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Spatiotemporal distributions of butyltin compounds in various intertidal organisms along the Samcheok and Tongyeong coasts of Korea

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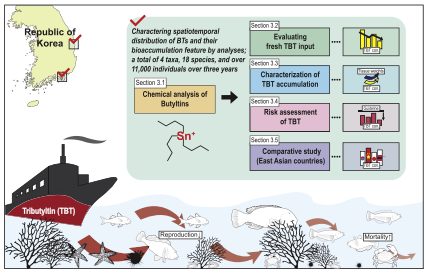
HIGHLIGHTS

- Butyltins (BTs) concentration differed in the two study areas and among species.
- Most intertidal organisms were less exposed to major concentrations of TBT.
- TBT accumulation was well correlated with the weight of the organisms.
- Fresh input of TBT was low in the study areas during the sampling period.
- Compared to other countries, concentrations of BTs were still greater in Korea.

GRAPHICAL ABSTRACT



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ABSTRACT

Thirteen years ago, the Korean Government introduced a regulation prohibiting the use of tributyltin (TBT), which was a component of antifouling paints. A subsequent decline in the concentration of butyltins (BTs) was recorded in seawater and the sediment, however, the current concentration of BTs in biota has not been well documented. The spatiotemporal distribution and concentration of BTs was recorded in biota from 2013 to 2015 along the coasts of Samcheok and Tongyeong using GS/MSD analysis. Crustaceans contained the greatest concentrations of BTs, followed by gastropods, fishes, and bivalves. We found that the concentration of BTs was greater at Tongyeong compared to Samcheok, because of the geographical characteristics of the area. We also confirmed that the regulation has been effective by showing that the TBT concentration decreased over the 3-year study period. The TBT levels of gastropods and bivalves fell within the limits of the guidelines and/or the effective concentration of the toxicological endpoint reported previously. The concentration of BTs also varied among species, being dependent on the weight of the soft tissue. Furthermore, the greater quantities of BTs degradation products compared to TBT confirmed the absence of recent inputs of pollutants during the study periods. However, compared with other Asian countries, biota BTs were greater in Korea, with noticeably greater concentrations along

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the south coast. Thus, further investigation of the distribution of BTs along the Korean coasts is required in the future. In conclusion, our results provide useful information about the recent trends of BTs in Korea.

1. Introduction

Butyltins (BTs) a component of hazardous chemicals that were first detected in the marine environment during the 1970s. Since the 1960s, these components have been widely used in pesticides and PVC preserved agents (Choi et al., 2009a). Tributyltin (TBT) is a type of butyltin that was mainly used in antifouling agents on fishing boats, vessels, and structures. Consequently, this chemical was released into the marine and fresh water environments, and negatively impacted the reproduction and development of marine organisms (Salazar and Salazar, 1991). For example, oyster exposed to TBT were subject to shell calcification (Waldock and Thain, 1983), while gastropods, such as *Reishia clavigera*, became infertile with females developing male organs (termed imposex) (Bryan and Gibbs, 1991). Because TBT is highly toxic, it also has major effects on the entire food chain, from phytoplankton to marine mammals (U'Ren, 1983; Bushong et al., 1988).

The accumulation of BTs depends on various factors. For instance, BTs negatively impacted the marine environment, with noticeably greater concentrations occurring along coastal areas near harbors and dockyards. BTs were also detected in semi-closed coastal areas where lower water circulation prevented the efficient flushing of this chemical. Affected areas included Ulsan, Masan, and Gohyun in Korea (Choi et al., 2009b). Biotic factors that impacted BTs accumulation included the size and age of organisms. Previous studies also reported significant correlations between biotic parameters and BTs accumulation (Choi et al., 2011, 2013a). Habitat type and the metabolism capability of biota also affect the extent to which BTs might accumulate (Lee, 1996; Jadhav et al., 2011).

Following confirmation of the harmful effects of BTs by many studies, the International Maritime Organization (IMO) adopted the ban in 2003. In Korea, the use of antifouling paints containing TBT was banned in March 2000 for small ships (<25 m), with the complete use of TBT being banned in November 2003 (Choi et al., 2010). However, most Asian countries have yet to implement such regulations.

Following the ban in the use of TBT in Korea, many studies have reported a decrease in BTs (Choi et al., 2013b; Kim et al., 2014). However, information about the recent trend in the distribution and concentration of BTs in Korea is lacking. Although several previous studies pointed out the species-specific accumulations of BTs in marine environment (Shim et al., 2005b; Jadhav et al., 2011), the bioaccumulation features of BTs cross varying taxa and/or within population have not been clearly examined until now. The present study analyzed a total of 4 taxa, 18 species, and over 11,000 individuals over three years, of which sufficient data provided a comprehensive understanding of bioaccumulation of BTs in coastal environment. The composition analysis and further calculations of BDIs provided the diagnosis on the recent input of TBT in the given areas. Thus, this study was designed to describe recent concentrations and occurrence of BTs in intertidal organisms to determine the effectiveness of regulations on TBT use in Korea. Then spatio-temporal trends and characterization of taxa containing BTs levels were analyzed. Comparison of our results with those of previous studies was expected to clarify the current status of BTs contamination in Korean coastal areas.

2. Materials and methods

This study aimed to determine the concentrations of BTs in various intertidal organisms, including gastropods (*Reishia clavigera*, Patellogastropoda sp., etc.), bivalves (*Mytilus galloprovincialis*, *Crassostrea gigas*), crustaceans (*Hemigrapsus sanguineus*, *Gaetice depressus*, etc.), fish (Gobiidae sp.), and ascidian (Pyuridae sp.). Of note, sedimentary BTs are out of scope in the present study.

2.1. Study area

Various intertidal organisms were collected from two coastal areas of Korea; namely, Samcheok (East coast) and Tongyeong (South coast) (Fig. 1). Sampling was conducted at three sites (S1–S3) in Samcheok from 2013 (November) to 2015 (December), and at three sites (T1–T3) in Tongyeong from 2013 (October) to 2015 (December). Samcheok is an exposed site located on the east coast of Korea (Fig. 1a). Despite the open sea enhancing its flushing efficiency with offshore waters, activities by military and coast guard ships affect this area. Military ships dock in the Sokcho and Uljin harbor near Samcheok (Lee et al., 2011). Thus, this area might be impacted by shipyard activity leading to the continuous accumulation of BTs. Tongyeong is located in the south coast of Korea, which represents the typical industrialized coastal region with semi-closed bay system. Accordingly, the bay experience relatively gentle seawater circulation with lack of flushing with offshore waters. Tongyeong Bay is one of the highly industrialized and urbanized areas in Korea, say numerous pollutants being released into the water and on the beach via various human activities such as neighboring industries and cities, shipyards, commercial fishing, and oyster farming etc. (Fig. 1b). Therefore, Tongyeong might be widely exposed to BTs pollution and other contaminants (Newton et al., 2014).

2.2. Sampling and sample preparation

Intertidal organisms, including gastropods (n = 7134), bivalves (n = 2881), crustaceans (n = 605), and fishes (n = 200), were collected form the intertidal zone at each sampling location over the 3 years (2013–2015). Details of the field study and species collected are shown in Tables S1 and S2 of the Supplementary Materials (S). The samples were immediately transported to the laboratory with dry ice. The shells of the bivalves, chitons, and gastropods were removed and whole somatic soft tissues were pooled and homogenized. The whole bodies of crabs and fishes were pooled and homogenized. Samples were stored at −20 °C and then freeze dried.

2.3. Analytical procedures

The analytical procedure was modified from that suggested by Shim et al. (1998) and Choi et al. (2009b). To analyze the samples, freeze dried samples (1 g) were extracted twice by mechanical shaking for 3 h with 20 mL of 0.1% tropolone-methylene chloride (Sigma Aldrich, Saint Louis, MO) and 10 mL of 6 N HCl (Sigma Aldrich) in 50 mL Teflon tubes. Diphenyltin dichloride was spiked in