Dioxin '97, Indianapolis, Indiana, USA

Three dimensional distribution of polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans and polychlorinated biphenyls in sea water using *in-situ* filtration/adsorption water samplers

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Introduction

Among the all man-made chemicals, polychlorinated dibenzo-*p*-dioxins (PCDDs) and some related compounds (polychlorinated dibenzofurans ; PCDFs and polychlorinated biphenyls ; PCBs) became subjects of world attention. Because of its special nature; high toxicity, high persistency and ubiquitous distribution on the earth. It is urgent task for mankind to make clear the global distribution of dioxin like compounds and eliminate their discharge into human environment.

However, few informations about dioxin-like compounds residues are available in sea water because of its very low concentration. Therefore it is very difficult to collect enough volume of water without procedural contamination using common water sampler on contaminated board. Even in a few informations [1, 2, 3] , most of the researcher investigated dioxins and related compounds in surface water only. However, everybody knows that the marine environment is three dimensional system. Monitoring on the surface water only looks on the surface of the global environmental problem.

Considering these situations, we applied automatic *in-situ* filtration/adsorption water samplers (ISFAWS) ; Kiel *in-situ* pump (KISP) [4] and INFILTREX II (AXYS environmental system) to Tokyo Bay and coastal area in Japan. In this report, we present the result of isomer specific analysis of PCDDs/PCDFs/PCBs in different layers of sea water around Tokyo Bay and coastal area, and reconstruct three dimensional distribution of these compounds in the marine environment.

Materials and Methods

Several water samples were collected around Tokyo Bay and coastal area (Table 1). Water samples were collected using KISP at station A, B, D, E and F. The *in-situ* filtration/adsorption system for KISP is shown Figure 1. Up to three of KISP were set to an oil-less stainless steel wire and sunken down to destined depth and maintained up to 9 hours filtration. KISP system was constituted of following equipments; Teflon filter holder (for glass-fiber filter), adsorbent column (for XAD-2), pump, control CPU, flow rate counter and power supply.

Another *in-situ* filtration/adsorption system for INFILTREX II was applied at station C

(Figure 2). INFILTREX II was constituted of similar equipments to KISP, but it was optimized for lower flow rate and longer pumping periods.

During collection of samples, suspended particulate matter was filtered out from sea water by glass-fiber filter and PCBs/PCDDs/PCDFs from them were adsorbed using XAD-2 resin. These resin was extracted in laboratory using Soxhlet extractor with methanol and toluene. Isomer-specific analysis of these compounds were performed using HRGC (HP5890II) - HRMS (VG AutoSpec-Ultima system). This combination of ISFAWS and HRGC-HRMS enable to determine individual isomers of PCDDs/PCDFs/PCBs in sea water at ultra-trace level (detection limit = 1-14fg/L of sea water, depends sample volume and background interferences).

Results and Discussion

Concentration of dissolved fraction of total PCBs/PCDDs/PCDFs in sea water around Tokyo Bay and coastal area are shown in Table 2, Figure 3 and 4.

PCBs concentration of surface waters from outside of Tokyo Bay (D, E, F) were comparable to or lower than that around North Sea in 1988 (13 - 415 pg/L) reported by Schulz-Bull [5]. On the other hand, PCBs concentration of surface waters from inside of Tokyo Bay (A, B) were higher than that around North Sea in 1988 but lower than the maximum concentration (2859 pg/L) reported in Baltic Sea in 1991 [6].

There is few informations on PCDDs/PCDFs levels in sea water around Japan. Matsumura reported 1.0 pg/L of total PCDDs in open ocean surface water near to Japan in 1994 [3]. Broman reported PCDDs and PCDFs concentrations in surface water around Baltic Sea in 1988 as 0.086 pg/L - 0.46 pg/L and 0.077 pg/L - 0.151pg/L respectively [2]. Concentration of total PCDDs and PCDFs (dissolved fraction + particle associated fraction) in surface water from Station E were 0.44 pg/L and 0.17pg/L respectively in this study. Although it is difficult to compare the result of on-site filtration/adsorption system on board they used with the result of our ISFAWS, this kind of large volume water filtration system is necessary to measure ultra-trace level organic pollutant in sea water.

It is interesting that the middle layer of sea water contained larger amount of PCDDs/PCDFs/PCBs than the surface layer in Station E. There was same situation in Station D for PCBs. This phenomenon might be under the influence of a particle transporting system by "Tidal Pump" suggested by Yanagi in 1992 [7].

It is necessary to discuss with particle associated fraction of dioxin like compounds for more consideration, because individual isomer of these has wide variety of hydrophobic nature.

As a result, it was revealed that the surface sea water did not always represents PCDDs/PCDFs/PCBs pollution in the marine environment. Each layer of water mass have its own nature influences the dynamics of dioxin like compounds in the marine environment.

It was also made clear that the combination of ISFAWS and HRGC-HRMS enable an isomer specific determination of PCDDs/PCDFs/PCBs in each layer of sea water at 0.001ppq levels. It is useful to investigate the vertical profile of these chemicals in the marine environment which is necessary to understand three dimensional dynamics of dioxin-like compounds on the globe.

Table 1. Sample list

Sample name	Latitude / Longitude	Depth (m)	Layer (m)	Period	Volume (L)	Sampler
A / 2	N 35`34" / E 139`50"	10	2	1995 / 8 / 18	240	KISP
B / 2	N 35`31" / E 139`49"	12	2	1995 / 8 / 25	348	KISP
C / 10	N 35`17" /	40	10	1995 / 5 / 29 -	1230	INFILTREX II
C / 30	E 139`42"		30	1995 / 6 / 8	1430	
D / S	N 34`53"-54" /	940-1021	100	1996 / 4 / 22 -	316	KISP
D / M	E 139`33"-34"		400	1996 / 4 / 23	702	
D / B			750		260	
E / S	N 35`03"-04" /	1450-1452	100	1996 / 4 / 22	262	KISP
E / M	E 139`20"-21"		600		253	
E / B			1200		328	
F / S	N 34`39"-40" /	1608-1743	100	1996 / 4 / 23 -	504	KISP
F / M	E 139`34"-35"		700	1996 / 4 / 24	240	
F / B			1500		228	

Table 2. Concentration (pg/L) of dissolved fraction of total PCBs, PCDDs, PCDFs in sea water around Tokyo Bay and coastal area.

Sample name	PCBs	PCDDs	PCDFs
A / 2	602	1.2	0.72
B / 2	299	1.2	0.80
C / 10	10	0.23	0.30
C / 30	11	0.32	0.29
D / S	11	n.a.	n.a.
D / M	15	0.055	0.059
D / B	6.4	n.a.	n.a.
E / S	11	0.11	0.061
E / M	23	0.27	0.34
E / B	8.4	0.12	0.036
F / S	9.7	0.10	0.11
F / M	4.5	0.11	0.044
F / B	1.6	0.095	0.049

n. a. ; not analyzed because of accidental missing of samples

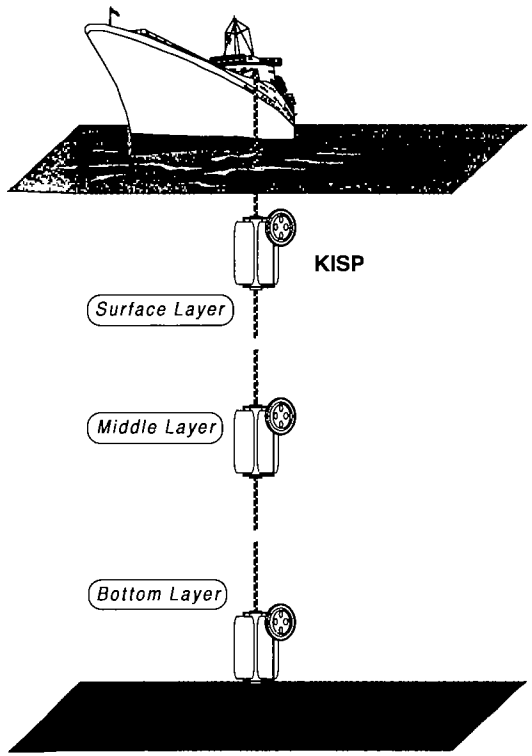

Figure 1.
In-situ filtration/adsorption system for KISP

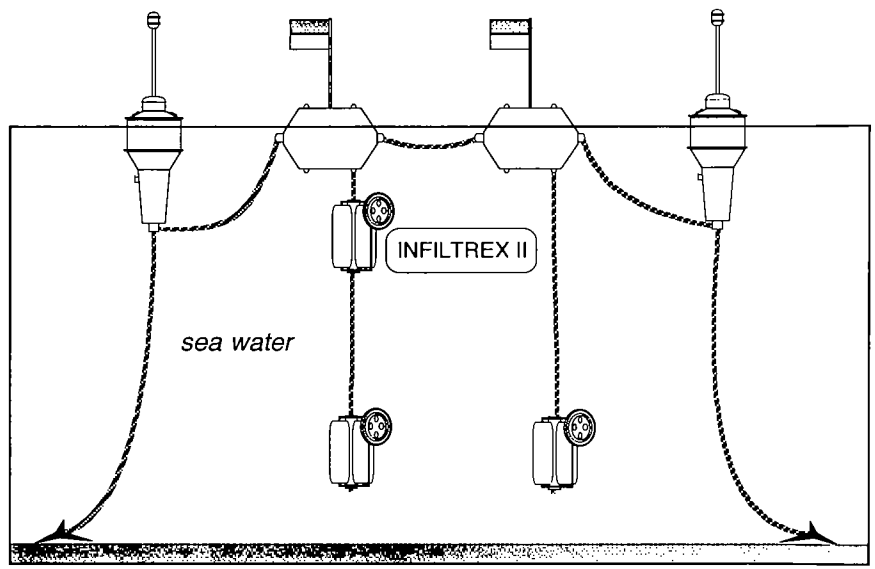

Figure 2.
In-situ filtration/adsorption system for INFILTREX II

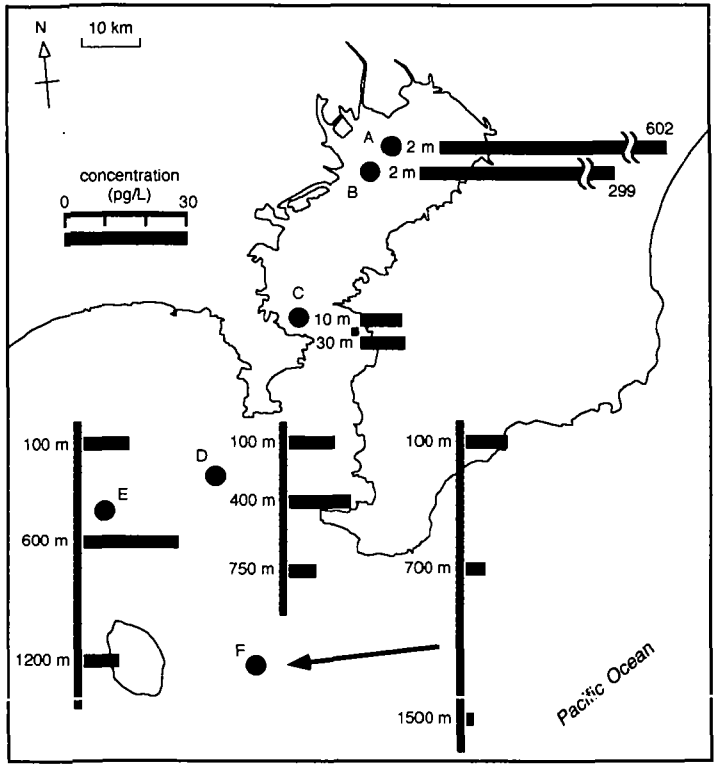

Figure 3.

Three dimensional distribution of dissolved fraction of PCBs in sea water around Tokyo Bay and coastal area.

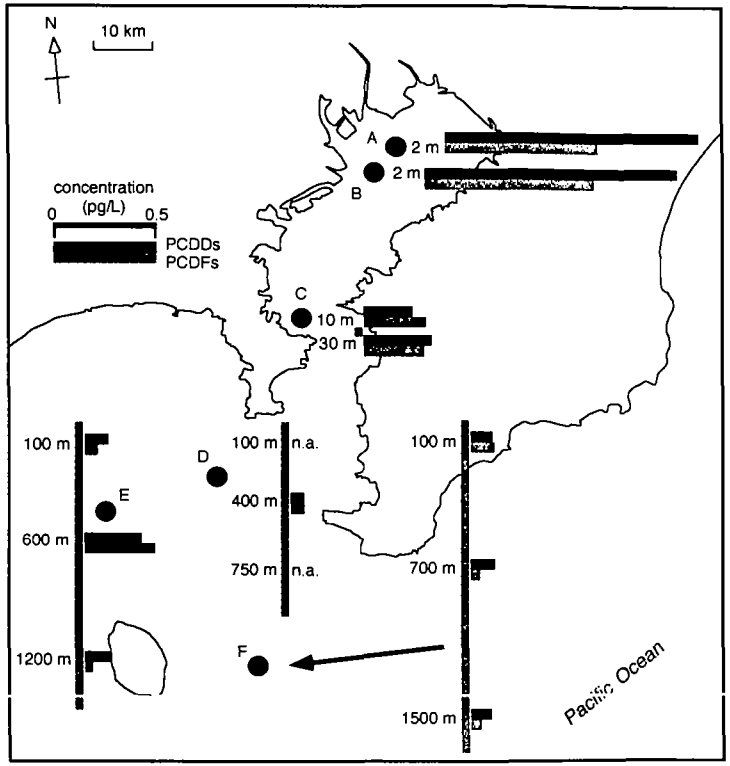

Figure 4.

Three dimensional distribution of dissolved fraction of PCDDs/ PCDFs in sea water around Tokyo Bay and coastal area.

Acknowledgment

Dr. Kannan and Mr. Petrick at Kiel University are gratefully acknowledged for supporting the KISP. Dr. Sakurai at Yokohama National University is acknowledged for assistance in the operation of HRGC-HRMS.

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