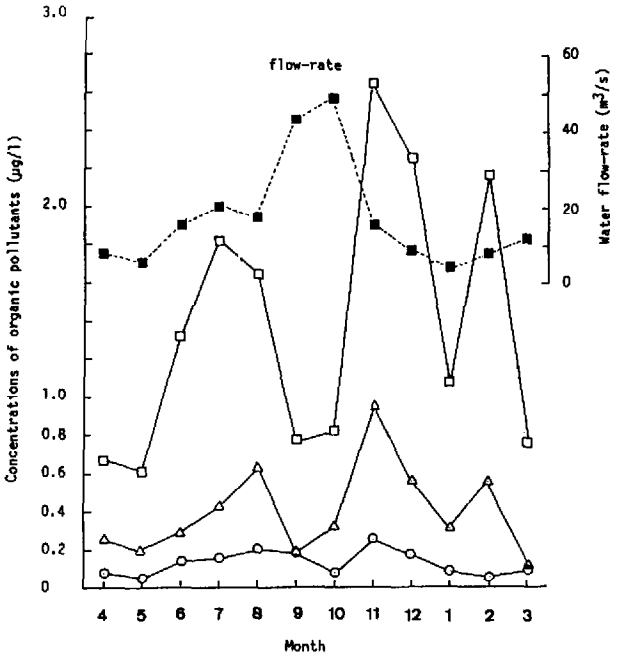

Fig. 5. Seasonal variations in the concentrations of ○ = PAHs, △ = phthalates and □ = total organic contaminants in drinking water, and ■ water flow-rate in the Tone River as source water.

TABLE V

CHROMATOGRAPHIC DETERMINATIONS OF PAHs, PHTHALATES AND OTHER COMPOUNDS IN THE XAD-2 RESIN EXTRACTS OF DRINKING WATER COLLECTED DURING APRIL 1988 to MARCH 1989

Compounds tested	Concentration (μg/l)												
	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Jan.	Feb.	March	Average
PAHs													
Naphthalene	0.012	0.022	0.020	0.051	0.013	0.060	0.003	0.002	0.003	0.002	0.001	0.002	0.016
2-Methylnaphthalene	0.004	0.004	0.008	0.018	0.024	0.026	0.024	0.070	0.044	0.025	0.001	0.006	0.021
Biphenyl	0.005	0.004	0.004	0.005	0.008	0.005	0.009	0.017	0.014	0.005	0.002	0.004	0.007
Benzophenone	0.011	0.010	0.005	0.006	0.023	0.005	0.008	0.081	0.058	0.032	0.027	0.015	0.023
Dibenzofuran	0.004	0.003	0.018	0.018	0.039	0.020	0.013	0.019	0.008	0.005	0.003	0.004	0.013
Fluorene	0.006	0.004	0.002	0.001	0.001	0.001	0.001	0.004	0.002	0.005	N.D.[a]	0.010	0.004
9-Fluorenone	0.005	0.003	0.011	0.011	0.024	0.021	0.008	0.023	0.014	0.008	0.005	0.010	0.012
Anthracene	0.001	N.D.	0.001	0.001	0.001	0.004	0.001	0.001	0.001	N.D.	N.D.	0.001	0.001
Anthraquinone	0.019	0.007	0.030	0.002	0.027	0.025	0.012	0.021	0.039	0.026	0.012	0.024	0.020
Phenanthrene	0.004	N.D.	0.018	0.019	0.024	0.014	0.006	0.019	0.010	0.001	0.002	0.007	0.010
9,10-Phenanthraquinone	0.005	N.D.	0.022	0.020	0.020	0.015	0.001	0.001	0.001	0.001	0.002	0.003	0.007
Fluoranthene	0.001	N.D.	N.D.	0.001	0.001	N.D.	N.D.	0.004	0.001	N.D.	N.D.	0.001	0.001
Subtotal	0.077	0.057	0.139	0.153	0.205	0.196	0.086	0.262	0.195	0.110	0.055	0.087	0.135
Phthalates													
Dimethyl phthalate	0.020	0.005	0.014	0.046	0.031	0.074	0.043	0.092	0.054	0.008	0.028	0.010	0.035
Diethyl phthalate	0.009	0.032	0.072	0.072	0.017	N.D.	0.007	0.037	0.060	0.034	0.048	0.016	0.034
Di-*n*-propyl phthalate	0.001	N.D.	N.D.	0.001	0.008	N.D.	0.010	0.018	0.020	0.011	0.036	0.004	0.010
D-*n*-butyl phthalate	0.140	0.046	0.110	0.134	0.197	0.073	0.147	0.279	0.180	0.159	0.403	0.008	0.156
Di-*n*-amyl phthalate	0.008	0.005	0.028	0.051	0.024	0.001	0.037	0.001	0.001	0.001	0.022	0.005	0.015
Benzyl butyl phthalate	0.001	0.074	N.D.	0.006	0.006	N.D.	0.001	0.031	0.016	0.007	0.037	0.031	0.017
Di-*n*-heptyl phthalate	0.013	N.D.	N.D.	0.001	0.019	0.014	0.001	N.D.	N.D.	0.001	N.D.	0.023	0.006
Dicyclohexyl phthalate	0.008	0.006	0.020	0.012	0.023	N.D.	0.016	0.032	0.006	0.027	N.D.	0.008	0.013
Di(2-ethylhexyl) phthalate	0.062	0.039	0.049	0.097	0.307	0.031	0.042	0.462	0.230	0.048	0.075	0.027	0.122
Subtotal	0.262	0.227	0.253	0.420	0.632	0.193	0.304	0.952	0.567	0.296	0.649	0.132	0.409
Unknown compounds[b]	0.331	0.360	0.906	1.244	0.811	0.401	0.446	1.428	1.494	0.679	1.462	0.573	0.845
Total	0.670	0.624	1.338	1.817	1.648	0.790	0.836	2.642	2.256	1.085	2.166	0.792	1.389

[a] Not detected.

[b] Amounts of these compounds were derived from GC–FID peak areas, relative to the area of di-*n*-butyl phthalate.

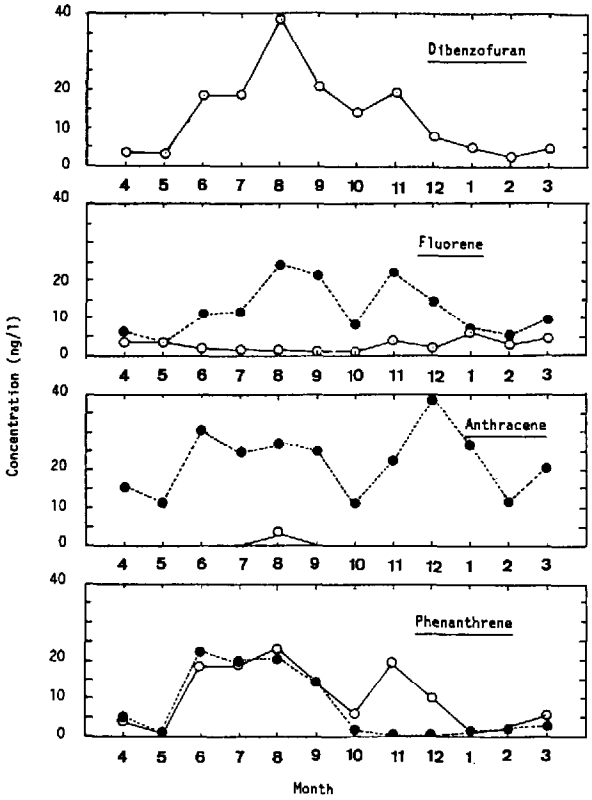

Fig. 6. Seasonal variations in the concentrations of PAHs in drinking water. Open circles represent the parent compounds and closed circles their oxygenated derivatives.

variations in the concentrations of total phthalate esters in drinking water were similar to those of total XAD-2-extractable and chromatographable compounds. The source of the phthalate esters is not yet known. Their concentrations are variable and seem to be correlated with the effective run-off. Locating their sources is of particular interest because their unusual ubiquity, their possible teratogenicity [35,36] and their mutagenicity [37].

The range of total PAH levels in water samples was from 0.055 to 0.262 μg/l with a mean concentration of 0.135 μg/l, depending on the sampling periods (Table V and Fig. 5). High concentrations of total PAHs were detected in the waters during the warmer months whereas low values were observed in those collected during the cooler months. This can be explained by an increase in water temperature (Table I), which may cause the leaching of PAHs from the coal tar coating inside pipes and water storage tanks [38,39] during warmer seasons. In addition, higher concentrations of fluorenone, anthraquinone and phenanthraquinone were detected in drinking water samples, as compared with the parent PAHs (Fig. 6). In general, reaction of chlorine with model PAHs produces oxygenated and chlorinated derivatives [40–43].

Fluorenone, anthraquinone and phenanthraquinone were reported as oxidation products of fluorene, anthracene and phenanthrene, respectively. PAHs have

also been suggested as the precursors of at least a portion of the mutagens produced in some chlorination processes [44].

CONCLUSION

Amberlite XAD-2 resin was used for the extraction of organic compounds from drinking water, in order to characterize and determine the organic pollutants. The XAD-2 extracts were further separated into several fractions on Polyamid TLC plates with chloroform as the developing solvent for GC–MS and HPLC analyses. The major organic pollutants were phthalate ester plasticizers such as dibutyl and di(2-ethylhexyl) phthalate. Several PAHs such as naphthalenes, biphenyl, benzophenone, dibenzofuran, fluorene, anthracene, phenanthrene and fluoranthene and their oxygenated compounds such as fluorenone, anthraquinone, phenanthraquione and chloromethylanthraquinone were also detected in drinking water samples. In addition, fatty acid methyl esters (palmitate, stearate and chlorohydroxystearate) were identified at low concentrations. The mean concentration of PAHs was 0.136 μg/l (*ca.* 10% of the total amount of organic compounds detected), phthalates comprised 0.405 μg/l on average (*ca.* 30%) and other components 0.845 μg/l on average (*ca.* 60%). The concentrations and compositions of organic pollutants were correlated with the effective rainfall content of the river and with the water temperature.

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