

Occurrence of Butyltin Compounds in Seawater, Sediment and Biosamples from the South Coast of Korea by GC-QFAAS

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ABSTRACT

The occurrence and level of contamination by butyltin compounds, tributyltin (TBT) and its degradation products, monobutyltin (MBT) and dibutyltin (DBT), in seawater, sediment and biosamples collected on the south coast of Korea have been determined. The butyltins, concentrated in the organic layer, were derivatized with PeMgBr ($\text{C}_5\text{H}_{11}\text{MgBr}$) and analyzed by GC/QFAAS (Gas Chromatography/Quartz Furnace Atomic Absorption Spectroscopy). Analysis of the samples collected in April, June and December 1994 confirmed the occurrence of butyltin compounds in the aquatic environments of two bays and one harbor in seawater and biosamples on the south coast of Korea. The TBT concentrations ranged from below detection limit to 22.5 ng Sn/L in seawater, and $\mu\text{g Sn/Kg}$. dry wt. level in sediment and biosamples. The highest concentration of TBT was found to be 56.6 $\mu\text{g Sn/Kg}$. dry wt. in the sediment near wharf facilities in Kwangyang Bay. TBT, the most toxic to aquatic life of the butyltin species, was found at concentrations sufficient to retard growth of sensitive aquatic organisms upon chronic exposure. Partitioning of TBT between seawater and sediment showed a high increase of $\text{TBT}_{\text{sed}}/\text{TBT}_{\text{sw}}$ in June compared to April and December.

INTRODUCTION

Organotin compounds are used for various industrial applications such as biocides, thermal stabilizers for PVC, and catalysts in the production of polyurethane foams. In biocides, triorganotin compounds (R_3Sn^+) having the highest biological activity are more common than nontoxic di- or mono-organotin compounds (Craig, 1986). Because of the acute toxicity of tributyltin, it is used as an antifouling additive in paints to prevent the attachment of barnacles and sea grasses to ships' hulls.

Tributyltin is slowly leached into the surrounding water and has toxic effects on the ecological system. For the past 20 years, increased use of butyltin compounds and their reported environmental problems have attracted the attention of environmental scientists. Because of the many investigations about the detrimental effects (Alzieu, 1986; Hall et al., 1988) of organotin compounds on nontarget aquatic lives, many countries including France (1982), the U.K. (1987) and Japan (1990) have already restricted the application of TBT-based antifouling paints for small ships of less than 25 m in order to protect the aquatic environment from organotin contamination. Several monitoring data sets show that concentrations of tributyltin in affected waters have significantly decreased since the regulations went into effect (Valkirs et al., 1991; Huggett et al., 1992). However, in spite of the ban on its use in many countries, TBT and its contaminating products can still be measured in sediment and biosamples from many coastal and estuarine environments (Page and Widdows, 1991). Moreover, other uses of organotins have resulted in a significant increase in their industrial production during the past decade (Blunden et al., 1984). Consequently, continuing research on the occurrence and fate of TBT in the aquatic environment is

needed in order to recognize potential sources and evaluate the effects of this contaminant.

In Korea, regulations concerning the use of TBT-based antifouling paints have yet to be established. Also, data for organotin compounds in the natural aquatic environment are scarce. Thus, there is a need to investigate the distribution and concentrations of organotin compounds, especially TBT, in aquatic environment and to assess the associated environmental risk. Restrictions on the use of TBT in Korea are needed to protect the aquatic environment. In this study, the occurrence of butyltin compounds in seawater, sediment and biosamples collected from two bays and one harbor on the south coast of Korea (Fig. 1) was investigated using a GC/QFAA system. In order to determine the fate of the butyltin compounds, the partition coefficient (K_d) between sediment and seawater, as well as the bioconcentration, were assessed. This paper reports the occurrence and the concentration of butyltin compounds present in seawater, sediment and biosamples in Korea's Kwangyang Bay, Chinhae Bay and Pusan Harbor.

MATERIALS AND METHODS

Chemicals

The standards BuSnCl_3 (MBT), Bu_2SnCl_2 (DBT), Bu_3SnCl (TBT), and tropolone were used as supplied by Aldrich Chemical Co. Other reagents were of analytical grade; water was deionized and doubly distilled. Butyltin standard solutions ($100\mu\text{g/mL}$) were prepared by dissolving 0.0119g, 0.0128g and 0.0137g of MBT, DBT and TBT, respectively, in 100 mL ethanol/water (96/4) solvent. The Grignard reagent, PeMgBr ($\text{C}_5\text{H}_{11}\text{MgBr}$), was prepared in the normal manner by the reaction of $\text{C}_5\text{H}_{11}\text{Br}$ and magnesium metal.

Equipment

The GC/QFAA system used was a Carlo Erba Fractovap

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