CONTAMINATION OF CHLORINATED COMPOUNDS IN THE WATER ENVIRONMENT

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ABSTRACT

Concentrations of polychlorinated biphenyls(PCBs), polychlorinated terphenyls(PCTs), chlordanes and chlorinated pesticides were measured in the water environment. Measurements of air, rain, snow, water and sediments were obtained and used to determine PCB fluxes to the sea-sediment. PCB fluxes to Harima-nada were estimated to 17$\mu g/m^2$ year for sedimentation and 2.5$\mu g/m^2$ year for wet deposition. The wet flux of chlordane was found to be 0.2$\mu g/m^2$ year.

KEYWORDS

Water; air; sediment; PCB; PCT; chlordanes; flux; deposition

INTRODUCTION

PCB had been used for about 20 years from 1954 to 1972 in Japan. Because the production amount is almost known by year and by composition, PCB is considered as a very useful index to deduce the diffusion of sediments. Residual isomeric pattern of these compounds in the environmental samples reflects the general abundance of isomer component of their commercial products.

The factors affecting the concentration of PCBs can be given as (1) the distance from the sources, (2) the diameter of sediment particle, (3) physico-chemical property of the sediment particle, (4) geographical feature, (5) tidal effect etc. Therefore, these factors have to be considered to estimate the PCB contamination of a sea area. On the basis of the results obtained by analyzing the particles of the same point of the sea area, it is clear that the concentration of sediment PCB is proportional to the particle size. That is, the PCB concentration in the sediment is greatly affected by the particle size of sediment. Consequently, it is necessary to estimate the sediment contamination by excluding differences caused by sediment features and comparing the PCB concentration in the sediment of the same particle size. PCB concentration in sediment was defined as that in fine particle.

The core-sample was collected with Smith-Mckintyre sampler, frozen in a acryl cylinder after sampling, and cut to 1cm segments before analysis. To investigate the vertical distribution of sediment, PCB contamination is important to make clear the yearly accumulation of the contaminant and the mechanism of the diffusion (Nakano et al., 1990c). The PCB concentration

in sediment decreased in proportion to the distance from the source.

MATERIAL AND METHODS

PCB and related compounds in environmental samples were analyzed by high-resolution GC/ECD and GC/MS-SIM. Water, sediment and biological samples were collected from the monitoring area in Harima- nada and Osaka-bay. Water samples were collected with a pail, sediment and benthos with a Smith-McIntyre sampler and plankton sample with a plankton-net. Air samples were collected at urban area in Kobe with a high volume air sampler.

GC/MS conditions. Column : PTE-5 capillary column (SUPELCO) $30m \times 0.25mmID$. $50°C$ (1 min hold) $\longrightarrow$ $30°C/min$ $\longrightarrow$ $200°C$ $\longrightarrow$ $5°C/min$ $\longrightarrow$ $250°C$. Column injector: splitless injection, $200°C$. Carrier gas :flow rate, $2ml/min$ helium (10 psi) Mass ionization: $70eV, 250°C$.
More than two monitoring ions of each chlorinated compounds were analyzed simultaneously by GC/MS-SIM.

RESULTS AND DISCUSSION

The distribution of these chlorinated compounds in Harima-nada, Osaka bay were investigated. The levels of these compounds in the sea-water, sea-sediment and atmosphere were monitored isomer-specifically (Table 1).

Distribution of PCBs in the Sediment Regional dispersion of pollutants in the sediment are found to be described by the following empirical equation,

$$C = \beta S^{-n}$$

where C is the pollutant concentration in the surface sediment, and S is the polluted area with concentration higher than C. The parameters n and β appear to become constant for given location and pollutant (Hiraizumi et al., 1978). Relationship between concentrations of PCBs in the sediments and dispersed area are listed in Table 2.

Sedimentation Most Suspended Solids(SS) are deposited on the sea bed within 5km from the discharge source on the coast (Hiraizumi et al., 1978). Table 3 provides a summary of the fluxes data for sedimentation determined by this study.
The PCB flux in the (C) area was approximately 10 times as much as the PCT flux. The total accumulation of PCBs in sediment cores ranged from 13μg/m2 to 520μg/m2 for Great Lakes (Swackhamer et al., 1986). In this study, PCB flux to Harima-nada was 17$\mu g/m^2$ year for sedimentation.

Deposition Wet deposition was dominated by particle washout, and volatilization was more important than sedimentation in the Great Lake. The main source of PCBs to rain is due to washout of the particulate phase rather than vapor scavenging (Swackhamer et al., 1988).
For many of these compounds, a few specific rain events would significantly affect the concentration of material in vapor-phase and particulate. The daily variability of the concentration of organics in the atmosphere has been discussed (Nakano et al., 1990a, 1990b) with meteorological conditions. These results indicate that wet deposition, rainfall of both particulate and vapor phases. has been played an important role in the behavior of chemicals.
Atmospheric PCB concentrations have remained relatively constant over the Great Lakes during the past 10 years. PCB congener fugacity gradients suggest PCB volatilization from Lake Superior. Mean volatilization fluxes of total PCBs (19 ng/m^2 day) are similar to estimates of gross atmospheric deposition to the lake (Baker et al., 1990). Concentrations of suspended particle in air to estimate areal fluxes are listed in Table 4.

Mass Balance Table 5 provides a mass balance of compounds in Harima-nada. The mass balance approach assumed a steady-state one-box model, and it equated total sources and sinks of each compound. The total yearly deposition of these compounds to the enclosed sea has been

TABLE 1 Average Concentration of Trace Organics in Air, Rain, Water, and Sediments of Harima-nada

Compounds	Snow ng/L	Water ng/L	Sediment ng/g	Rain ng/L	Air ng/m³	year
t-chl	0.08	0.07	0.01	0.03	0.42	1986-1990
c-chl	0.04	0.12	0.01	0.09	0.36	1986-1990
t-nona	0.06	0.08	0.03	0.69	0.28	1986-1990
DDE	0.03	0.05	0.42	8.16	0.005	1986-1990
HCHs	46	0.13	<0.01	11.4	<0.01	1986-1990
HCB	<0.01	0.007	0.02	<0.01	0.013	1986-1990
PCTs	n.a	n.a	1.4	n.a	n.a	1977-1979
PCBs	0.334	0.806	8.222	1.745	0.434	1988-1990
18	<0.001	0.026	0.060	0.008	0.025	
16/32	<0.001	0.023	<0.001	0.001	0.012	
31/28	0.007	0.169	0.760	0.089	0.041	
20	<0.001	<0.001	0.224	0.069	0.001	
52	0.017	0.061	0.447	0.056	0.032	
49	0.006	0.025	0.406	0.025	0.010	
44/42	0.012	0.029	0.145	0.032	0.047	
41/64	0.023	0.046	0.412	0.064	0.020	
70	0.030	0.055	0.342	0.072	0.033	
66	0.034	0.045	0.615	0.079	0.017	
60	0.031	<0.001	0.288	0.053	0.023	
91	<0.001	0.032	0.333	0.054	0.025	
101	<0.001	0.039	0.502	0.114	0.026	
99	<0.001	0.034	0.564	0.170	0.013	
113	<0.001	<0.001	0.178	0.029	0.021	
118/108	0.164	0.058	0.662	0.164	0.018	
149/144	<0.001	0.035	0.636	0.103	0.015	
153	<0.001	0.039	0.642	0.279	0.015	
138	0.006	0.034	0.403	0.190	0.011	

t-chl: trans-chlordane; c-chl: cis-chlordane; t-nona: trans-nona chlor; DDE:p,p'-DDE; HCHs:hexachlorocyclohexanes; n.a : not analysed

TABLE 2 PCB flux to the Harima-nada

Conc. μg/g	S km2	ΔS km2	loading kg/year	flux mg/m² year
0.05	168	168	7.64	0.046
0.04	473	305	11.1	0.036
0.03	1000	527	14.4	0.027
0.02	1860	860	15.7	0.018
0.015	2470	610	8.33	0.014
	3426		57	0.017

TABLE 3 Flux to the Sediment of PCBs in Enclosed Coastal Sea

PCB	flux μg/m² year	flux μg/m² day	area km²	PCB kg/year	year
Harima-nada (A)	17	0.046	3426	57	1978-1979
Harima-nada (B)	14200	39	0.45	6.4	1978-1979
Harima-nada (B)	19600	54	0.45	8.8	1954-1979
Harima-nada (C)	266	0.73	7	1.9	1954-1979
Osaka-Bay	91	0.25	1529	140	1978-1979
PCT	flux μg/m² year	flux μg/m² day	area km²	PCT kg/year	year
Harima-nada (C)	27	0.074	7	0.188	1954-1979

(A) overall; (B) close to PCB source (lower chlorinated PCB);
(C) close to PCB source (high chlorinated PCB)

TABLE 4 Concentrations of Compounds in Particulate

	1986	1988	1988
	air	air	
	V+P	Vapor	Particle
	ng/m³	ng/m³	ng/g
t-chl	0.16	0.67	230
comp.5	0.04	0.17	91
c-chl	0.12	0.58	68
t-nona	0.09	0.46	37
c-nona	0.014	0.055	23
DDE	0.006	0.033	23
HCHs	0.3	n.a	n.a
PCDFs	0.0086	0.0005	53
PCDDs	0.0088	0.0006	79
PCBs	2.8	0.43	272
C12	0.04	0.009	0
C13	0.55	0.081	0.5
C14	1.1	0.18	66
C15	0.77	0.1	84
C16	0.25	0.041	43
C17	0.09	0.016	58
C18	0.004	0.0006	21

t-chl: trans-chlordane; c-chl: cis-chlordane;
comp.5:12346788-octachloro-isomer(Miyazaki et al.,1985);
t-nona: trans-nonachlor; c-nona: cis-nonachlor;
DDE:p,p'-DDE; HCHs:hexachlorocyclohexanes

TABLE 5 Mass Balance of Compounds in Harima-nada

Compounds	Water ng/L	Sediment ng/g	Rain ng/L	Air ng/m³	River ng/L
CHL	0.19	0.02	0.12	0.78	0.19
DDE	0.05	0.42	8.16	0.005	
HCHs	0.13		11.4		
HCB	0.007	0.02		0.013	
PCBs	0.806	8.22	1.75	0.43	0.336

Compounds	Water kg	Sedimentation kg/year	Rain kg/year	Air kg	River kg/year
CHL	17	n.a	0.6	2.7	0.8
DDE	4.4	n.a	39	0.02	0.2
HCHs	12	n.a	55		0.5
HCB	0.6	n.a		0.04	0.3
PCBs	71	57	8.4	1.5	1.4

n.a : not analysed ; CHL : trans- and cis-chlordane;
Surface area: 3426 km^2; rainfall: 1400mm/year (1951-1980);
volume: $8.87 \times 10^{10} m^3$; inflow(from river): $4.2 \times 10^9 m^3$/year;
rainfall: $4.8 \times 10^9 m^3$/year

calculated by taking the mean concentration and multiplied by the total yearly amount of rain over Harima-nada of 1400 mm/year.

Chlordane had been used mainly in urban areas of Japan for termite control. Since 1986, chlordane is no longer used in Japan, but it is the most abundant chlorinated organics in urban atmosphere. The wet flux of chlordane to Harima-nada was 200ng/m2 year. Knap et al.(1988) also reported the flux of chlordane in the ocean, and gives a range for wet flux of 78–115 ng/m^2 year.

$$F(\text{rain}) + F(\text{snow}) + F(\text{dry, aerosol}) + F(\text{dry, vapor}) + F(\text{river}) + F(\text{point source})$$

$$= F(\text{sedimentation}) + F(\text{evaporation}) + F(\text{degradation})$$

$$F(\text{sedimentation}) = F(\text{settling}) + F(\text{saltation}) + F(\text{rolling})$$

where F refers to the flux of compound for each process.

Hoisen et al.(1991) reported that the dry deposition flux of PCBs in Chicago to a smooth greased surface varied between 2.8 and 9.7 μg/m^2 day. The calculated overall PCB dry deposition velocity for Spring averaged 0.5 cm/sec. This value did not increase with increasing PCB flux or airborne PCB concentration.(Hoisen et al., 1991)

Comparing with the estimation of other process , these results indicate that dry deposition, the fallout of coarse particles and the sorption of vapor-phase materials, has been play an important role in the total PCB flux.

CONCLUSIONS

Concentrations of chlorinated organics were measured in the atmosphere, rain, snow, surface waters and sediment at the enclosed coastal sea; Harima-nada and Osaka bay. PCB fluxes to Harima-nada were estimated to 17μg/m^2 year for sedimentation and 2.5μg/m^2 year for wet deposition. The wet flux of chlordane was found to be 0.2μg/m^2 year. Dry deposition, the fallout of coarse particles and the sorption of vapor-phase materials, has been play an important role in the total PCB flux.

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