PCDDs Concentration in Open-Ocean Water

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1. Introduction

In the last decade, significant advances have been made in determining the concentrations of PCDDs for various kinds of environmental samples (e.g., ash, waste water, pesticide, sludge, food, industrial material, organism, air, etc.). However, there have been no reports with respect to the open-ocean seawater caused by their low concentrations and sampling difficulties.

Accurate data on the concentrations of PCDDs in the open-ocean, in particular the upper layers of water columns, are indispensable in understanding their role in various biochemical and geochemical systems.

We developed special "Pre-concentration system" [1] in order to determine the concentrations of PCDDs in open-ocean seawater and applied to open-ocean seawater in the western North Pacific.

2. Methods

Sampling Locations

Open-ocean samples were collected at two stations in the western North Pacific (Fig. 1) on 25 November, 1994. These sampling site were located on the outside of the "Kuroshio" (the Japan Current). Depth of Sta. A and B was 4290 and 4700 m, respectively.

Pre-concentration System

Since the concentration levels of PCDDs in open-ocean seawater would be very low, large sample size and sensitive detection system is necessary. Schematic diagram of "Pre-concentration system" is shown in Fig. 2. The apparatus consists of the electric pump, pump controller, pulse smoother, cartridge filters, disk filters and adsorbent resin. Seawater sample flows into the cartridge filters (Toyo, TCW-CSS) after passing through a pulse smoother. Pore size of each cartridge filter was 5, 3 and 1 μ m, respectively. After passing through the cartridge filter, the water flow is drawn into glass fiber filter (Toyo, GC-50). Final stage is adsorption on macroreticular resin. Amberlite XAD-4 (Rohm and Haas) was employed for adsorbent and its volume was 5,000 mL. Flow-rate is continuously adjustable from 0 to 2,000 L/hr using by pump controller.

Sampling Methods

In order to avoid contamination by materials from the research vessel, seawater samples were corrected from the 50 m depth using pressure resistance pump. Flow-rate were regulated less than 600 L/hr This flow-rate is equivalent to 2.0 bed volumes/min. After the pre-concentration operation, cartridge filters, glass fiber filters and XAD-4 resin were stored in stainless or Teflon receptacles until they were analyzed in the laboratory.

Extraction from the Filters and Resin

Cartridge filters and glass fiber filters were Soxhlet extracted for 12 hr with methanol and n-hexane. PCDDs adsorbed on XAD-4 resin were extracted by methanol and n-hexane using special "Continuous extraction unit" (Fig. 3). Methanol and n-hexane were combined after the extraction, and concentrated to small volume using rotary evaporator. Finally, solvent was changed to n-hexane.

Cleanup

Concentrated sulfuric acid cleaning and column chromatograph technique (silica gel and alumina) were employed in order to separate the PCDDs from other impurities in sample. Descriptions in detail for cleanup technique are omitted here.

PCDDs Standards

The native and ^{13}C-labeled standard compounds (Cambridge Isotope Laboratories); 2,3,7,8-TetraCDD, 1,2,3,7,8-PentaCDD, 1,2,3,6,7,8-HexaCDD,

1,2,3,4,6,7,8-HeptaCDD and 1,2,3,4,6,7,8,9-OctaCDD were employed for the calibrations and recovery verifications.

HRGC/HRMS Determination

The final analysis of PCDDs in extracted sample was performed on a high resolution mass spectrometer (AutoSpec, VG Analytical) directly coupled to a high resolution gas chromatograph (5890 SERIES II, Hewlett Packard). The HRGC was equipped with a SP-2331 (Supelco), or DB-5 (J&W) fused silica capillary column. HRMS was operated in the electron ionization, selected ion monitoring and PFK lock mass procedure at 10,000 or more resolution. In order to gain high resolution and high sensitivity, the mass measurements were carried out one injection per one congener.

Contamination

Strict measures were taken to minimize contamination during the analysis. All analyses were carried out in the "Chemical hazard clean room". The air supplied into this room is passed through several pre- and charcoal-filters. All glass wares were applied to solvent cleaning and 400 W ultraviolet irradiation (65 $\mu W/cm^2$ at 254 nm) for more than 12 hr before in use. Cartridge filters and XAD-4 resin were cleaned by the Soxhlet extractor and "Continuous extraction unit". Grass fiber filters were heated in a muffle furnace for at least 2 hr at 400 ℃. Organic solvents were purified by distillation.

3. Results

Almost isomers of hexa- and hepta- CDD were detected. Some isomers of tetra- and penta-CDD were not detected in a reliable S/N ratio. Results obtained for total concentrations of PCDDs are shown in Table 1.

Table 1. Concentration of PCDDs in the surface water of Sta. B.

Congener	Concentration (fg* / L)
Tetra	40
Penta	60
Hexa	210
Hepta	350
Octa	390

* femto gram ; 10^{-15} g

4. References

1) Matsumura T., H.Ito, T.Yamamoto, and M.Morita (1994): Development of Pre-Concentration System for PCDDs/DFs in Seawater, Organohalogen Compounds 19, 109-112

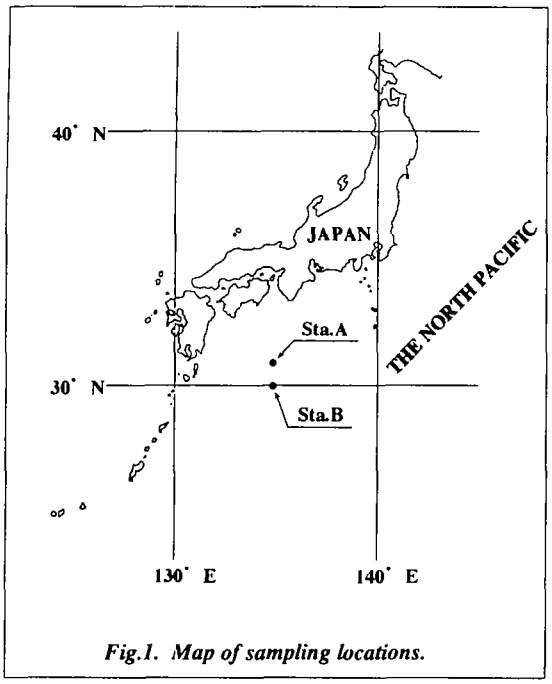

Fig.1. Map of sampling locations.

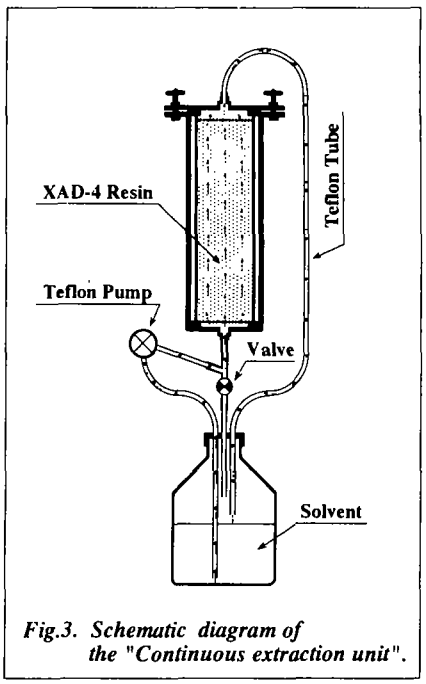

Fig.3. Schematic diagram of the "Continuous extraction unit".

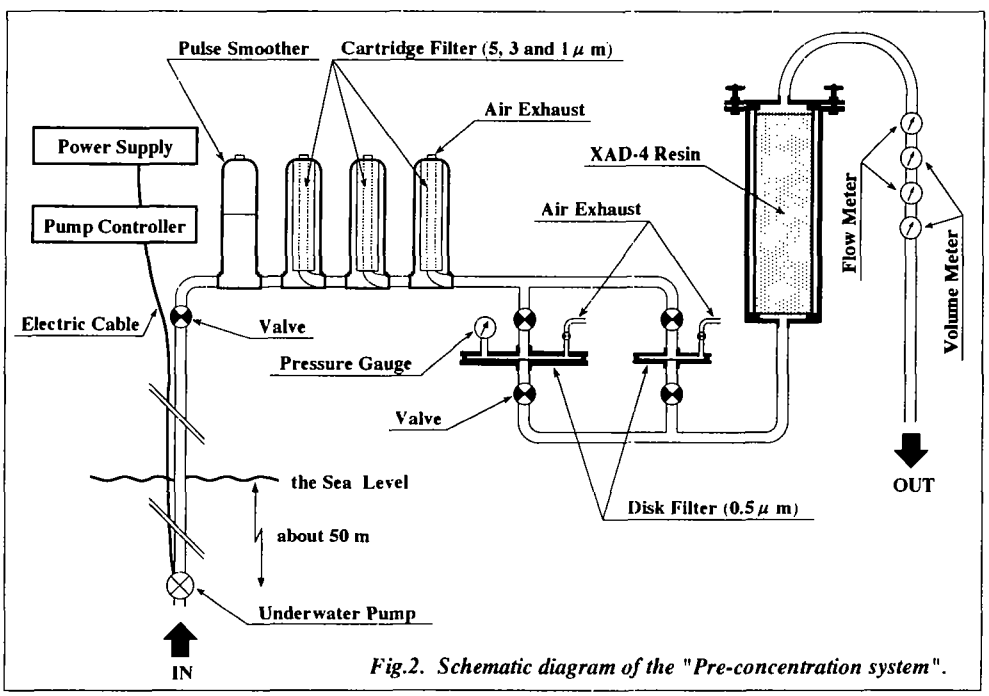

Fig.2. Schematic diagram of the "Pre-concentration system".