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Organochlorine Extraction Based on the Combination of Polyaluminum Chloride and Octadecyl Silica Powder: Application to Lake Water

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Two typical extraction methods of organochlorine compounds (OCs) have been suggested thus far: liquid-liquid extraction (LLE) and solid-phase extraction (SPE). LLE by manpower is a convenient pretreatment when a small number of samples are applied to the extraction. However, since most OCs in background water are present at relatively low concentrations, quantities of water must be pumped up to enable a sensitive analysis through gas chromatography-mass spectrometry (GC-MS). On the other hand, SPE-C18 disk methods are the official and widely used means of collecting hydrophobic materials in inland water. SPE has advantages over LLE; the former requires less manipulation of the sample and uses considerably smaller quantities of solvent. However, the disk requires the procedure that the particulates must be removed with another glass fiber filter when a sample includes a large quantity of suspended solids. Information has been provided on the application of SPE to adsorb some pesticides (Pujadas et al. 2001), whereas the sorption efficiency of the SPE-C18 disk for regulated organochlorines is still lacking. During the past years, miniaturization has become a dominant trend in analytical chemistry. Solid-phase microextraction (SPME) and stir bar sorptive extraction (SBSE) are representatives of the miniaturization in sample preparation techniques; they are based on partitioning of the analytes between aqueous matrices and sorbents (Boussahel et al. 2002; Peñalver et al. 2003). Although these new methods provide us with good performance in semi-volatile compounds, in some cases, strong interactions with sorbents may cause incomplete thermal-desorption of the analytes. Further, when we have to analyze much lake water including many particles for the OCs which are present at ppq level, it is not appropriate for these miniaturized methods as well as LLE than SPE-C18 disk methods.

Organic pollutants in environmental water tend to be distributed between two species on the basis of their vertical profiles. In this study, we designed a method to trap the two OC species (i.e., “free OCs” and “OCs adsorbed on suspended solids”) for collecting OCs from quantities of lake water (20 liters); our method is based on the combination between polyaluminium chloride (PAC) and octadecyl silica powder (ODS powder). The extraction efficiencies of different four methods including the standard C18 disk method were compared under various conditions.

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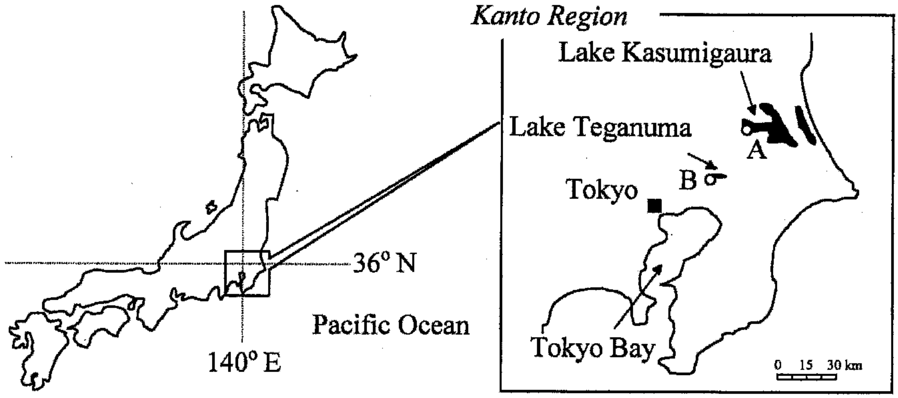

Figure 1. Map of Japan showing sampling locations. A and B: sampling locations.

MATERIALS AND METHODS

OC standards were purchased from AccuStandard Inc. (CT, USA) and Cambridge Isotope Laboratories Inc. (MA, USA). PAC and humic substances were obtained from Honmachi Chemical Industries (Tokyo, Japan) and from the Japanese Humic Substances Society, respectively. ODS powder (surface area, 520 m^2 g^{-1}) was purchased from Sigma-Aldrich (Supelclean LC-18, Tokyo, Japan). Empore™ C18 disk (90mm FF type, 3M, MN, USA) was also used to extract OCs. Purified water was obtained by a Milli-Q® system (Nihon Millipore, Tokyo, Japan).

Lake waters were collected at the shores of Lake Kasumigaura and Lake Teganuma in August 2003 (Figure 1). After hydrochloric acid was added to adjust the pH 4, the sample was stored at 4°C. ODS-PAC method: water (1 liter) was transferred to another glass container; 0.02 g of anhydrous sodium carbonate, 0.5 ml of acetone containing surrogate standards, and 4 ml of 10% (w/w) PAC were added into the container. After the water was stirred (700 rotations min^{-1}) for 30 min, 0.1 g of ODS powder were added to the stirred water. The pH 7.0 was adjusted with ammonia solution; the mixture was stirred for 24 hours at a room temperature. Residues were allowed to separate with a glass fiber filter. The weight of PAC and ODS powder were increased in proportion to the sample weight. ODS-powder method: water (1 liter) was transferred to another glass container; 0.02 g of anhydrous sodium carbonate and 0.5 ml of acetone containing surrogate standards were added into the container. After the water was stirred for 30 min, 0.1 g of ODS powder were added to the stirred water. The pH 7.0 was adjusted with ammonia solution. The mixture was stirred for 24 hours at a room temperature. Residues were allowed to separate with a glass fiber filter and were dried briefly for 1 min with vacuum. PAC method: water (1 liter) was transferred to another glass container; 0.02 g of anhydrous sodium carbonate, 0.5 ml of acetone containing surrogate standards, and 4 ml of 10% (w/w) PAC were added into the container. After the water was stirred for 30 min, the pH 7.0 was adjusted with ammonia solution. The mixture was stirred for 24 hours. Residues were allowed to separate with a glass fiber filter. C18 disk method: water (1 liter or 20 liters) was transferred to another glass container; 0.5 ml of acetone containing surrogate standards was added into the container. After the water was stirred sufficiently, the pH 3.0 was adjusted with hydrochloric acid. Washing C18 disk was carried out carefully with solvents. The order of used solvents was as follows: 10 ml of toluene, 10 ml of acetone, 10 ml of methanol, and 10 ml of purified water. The sample was loaded at a rate of 150 ml min^{-1}.

The disks or the slightly wet filters were transferred to a steel column for the pressurized liquid extraction system (ASE-200, Nippon Dionex, Osaka, Japan). OCs was extracted twice with acetone (100°C for 10 min at 1500 psi) and toluene (120°C for 11 min at 1000 psi). All the extracts were mixed. The aqueous layer was shaken for 10 min with 50 ml of dichloromethane. The dichloromethane layer was added to the mixture. Hexane was substituted for the final mixture. When purified water was used as a sample, the concentrate was transferred to centrifuge tubes and was directly reduced to 100 μl with dry nitrogen. Five hundred picogram of $^{13}C_{12}$-PCB 153 was added to the final concentrate. When lake water was used as a sample, the hexane-concentrate was further purified with a glass column (15 mm i.d., 300 mm length) containing from top to bottom: 2 g of anhydrous sodium sulfate, 10 g of activated Florisil®, 2 g of anhydrous sodium sulfate and a quartz wool plug. The concentrate was eluted with 100 ml of diethyl ether/hexane (5:95; v/v, Fraction 1, corresponding to the other OCs except dieldrin) and 100 ml of diethyl ether/hexane (1:4; v/v, Fraction 2, corresponding to dieldrin). After the mixture of both fractions was concentrated, $^{13}C_{12}$-PCB 153 was added to the final samples.

A mass spectrometer (5973N, Agilent Technologies Inc., DE, USA) equipped with a gas chromatograph (6890, Agilent Technologies Inc., DE, USA) was used. HT8 (50-m length, 0.22-mm i.d., 0.25 μm film thickness; SGE Japan Inc., Kanagawa, Japan) was selected for a column. Helium was employed as a carrier gas at a flow rate of 1 ml min^{-1}. Temperatures of an injector port and a transfer line in the gas chromatograph were maintained at 260°C and 280°C, respectively. The column temperature was maintained at 50°C for 0.3 min, ramped to 200°C at a rate of 20°C min^{-1}, to 280°C at a rate of 2.5°C min^{-1}, and maintained at 280°C for 1 min. Methane served as a reagent gas. Temperatures of an ion source and a quadrupole were maintained at 150°C and 106°C, respectively.

SPSS version 10.0J (SPSS Inc., Chicago, IL, USA) and FreeJSTAT 8.2 (Free software provided by M. Sato, Japan) were used for statistical analysis ($p < 0.05$).

RESULTS AND DISCUSSION

Without a cleanup, it was impossible to analyze directly the extracts of lake water samples by GC-MS. Therefore, Florisil® column chromatography was applied to removal of matrices derived from lake water. First of all, we have to inquire into the cleanup efficiencies. On the basis of the C18 disk method, hexane-base extracts

Table 1. Mean recoveries (%) of OCs in purified water (1 liter).

	C18 disk		ODS powder		PAC		ODS-PAC	
compound	Mean	R.S.D.	Mean	R.S.D.	Mean	R.S.D.	Mean	R.S.D.
HCB	74	24	50	13	1.1	8.5	59	12
aldrin	48	23	60	18	6.0	46	75	11
dieldrin	80	16	58	11	2.4	14	89	6.5
p,p'-DDD	79	1.2	66	11	nd	-	66	16
o,p'-DDE	70	1.7	61	19	7.8	31	71	11
p,p'-DDE	80	12	79	21	12	18	72	12
o,p'-DDT	81	10	79	17	12	33	72	6.5
p,p'-DDT	91	19	97	10	nd	-	102	2.3
t-chlordane	89	11	74	13	5.9	15	77	10
c-nonachlor	86	8.1	69	9.3	6.8	25	76	8.7
t-nonachlor	83	11	72	14	8.0	30	75	9.0
heptachlor	115	26	98	19	2.5	88	112	12
heptachlor epo.	99	5.1	66	12	1.0	88	86	6.1
oxychlordane	91	9.1	70	11	4.8	11	84	9.1
mirex	85	17	124	11	77	11	119	16

nd: not detected.

Table 2. Mean recoveries (%) of OCs in the water (1 litre) of Lake Kasumigaura.

	C18 disk		ODS powder		PAC		ODS-PAC	
compound	Mean	R.S.D.	Mean	R.S.D.	Mean	R.S.D.	Mean	R.S.D.
HCB	52	5.9	54	5.5	4.3	19	52	10
aldrin	54	6.4	66	11	13	36	76	13
dieldrin	60	8.2	54	12	8.4	47	67	14
p,p'-DDD	77	9.9	77	7.4	21	8.1	88	11
o,p'-DDE	59	6.3	64	8.3	23	22	72	12
p,p'-DDE	72	3.2	83	5.5	35	17	87	15
o,p'-DDT	78	14	73	18	30	32	80	21
p,p'-DDT	94	18	86	12	34	29	98	21
t-chlordane	80	5.0	79	10	23	31	88	10
c-nonachlor	84	8.0	78	9.6	31	23	87	10
t-nonachlor	77	2.2	77	11	25	28	85	9.3
heptachlor	104	3.6	47	11	3.4	110	87	45
heptachlor epo.	78	7.4	70	7.7	6.0	77	89	4.0
oxychlordane	78	6.8	76	9.2	14	43	86	6.7
mirex	83	25	107	5.7	85	24	109	15

including natural matrices were obtained from 20 liters of Lake Teganuma water. The lake is one of the most polluted lakes by human activities in Japan. The mean recoveries ($n = 3$) ranged from 90 to 117% (except for HCB, 68%) and had good repeatability (relative standard deviations; R.S.D. < 13%). Table 1 shows the mean recoveries ($n = 3$) obtained from 1 liter of purified water. The PAC method produced poor recoveries for all the OCs except mirex (77%). The OC mean recoveries were present in the range of 1.0–12%; further, the R.S.D. values exceeded those of the other methods. It is considered that lack of organic particles in the water prevented PAC from forming flocks. The dosage of mirex was 10 ng and was kept within its solubility (1.0 µg/L) in fresh water (Bell et al. 1978). The physicochemical properties (vapor pressure and an octanol-water partition coefficient) of mirex are similar to those of the others (Fisk et al. 1998); the reason of its recovery was unclear. The C18 disk method which is a candidate official method of PCDD/F analysis also permitted effective sorption of OCs. The mean recoveries by using the three methods except the PAC method were as follows: 48–115% for the C18 disk method, 50–124% for the ODS powder method, and 59–119% for the ODS-PAC method. Water solubility controls the volatilization rate of those OCs that have generally low vapor pressure, and DDT, whose water solubility is especially low, will become volatile faster than aldrin or dieldrin will. In fact, DDT volatility has a half-life of 73.9 hours (Mackay and Leinonen 1975). However, since the process is slow, we can ignore the diffusion of OCs into the atmosphere by stirring the samples.

The results ($n = 3$) obtained by different four methods in the water of Lake Kasumigaura are summarized in Table 2. In the three methods except the PAC method, no significant differences in the mean recoveries among the methods were found in twelve OCs, excluding three compounds (heptachlor, heptachlor epoxide, and aldrin). On the other hand, it is apparent that not almost all the OCs was sufficiently recovered with the PAC method; however, the application of this method to lake water provided obviously higher recoveries than those from purified water. It is considered that the presence of suspended solids promoted flocculation in lake water and led to this result. The mean recoveries of OCs except mirex by the PAC method ranged from 3.4 to 35%. Tables 1 and 2 led us to the conclusion that the PAC method is not capable of being a major OC sorption process in lake water, based on its extensive R.S.D. values. However, the ODS-PAC method tended to show high recoveries than the independent applications (the ODS powder method or the PAC method); the PAC method played an indispensable role. The C18 disk method delivered acceptable recoveries and repeatability; it was an effective tool for the collection of low-polarity compounds from lake water. The ODS-PAC method as well as the C18 method possessed the similar sorption efficiencies; judging from the good recoveries, we supposed that almost all the OCs except heptachlor were independent of hydrolysis concerning the methods except the ODS-PAC method. Heptachlor is rapidly hydrolyzed to 1-hydroxychlordane in water (WHO 1984); hydrolysis may be a factor of the large R.S.D. of heptachlor in Tables 1 and 2.

The influence of a surfactant on OC recoveries ($n = 3$) in the ODS-PAC method is shown in Figure 2. Because linear alkylbenzene sulfonate (LAS, wetted with water,

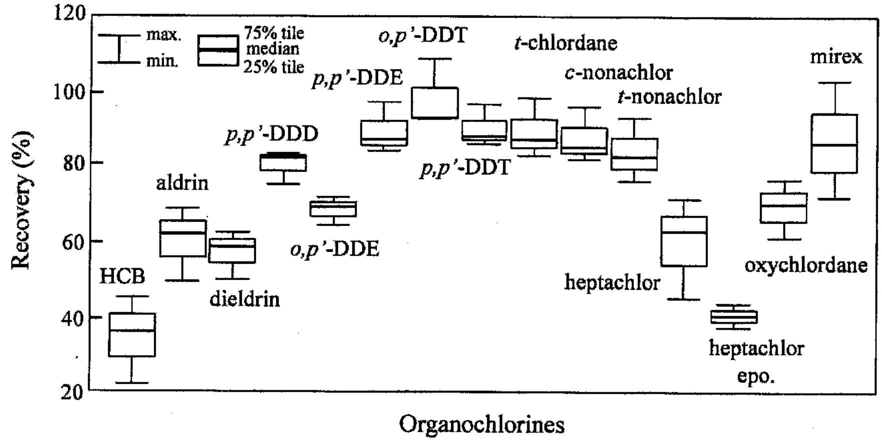

Figure 2. Application of the ODS powder-PAC method to the water (1 liter) containing LAS.

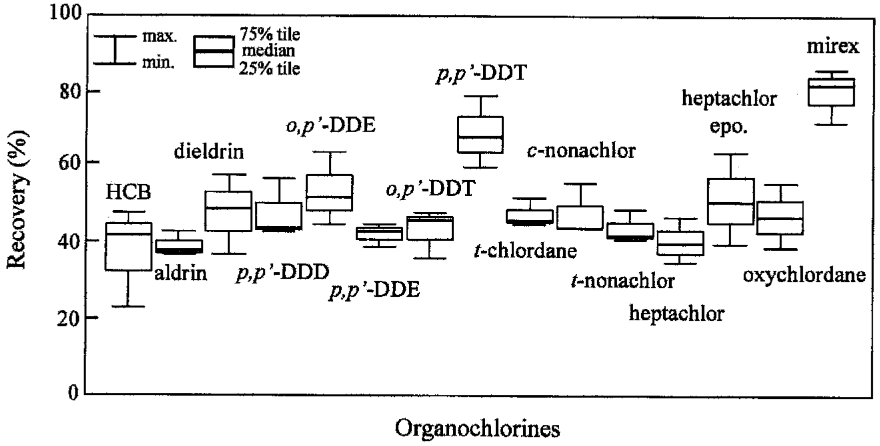

Figure 3. Application of the ODS powder-PAC method to the water (1 liter) containing humic substances.

soft type 65%, dodecylbenzenesulfonic acid sodium salt) was detected widely in natural water, it was selected as a model of anionic surfactants distributed in Japanese environments. In a small river flowing through residential areas having no sewerage, the concentration of LAS exceeds 1 ppm (Takada 1993). The concentration was set to 10 ppm in the present study. Comparisons with Table 1 from purified water indicated that dieldrin, heptachlor, and heptachlor epoxide were detected with obviously descending mean recoveries. Further, HCB (34%) and *p,p'*-DDT (90%) were led to similar significant declines. It seems reasonable to conclude that the coexistence of LAS with OCs leads to a negative effect because the increase in the water solubility of OCs due to micell formation weakens the interaction between some OCs and the ODS powder. Figure 3 illustrates the mean recoveries ($n = 3$) obtained by the ODS-PAC method in water

Table 3. Comparison of OC concentrations (pg/L) in Lake Teganuma water.

	sample #1				sample #2			
	C18 disk		ODS-PAC		C18 disk		ODS-PAC	
compound	Conc.	R.(%)	Conc.	R.(%)	Conc.	R.(%)	Conc.	R.(%)
HCB	74	86	393	55	138	65	263	35
aldrin	nd	48	nd	58	nd	58	nd	45
dieldrin	178	103	269	123	162	89	127	96
p,p'-DDD	nd	66	nd	62	nd	94	nd	61
o,p'-DDE	16	69	nd	88	nd	75	nd	62
p,p'-DDE	82	68	63	82	52	86	83	52
o,p'-DDT	nd	60	nd	107	nd	84	nd	76
p,p'-DDT	nd	71	nd	100	nd	109	nd	65
t-chlordane	632	81	846	80	556	77	771	53
c-nonachlor	108	75	98	79	73	75	84	54
t-nonachlor	349	75	351	87	330	70	361	51
heptachlor	22	118	nd	49	nd	78	nd	52
heptachlor epo	115	124	190	83	65	91	111	57
oxychlordane	21	102	40	76	30	78	44	53
mirex	nd	60	nd	87	nd	60	nd	64

nd: not detected.

(1 liter) containing humic acid (2 mg) and fulvic acid (2 mg) from a brown forest soil. The concentration of both acids was decided according to previously reported data on Lake Teganuma (Tatsumoto et al. 1990); these acids possess the ability to fix hydrophobics (high molecular weights) like PCBs, OCs, and polycyclic aromatic hydrocarbons, rendering them water soluble (Krishnamurthy 1992). The impact of humic substances increased remarkably for OCs in Figure 3. The mean recoveries, which ranged from 38 to 80%, were much inferior to those of purified water. These humic substances interfered with the hydrophobicity of OCs; as a result, the increased water solubility caused the poor recoveries. Controlling pH (by keeping it low) seems to be effective in preventing such a phenomenon, although the low pH inhibits the flocculation by PAC. The concentrations of humic substances were set to higher values than those of environmental waters; as seen in Table 2, the ODS-PAC method led to satisfactory OC recovery in 1 liter of lake water. It was supposed that at least the concentrations of humic substances correlated negatively with the collection efficiency of OCs.

Table 3 summarizes the mean OC recoveries and the mean concentrations ($n = 2$) from the water (20 liters) of Lake Teganuma; the concentrations were corrected by the recoveries. Samples #1 and #2 were collected on separate days. The C18 disk method had slightly better recoveries than those obtained by the ODS-PAC method. The mean recoveries of both samples by the C18 method were presented in the range of 48–124% (sample #1) and 58–109% (sample #2); in addition to this, the ODS-PAC method led us to the results that the OC recoveries ranged from 49 to 123% (sample #1) and from 35 to 96% (sample #2). Using the C18 disk provided the stable recoveries for the more soluble compounds, such as oxychlordane, whereas the recovery of aldrin was independent of the used method and was always recovered at low rates (45–58%). It is reported that amino acids and humic acids possess the ability to epoxidate aldrin under natural light (Ross and Crosby 1985). In fact, both methods gave rise to almost equal OC concentrations; thus the comparison between the ODS-PAC method and the C18 disk method emphasized the validity of the ODS-PAC method in lake water.

This study indicated the possibility of applying of the flocculation process to the OC analysis of lake water. The PAC method was not a major method for OC collection but a method to assist other methods. However, the recovery efficiencies of the established ODS-PAC method were acceptable enough.

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