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Assessment of butyltin contaminants in sediments from Busan Bay with the largest harbours in Korea

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Introduction

The tributyltin (TBT) is effective as an anti-fouling agent, and has therefore been added to many ship-paint formulations to keep ship hulls free from algae, barnacles and other fouling organism. However, the use of tributyltin (TBT) has been restricted since 1980s in many counties because of its ability to cause toxicity at very low water concentrations (Meador, 1997). Notwithstanding the ban of TBT in antifouling paints, TBT remains an important pollutant in areas with high ship traffic. Recent studies have shown the widespread occurrence and accumulation of butyltin compounds in the sediment and organism (Kannan and Falandysz, 1997). In Korea, the ban on the use of TBT-based paints was initiated in 1999. Busan Harbour located at the southeastern end of the Korean Peninsula is the foremost harbour in Korea. Busan Harbour processes 40% of total marine export cargoes and 81% of container cargoes in Korea as well as 42% of marine products domestically produced. Therefore, the study to assess the distribution and patterns of BTs (butyltins) compounds in sediments from Busan Bay with very high potential on the butyltin contamination is very important.

Materials and Methods

Samples were collected from Busan Bay in March and September 2002: surface sediment (40 stations) and sediment core (1 station). The samples were immediately transported to the laboratory in a cooler box with ice or dry ice. Samples were stored -20°C and later freeze-dried. The analytical procedure was performed after combing and modifying the procedures of Wade et al. (1988) and Harino et al. (1992). Briefly, the freeze-dried samples were extracted with 0.1% tropolonemethylene chloride, hexylated with Grignard reagent and then purified by Florisil

column. Tripentyltin chloride was spiked before extraction as surrogate standard. The extract eluted with n-hexane was concentrated and tetrabutyltin (internal standard) was added. The butyltin level was determined on a Hewlett-Packard 6890 gas chromatograph (GC) with a flame photometric detector. The recovery in the reference material was more than 90% for TBT. Organic carbon (OC) was measured by a CHN analyzer (Perkin Elmer 2400) and particle size was determined using standard wet sieving techniques. Sedimentation rates using ²¹⁰Pb profiles and a ¹³⁷Cs-time marker were determined.

Results

Tributyltin (TBT) was detected at all stations of 40 stations in the surface sediment. The estimated TBT concentrations for 40 sediments ranged from 0.08 to $4.10 \mu g$ Sn/g dry. Very high concentrations of TBT were found in two sites near shipyards and Gamcheon Harbour, suggesting that these samples represented the TBT contaminated "hot spots". However, the concentration of TBT decreased rapidly seaward. With regard to the composition of BTs, the contributions of TBT were high in the inner stations (34-56%) and low in the outer stations (8-40%). The historical trend of Gamcheon Bay was dominated by a distribution of a subsurface maximum with decreased contaminant levels both to the surface and with depth in the core. Three TBT peak presented at depths of 18-20 cm, 24-26 cm and 34-36 cm layers. The surface sediment exhibited similar to TBT level at 40-42 cm layer with more than 3 μg -Sn/g.dry. It means the present-day situation has not largely improved compared with past. The contributions of TBT in sediment cores exhibited a weak variation among layers, ranging from 37 to 71% (mean 51%). These results indicate that the sampling sites have had continuous influence from pollution sources such as harbors, shipyards or industrial complexes and the elevated butyltin contamination still remains at several sites in Busan Bay.

Reference

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