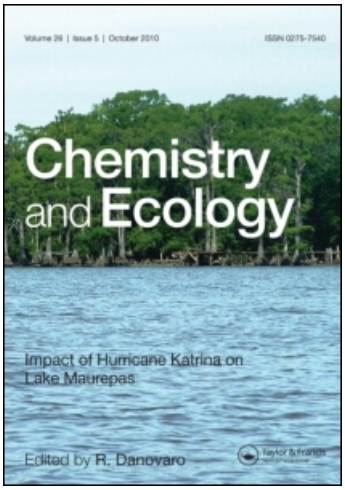

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POLYCHLORINATED BIPHENYLS (PCBs) POLLUTION IN SEA OF JAPAN

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Deep waters of the Sea of Japan and surface waters of the Pacific Coast of Honshu and the northeast Sea of Japan were analysed for polychlorinated biphenyls (PCBs) pollution. The ΣPCB concentrations in solution in the Sea of Japan (50–3000 m) were between 140 and 1230 fg dm^{-3}. The space-integrated surface water concentration near the Pacific coast of northern Honshu was 140 fg $dm^{-3}$and for the surface water of the Sea of Japan was 230 fg dm^{-3}. Based on these analyses four water masses were deduced in the Sea of Japan during the summer months. It is shown for the first time in the Sea of Japan that polychlorinated biphenyls are excellent chemical indicators of not only the anthropogenic pollution, but also water masses.

Keywords: Kiel in-situ pump; PCBs; Sea of Japan; chemical tracer

1. INTRODUCTION

Polychlorinated biphenyls (PCBs) are used successfully as chemical tracers in identifying population structure, migratory routes and physiological parameters of certain marine mammal species (Subramanian *et al.*, 1988a; Subramanian *et al.*, 1988b). Their use as indicators of ecotoxicological effects are also reported (Boon *et al.*, 1994; Kannan *et al.*, 1995a; Kannan *et al.*, 1995b; Reijnders, 1994; Safe, 1991). However, their application in the biogeochemistry of

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oceans are very limited because of difficulties in measuring PCBs in water. A high volume, low contamination pumping system, "Kiel In-Situ Pump" (KISP) has been developed recently (Petrick *et al.*, 1996) to analyse ocean waters for PCB contamination. For the first time, this system was deployed in the deep waters of the Sea Japan to study the vertical profile. Bounded by Japan, Korea and Russia, the Sea of Japan is a region of great practical interest. Halloway *et al.* (1995) described this as a semi-enclosed "small ocean", roughly 1600 km long by 900 km wide with depths exceeding 3700 m with shallow straits (Tsushima, Tsugaru, Soya) connecting the China, Pacific and Okhotsk seas. The Sea of Japan provides a natural "laboratory" for testing ocean circulation theories.

2. MATERIALS AND METHODS

Sampling Water samples were collected during the geological survey of the Department of Geological Survey of Japan with R. V. "Hakurei-maru" in June-July 1995 (see map in Fig. 1).

Surface water was taken in from the 6 m depth horizon from the bow of the ship while sailing. Deep water was sampled with KISP, using several units attached to the hydrographic wire at 50, 100, 1500 and 2500 m (Siribesi Trough: 42.58N 139.32 E) and at 500, 1000, 2000 and 3000 m (Siribesi Trough: 42.55N 139.32E). PCBs from water were extracted in XAD-2 resin column attached in the KISP. These columns were kept air–tight and covered with sea water after sampling in a refrigerator until analysis in the home laboratory.

Extraction and Cleanup: The XAD-2 resin was extracted in a modified soxhlet apparatus with water/acetonitrile (10:90). The extraction procedure is given in detail in an IOC manual (Anonymous, 1993). Organics in the extracted solution were separated into classes according to the procedure of Petrick *et al.* (1988).

Gas chromatographic separation and detection: Gas chromatography-electron capture detection analyses were carried out with Siemens Sichromat-1 (single column)-^{63}Ni ECD and a cold on-column injector (PTV). A SE-54 fused silica column (50m, 0.25mm i.d., ICT, Frankfurt) was used for identification of 30 CBs that elute from this

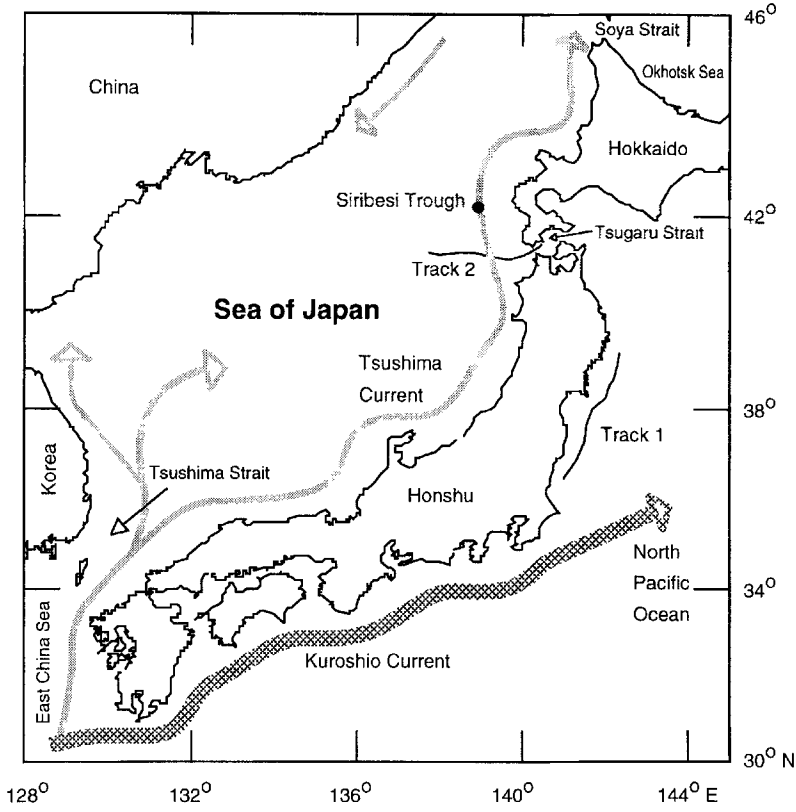

FIGURE 1 Map showing the sampling location in Japan. Deep water samples were taken at Siribesi Trough. Space-integrated surface water samples (6m) were collected at Track 1 and 2. The flow of Tsushima Current in the Sea of Japan is shown in darker shade. Kuroshio, the major current that flows towards northern Pacific Ocean, is shown in lighter shade.

column as single peaks (Schulz *et al.*, 1989). Temperature: 140 – 170°C at 5°C min^{-1}, then temperature ramp to 240°C at 30°C min^{-1}. Carrier gas: H_2(2 ml min^{-1}).

3. RESULTS AND DISCUSSION

The sum of PCB concentrations in the surface water of the Japanese area is given in Figure 2. These values are compared with other values

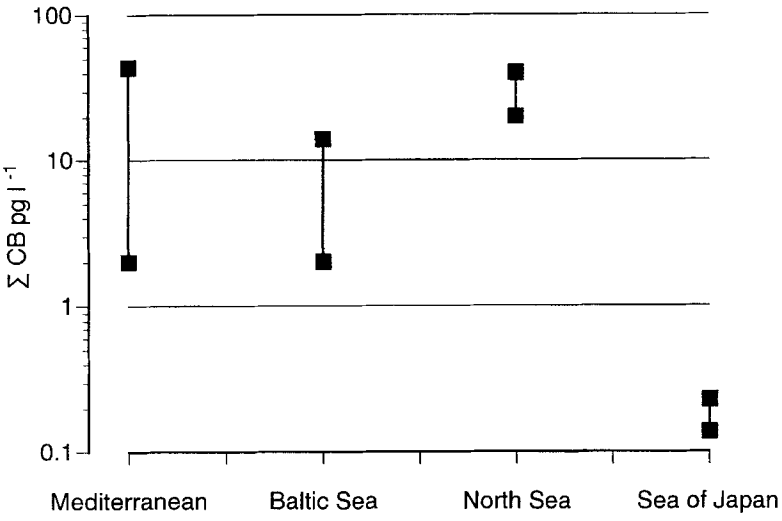

FIGURE 2 Space-integrated surface water concentrations in the Mediterranean (Schulz-Bull *et al.*, 1997), the Baltic Sea (Schulz-Bull *et al.*, 1995), the North Sea (Schulz-Bull *et al.*, 1991) and the Sea of Japan.

in the Mediterranean, Baltic Sea and North Sea taken from our previous studies (Fig. 2). The PCB contamination in the Japanese water is at least two orders smaller than in the European environment. The space integrated PCB concentrations in Japanese surface waters were in the range of 190 to 340 fg dm^{-3}.

The vertical profile of PCB pollution in the Sea of Japan was studied. The detailed congener-specific concentration profile at different depths is given in Figure 3. Samples from 50, 100, 500, 1000, 1500, 2000, 2500 and 3000 m depths were taken from a location called Siribesi Trough. The first level (50 m) concentration (ΣPCB) was in the range found in the Japanese surface waters. However, a different picture emerged when deep water samples were analysed. The highest concentrations were recorded at depths of 500 and 1000 m. After a small dip in concentration at 1500 m, it went up again at 2000 and 2500 m depths. The vertical profile of ΣPCB concentrations at Siribesi Trough is presented (Fig. 4) along with a vertical profile in the Atlantic for comparison.

An unpublished study in Tokyo Bay using PCDDs/PCDFs/PCBs as tracers confirm the observation that deeper waters carry higher

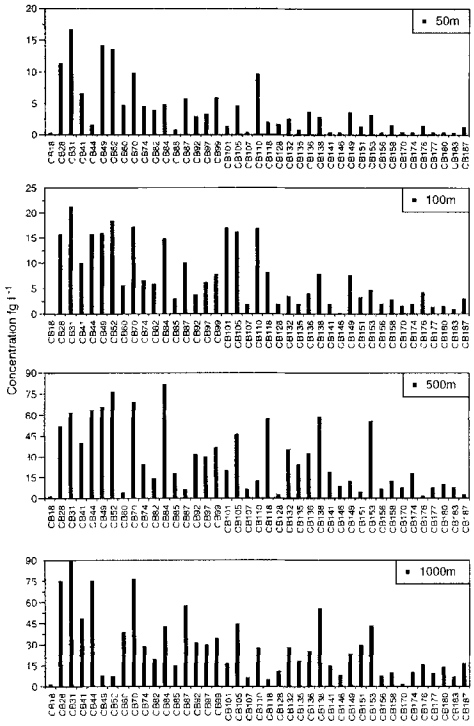

FIGURE 3 Concentration profiles of polychlorinated biphenyls (PCBs) at various depths in the Sea of Japan.

concentrations of these contaminants (Yamashita *et al.*, 1997). This interesting situation may either be due to the "Tidal Pump" as proposed by Yanagi *et al.* (1992), or due to underwater currents.

It is well known that Kuroshio current that originates from East China Sea branches off at the Tsushima islands and enters the Sea of Japan as the Tsushima Current (Moriyasu, 1972). This carries water of high salinity and high temperature toward the north. Branches of this current flow out of the Sea of Japan through the Tsugaru Strait in between the northern Japanese islands and part of the water continues along the west side of Sakhalin Island (Russia), then turns around and flows south after having been cooled and diluted. Tsushima Current brings waters of East China sea to coastal waters of Korea and Primorskaya when it arrives in the north eastern Sea of Japan. The

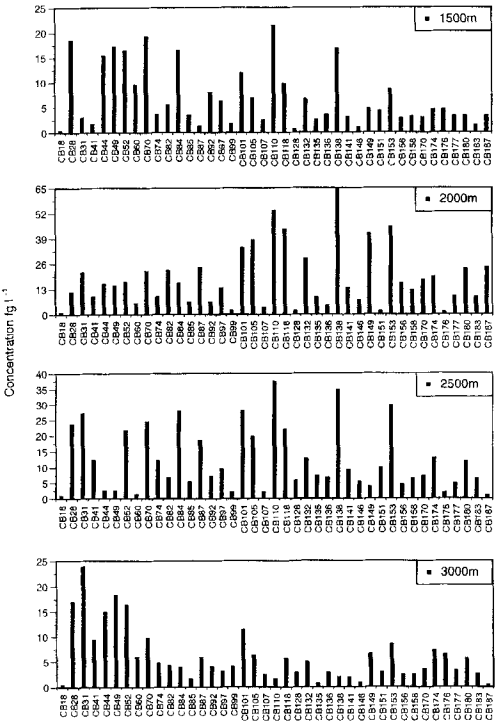

FIGURE 3 (Continued).

water masses in the Sea of Japan may be due to these currents. In summer, vertical convection currents add complexity to this situation by mixing the water of Sea of Japan, with cold, diluted waters of the north (Gamo *et al.*, 1986). The existence of such strong seasonal current with the speed over 30 cm/sec has been verified by the deep-sea current metre mooring, carried out for more than three years during Circulation Research of the East Asian Marginal Seas (CREAMS) studies (Takematsu *et al.*, 1996).

There is no regular vertical gradient in the concentration of PCBs in Siribesi Trough samples (Fig. 4) suggesting that Sea of Japan is stratified in summer months into several layers. For example, the uniform ΣPCB concentrations in solution up to a depth of 100 m suggest a surface layer, with high concentrations recorded in 500 and

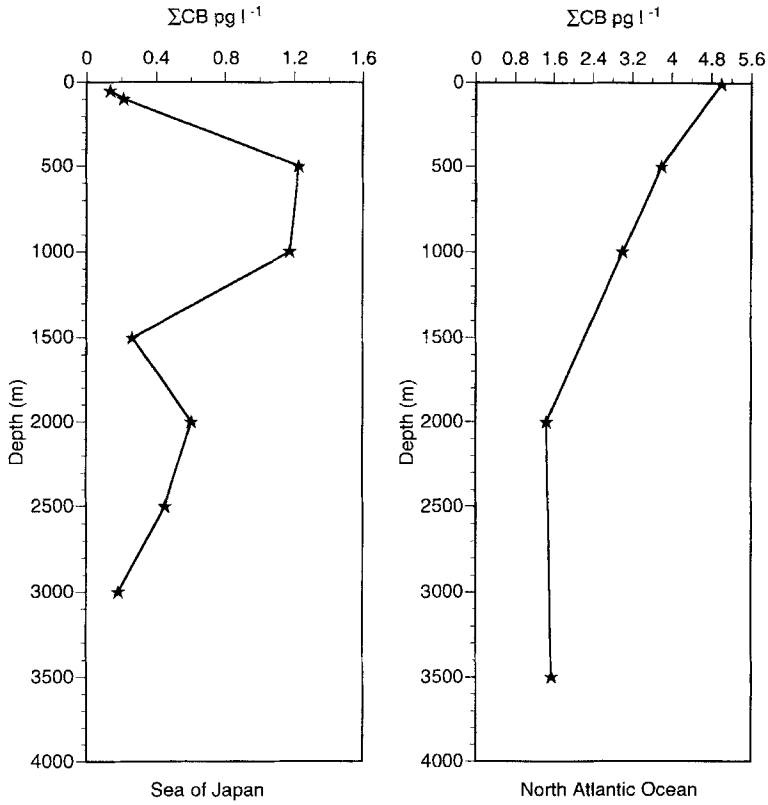

FIGURE 4 ΣCB concentrations at various depths in the Sea of Japan [42.55°N, 139.32°E] (shown left) and North Atlantic [42.55°N, 139.32°E] (Petrick *et al.*, 1996) (shown right).

1000 m, suggest a central water (100–1000 m), and low but similar concentrations in 1500 and 2000 m suggest a deep water (1000–2000 m). The lowest concentrations in 2500 and 3000 m suggest a bottom water (2000–3000 m). CTD data for summer supplied by Japan Oceanographic Data Centre, indeed, supports our conclusion.

In fact, water mass analysis has been carried out in the Sea of Japan using physical measurements as early as in 1954 (Akagawa, 1954; Kajiura *et al.*, 1958; Miyata, 1958). However, most recent results come from CREAMS expeditions carried out jointly by Korean-Japan-Russian oceanographers during 1993–1996. Temperature-Salinity

plot obtained in Japan basin during CREAMS studies clearly reveal unequivocal evidence that the East Sea Proper Water (ESPW), previously known as a single homogenous water mass, consists of several distinct water masses (Kim, 1996). The proposed names for these water masses are East Sea Surface Water, East Sea Central Water, East Sea Deep Water and East Sea Bottom Water.

These results suggest that PCBs could be used effectively as chemical tracers by virtue of their environmental persistence in understanding biogeochemical processes such as water mass formation in deep regional seas and oceans.

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