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## Polychlorinated Biphenyls (PCBs) in a Sub-tropical Marine Environment: A Case Study in Seawaters Collected around Ryukyu Islands, Japan

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### Abstract

Seawater samples collected around Ryukyu Islands during the Nagasaki Maru expedition in September 22 to October 2, 2001 were analyzed for total PCBs and some nutrients. The PCBs were detected in all stations (W-1 to W-4), in concentrations ranging between 0.053-0.28 ngL<sup>-1</sup>. The concentration of PCBs increased from surface water down to 600 m, thereafter decreasing with depth to 1200 m at W-4. At W-1, PCBs increased from surface water down to 55 m. Chromatogram patterns varied among the sampling stations, implying the possibility of having different compositions of PCBs. The trend of the nutrients such as phosphates (PO<sub>4</sub>-P) and silicates (SiO<sub>4</sub>-Si) showed a general increase with depth.

Key words: PCBs; Nutrients; Ryukyu Islands; Nagasaki maru; XAD-2; Homolog; Seawater.

### 1. Introduction

Polychlorinated biphenyls (PCBs) are chlorinated hydrocarbons with a biphenyl nucleus on which one to ten of hydrogens have been replaced by chlorine. PCBs synthesis was first described by Schmidt and Schultz in 1881 (Waid, 1986). The first findings of PCBs in the environment were reported by Janseen in 1966 (Tanabe, 1988). The role of some PCBs congeners in cancer genesis have led to the inclusion of this class of compounds in the list of priority pollutants, hence making their environmental monitoring of prime importance (Fuoco *et al.*, 1996).

Open ocean water serves as a vast reservoir and final sink of PCBs (Tanabe, 1988). PCBs are found ubiquitously in many environmental matrices, including marine plants and animals, fish, mammals, birds, wildlife, soil, air, and water. The concentration of PCBs increases through the food chain (Erickson, 1997). PCBs production was stopped in many countries in the 1970s. However, there is still a big load already existing in the environment, and they tend to accumulate in the fatty tissues of organisms. Furthermore, PCBs can still be produced unintentionally, through several processes, such as incomplete combustion of high chlorine content wastes (Riley, 2001).

The Ryukyu Islands are subtropical climate islands situated in the south west of Japan, which experience high rainfall and frequent typhoons. The agriculture and fishing are important economic activities. Some light industries and several US military bases are found on Okinawa Main Island. This work was aimed at elucidating the status and behavior of PCBs in the seawater around Ryukyu Islands.

## 2. Materials and Methods

### 2.1 Sampling stations.

The expedition was conducted using the R/V Nagasaki Maru, from September 22 to October 2, 2001. The routes of this survey covered some points in the Pacific Ocean and in the East China Sea (Fig. 1). Seven seawater samples of 25 L to 90 L were collected during this expedition.

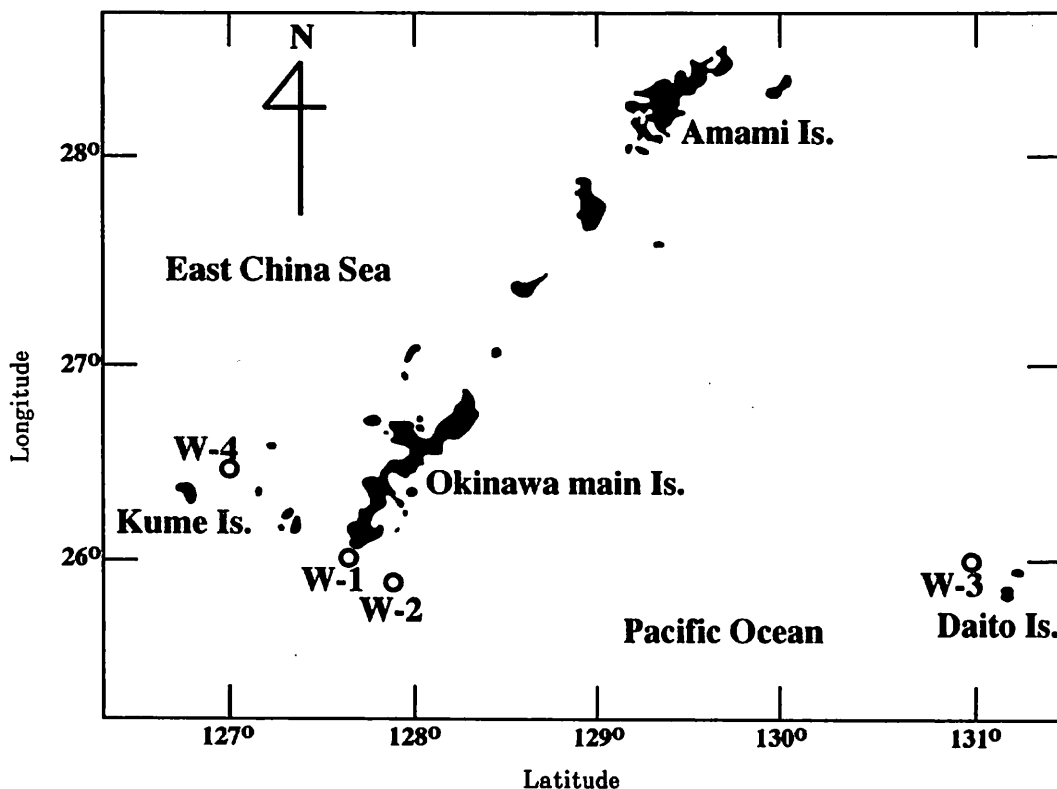


Fig. 1. Sampling points.

### 2.2 Sampling.

Pre-cleaned 50 g XAD-2 (styrene-divinylbenzene copolymers) columns were used to extract the PCBs from the seawater. First XAD-2 resins were cleaned by analytical grade ethanol for more than seven days using Soxhlet apparatus and exchanged four times. The last part of ethanol was exchanged by hexane and then concentrated to 100  $\mu$ L, which was

then utilized to check for contamination using gas chromatography equipped with an electron capture detector (GC/ECD). If any interference peaks appeared, the cleaning was continued until a satisfactory blank was obtained. A metallic bucket was used to collect the surface seawater samples, and for the deep seawater samples the CTD Rosette System Sampler was used throughout the survey. All tools and devices used for the sampling were pre-washed by using detergent and water, and finally rinsed with analytical grade organic solvents such as methanol, hexane and ethanol. The ship environment has been identified as possible source of contamination (Schulz *et al.*, 1988). To minimize the risk of contamination, all samples were immediately processed on board. Furthermore, all organic solvents used in sampling were measured for their blank before the sampling.

The unfiltered seawater was immediately extracted by XAD-2 columns at the flow rate of about 300 mL/min, and then columns were kept refrigerated at 4 °C in the ship. The columns were frozen at -20 °C in the laboratory until analysis.

### 2.3. Samples analysis.

The PCBs were eluted by 300 mL of ethanol and then exchanged with 100 mL of hexane (Iwata *et al.*, 1993). The hexane extract was concentrated using a rotary evaporator under a nitrogen gas stream, and cleaned by concentrated sulphuric acid (Per Larsson *et al.*, 1987). Activated florisil columns were used to remove possible interfering substance like pesticides. All organic solvents used in this study were reagent grade for pesticide residues and PCBs analysis and obtained from Kanto Chemical. Co. Inc, Tokyo-Japan. Kanechlor standards were obtained from GL Science Inc. Tokyo, Japan.

Quantitative analyses of total PCBs were accomplished by a Hewlett-Packard 6890 gas chromatography equipped with a <sup>63</sup>Ni electron capture detector (GC/ECD). Samples of volume 3  $\mu$ L were injected using autosampler in the splitless mode at 250 °C. Helium gas was used as carrier gas at the flow rate of 60 mL/min. Detector temperature was 300 °C. The column used for analysis was Capillary column (J & W Scientific, USA: DB-5, 15 m (length) x 0.53 mm (inner diameter) x 1.5  $\mu$ m film (thickness)). A mixture of Kanechlors (KC-Mix) 300, 400, 500, 600 in a 1:1:1:1 ratio was used as the external standard to quantify the total PCBs. HP Chemstation software was used to determine the levels of PCBs. The triplicate recovery tests of total PCBs spiked in Milli-Q water yielded 84 %. All PCBs concentrations were corrected for blank levels but not recovery percentage. Nutrients were determined immediately after sampling using the HITACHI C-2001 Spectrophotometer.

## 3. Results and Discussion

### 3.1 PCBs levels in the seawater.

PCBs were detected in all sampling stations (W-1 to W-4) in concentrations ranging between 0.053-0.28 ngL<sup>-1</sup> as shown in the Table 1.

The levels of PCBs in this study are relatively low compared to previous studies (Table 2).

Table1. Description of the samples.

Station	Location	Date	Depth (m)	Volume (L)	PCBs concentration (ngL <sup>-1</sup> )
W-I	26°09' N-127°35' E	22/9/2001	0	90	0.069
W-1	26°09' N-127°35' E	22/9/2001	55	36	0.15
W-2	25°50' N-127°49' E	22/9/2001	0	72	0.24
W-3	26°00' N-130°57' E	23/9/2001	0	54	0.053
W-4	26°29' N-126°59' E	24/9/2001	0	72	0.057
W-4	26°29' N-126°59' E	24/9/2001	600	25	0.28
W-4	26°29' N-126°59' E	24/9/2001	1200	30	0.26

Table2. Comparison of PCBs concentrations in seawater from different oceanic regions.

Location	Sampling date	No. of samples	PCBs range (ngL <sup>-1</sup> )	PCBs mean (ngL <sup>-1</sup> )	Reference
East China Sea and Pacific Ocean	2001	7	0.053-0.28	0.15	This study
Mediterranean Sea	1975	80	<0.2-8.6	2.0	Elder <i>et al.</i> , 1977
N.W. Mediterranean Sea	1975	11	1.5-3.8	13	Elder, 1976
Sargasso Sea	1973	8	<0.9-3.6	1.1	Bidlema <i>et al.</i> , 1974
North Sea and Scottish Coast	1974	5	<0.15-0.52	0.23	Dawson <i>et al.</i> , 1977
Antartic 48-65°S, 124-163°E	1980/81	7	0.042-0.072	0.058	Tanabe <i>et al.</i> , 1982

This may reflect the fact that production and use of these compounds have ceased in the world since 1970s.

The total PCBs concentrations were found to have variations through the water column (Fig. 2). The total PCBs at 600 m are relatively high compared to surface water, but the PCBs concentration decreased down to 1200 m at W-4. At W-1, PCBs concentration increased from surface to 55 m (Fig. 2). The vertical distribution pattern obtained in this study supports the previous study (Tanabe *et al.*, 1986). The PCBs from surface to deep seawaters are strongly associated with sinking of the particles in the water column. Transport of PCBs from the surface to deep water may be considered to happen after their sorption to particles in surface water, which then sink in to deeper water with analogous

to the behavior of several inorganic substances. Another possible mechanism is oxidation/dissolution of biogenic particles, which tend to release part of their sorbed constituents at great depths, causing an increasing the concentration of nutrients and metals in deeper water. It can also be applied to organic contaminants like PCBs (Schulz *et al.*, 1988). Elder *et al.* (1977), found high concentrations of PCBs in fecal pellets collected in the Ligurian Sea. Since biogenic particulate products, especially fecal pellets, are known to sink rapidly in to the deep water, the transport of PCBs by such sinking particles could be an important route to deep sea. The nutrients (phosphates and silicates) analyzed in this study, clearly increased with increasing the depth (Fig. 2). which supports the above mentioned mechanisms.

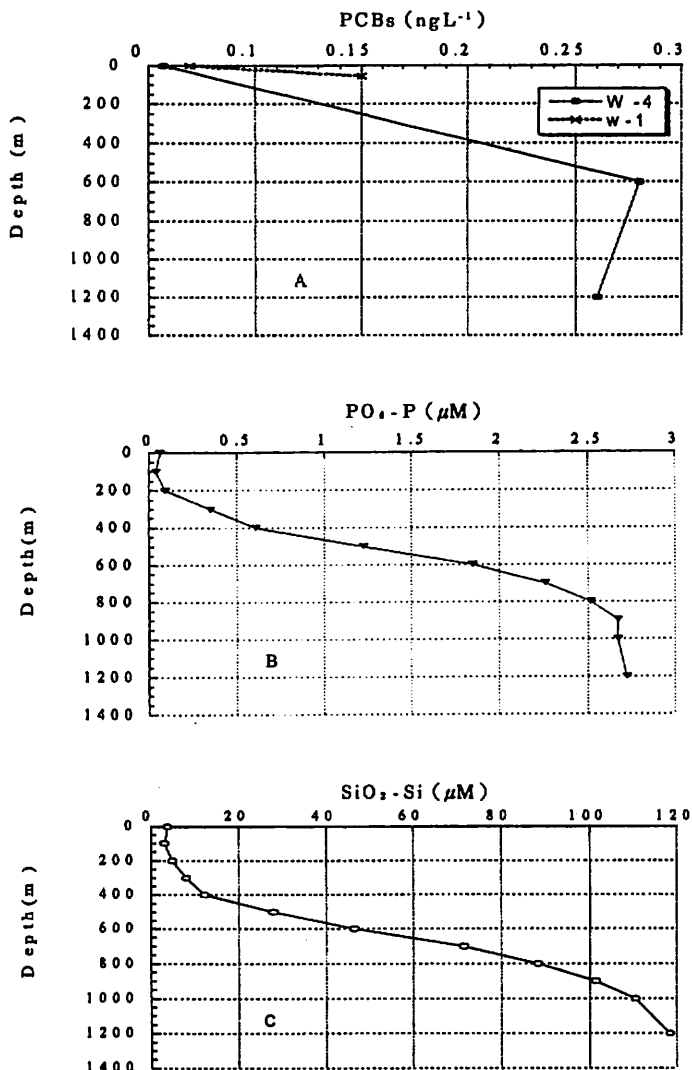


Fig. 2. Vertical profiles of total PCBs at W-1 and W-4 (A); vertical profile of Phosphates at W-4 (B); vertical profile of Silicates at W-4 (C).

In the case of surface seawater, higher intensive shipping movements around Okinawa Island may be related to the higher PCBs levels at W-1 and W-2, compared to W-3 and W-4. There was no significant difference in PCBs levels between the East China Sea and the Pacific Ocean (Table 1).

### 3.2 Homolog patterns of PCBs in seawater around Okinawa Islands.

Homolog composition is very important in studying PCBs behavior. As the number of substituted chlorine atoms in the PCBs increases, solubility in water and vapor pressure decrease, so they can remain in the environment for longer period (Jeong *et al.*, 2001). The chromatogram patterns of the seawater extracts in this study suggest possible different compositions between surface water and deep water, as well as between the East China Sea and the Pacific Ocean. Typical sharp peaks clearly observed in chromatogram of deep seawater at 600 m compared to broad peaks in surface waters are shown in Fig.3b. This gives important clue about the composition and fate of PCBs in this study; The chromatograms of surface waters (0 m) at W-3 and W-4 have relatively higher background compared to deep sea water at W-4 (600 m), this might be caused by the presence of relatively water soluble organochlorines such that HCHs, which are slowly scavenged at surface waters (Tanabe *et al.*, 1986). Deep seawaters were dominated with higher chlorinated PCBs than surface waters. Furthermore, almost all the sample chromatograms have common unidentified sharp peaks before the retention time of 5.6 min (Fig.3b). These peaks might be important in the distribution of PCBs homologs; however, more analysis using gas chromatography with high-resolution mode mass spectrometry (GC-HRMS) is necessary to further

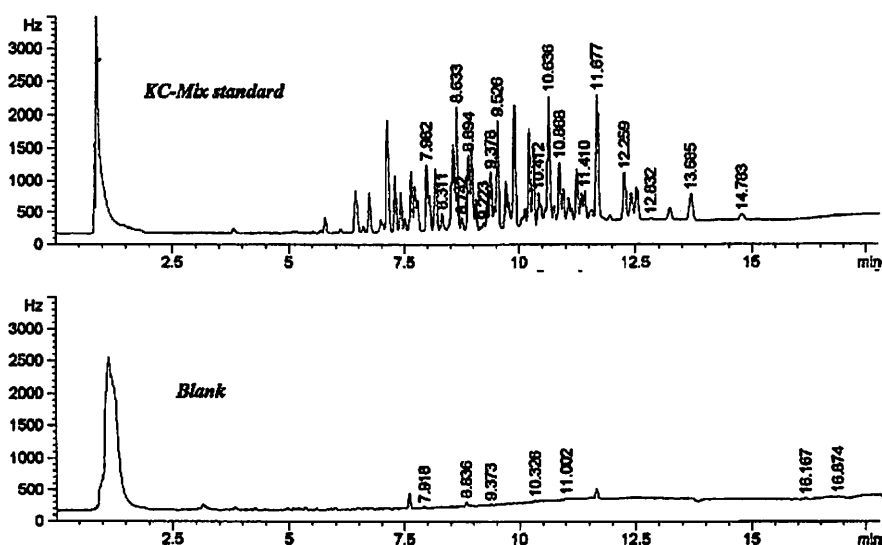


Fig. 3a. Chromatograms of KC-Mix standard and blank. The PCB compounds were eluted at retention time between 5.6 to 14.7min.

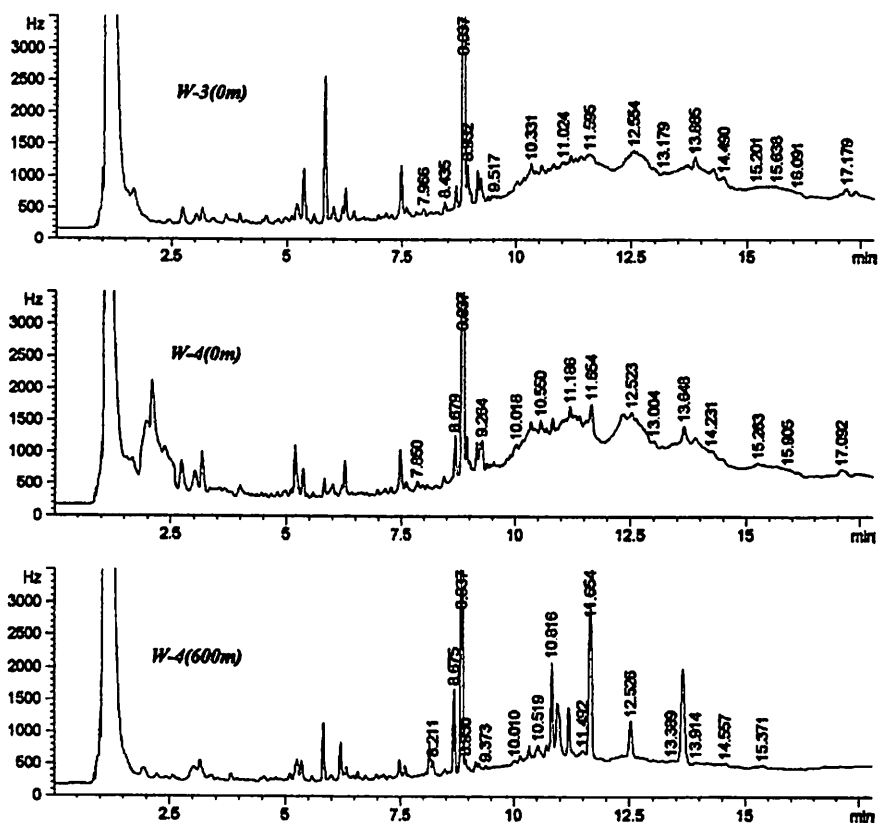


Fig. 3b. Chromatograms of W-3 (0 m), W-4 (0 m) and W-4 (600 m). The PCB compounds were eluted at retention time between 5.6 to 14.7 min.

confirm the exact compositions of PCBs.

Atmospheric deposition, continental runoff and river inputs are possibly main modes of PCBs transport in the open ocean; hence, these mechanisms should be considered in our study. However, further systematic studies are needed, involving larger volumes of seawater and sampling at greater depths in order to clarify the contribution of these mechanisms on the role of PCBs geochemistry in seawater around Ryukyu Islands.

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