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Organotins and new antifouling biocides in water and sediments from three Korean Special Management Sea Areas following ten years of tributyltin regulation: Contamination profiles and risk assessment

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ABSTRACT

A simultaneous monitoring study on organotins (butyltins and phenyltins) and most frequently used alternative antifouling biocides (Irgarol 1051, Diuron, Sea-Nine 211 and M1) in water and sediments (n = 44) collected from three Special Management Sea Areas operated by Korean government. The lower concentration of butyltins (BTs) than that of new antifouling biocides (NEW) was found in water but the significant greater concentration of BTs than that of NEW was still found in sediments. The tributyltin (TBT) levels in water exceeded the chronic criterion to protect seawater aquatic life at several sites. Even ten years after the ban of the use of TBT-based antifouling paint, the concentrations of TBT, Diuron and Irgarol 1051 in sediments from shipyards exceeded global sediment quality guidelines and potentially poses adverse risks on marine organisms and extremely high concentration of TBT up to 2304 ng/g was found for a sediment collected at a shipyard.

1. Introduction

Organotin compounds (OTs) have been used widely in antifouling paints to prevent adherence of sedentary organisms to ship hull and other structural surfaces immersed in seawater from the 1960s. High concentration of tributyltin (TBT), the most environmental concern OT, have detected in the areas with frequent shipping activities such as harbors, shipyards, fishing ports, and marinas (Harino et al., 2007; Garg et al., 2011; Cho et al., 2014). TBT can remain at high concentrations in sediment due to its persistence that was associated with the composition of the surrounding water and the benthic deposits. Half-life of TBT contamination in sediment near a commercial shipping area was reported to be up to 33 years (Langston et al., 2015). The release of OTs has caused deleterious effects on aquatic environment seen at concentrations as low as 1 ng/L (Alzieu, 2000). Particularly, imposex phenomenon in gastropods caused by the most toxic and environmental concern OTs of tributyltin (TBT) and triphenyltin (TPT) was well documented and approximately 150 species of gastropods had been reported to be affected by imposex worldwide as of 2004 (Horiguchi, 2009). In vitro studies suggest that TBT may cause immunotoxicity, teratotoxicity and neurotoxicity in mammals (Cooke, 2002; Tsunoda et al., 2006; Silva et al., 2014). OTs are also suspected to cause endocrine-disrupting effects in humans and rodents, partly as a result of the consumption of contaminated seafood (Keithly et al., 1999; Grote et al., 2004 and 2006; Graceli et al., 2013).

In response to the toxicity of OTs, the application of TBT-based antifouling paints to ships < 25 m in length was banned in the mid-1980s in many countries (Sonak et al., 2009). In Korea, the national restriction on the use of TBT-based antifouling paints was introduced in 2000 for small boats, and they were totally banned in 2003. Additionally, International Maritime Organization (IMO) has done the International Convention on the control of harmful anti-fouling system on ships (AFS 2001) in October 2001, and then introduced a ban on the application of organotin-based antifouling paints in ocean-going vessels from 2003. The use of OTs-based antifouling paints on any size of ships globally was banned from 2008 and forced to completely remove OTs-based antifouling paint on ship hulls until 2013 (Kim et al., 2014a). As of 2016, 73 states had accessed the AFS 2001 and the combined merchant fleets of these states constitute approximately 93.26% of the gross tonnage of the world's merchant fleet (IMO, 2016).

After the ban of OTs, a number of chemical compounds including herbicides and fungicides have been introduced as TBT alternatives and are currently used worldwide (Bellas, 2007). Investigations revealed that Diuron, Irgarol 1051, and Sea-Nine 211 were included in the most

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frequently used new antifouling biocides (NEW) in many countries (Readman, 2006). Although these NEW were used to prevent from the effects of TBT toxicity in environment, their toxins in environment have been reported.

Among these biocides, Irgarol 1051 is the most widely detected booster biocide worldwide (Sapozhnikova et al., 2013). Generally, NEW have less toxic than OTs; however Irgarol 1051 was reported to be more toxic than TBT in the growth of autotrophic species (Bao et al., 2011). Since mid-1990s, the high concentration of Irgarol 1051 as an alternative antifoulant has been globally reported in the harbors or marinas (Omae, 2006). Diuron is an herbicide that is commonly used in agriculture and in some antifouling paint formulations as an organic booster biocide (Sapozhnikova et al., 2013). Relatively long half-life in seawater of up to 2180 days for Diuron (Moncada, 2004) and up to 350 days for Irgarol 1051 (Omae, 2003) were reported. Irgarol 1051 and Diuron were suggested to be likely to cause damage to non-target organisms, especially phytoplankton, periphyton and corals (Readman, 2006). Since Irgarol 1051 and Diuron are photosynthesis-inhibiting herbicides, they are much more toxic to primary producer communities than aquatic animals (Hall and Anderson, 1999; Bao et al., 2011). Irgarol was generally more toxic than Diuron for eight native species of subtropical Hongkong including cyanobacteria, sea anemone, tubeworm, barnacle, amphipod, copepod and coral (Bao et al., 2011). Reported toxicity benchmark of Irgarol 1051 used for risk characterization was 136 ng/L (Hall and Anderson, 1999) and acute 96 h EC50s of Irgarol 1051 on cyanobacteria and marine diatom range from 0.29–7.71 μg/L (Zhang et al., 2008). Sea-Nine 211 is a rapidly degradable antifoulant in the environment by microorganisms. Its half-life in aerobic and anaerobic microcosm studies was < 1 h (Jacobson and Willingham, 2000). Although no bioaccumulation in fish were reported for Sea-Nine 211 (Jacobson and Willingham, 2000), the toxicity of Sea-Nine 211 to ecologically relevant species has been reported. The long-term exposure of 28 day LC_{50} of Sea-Nine 211 was determined to be 14 μg/L (Okamura et al., 2002). In addition, greater toxicity of Sea-Nine 211 than Diuron and Irgarol 1051 to juvenile rainbow trout was also reported (Okamura et al., 2002). Last but not least, M1 is a major metabolite of Irgarol 1051 under photodegradation and biodegradation processes and has long half-life as over 200 days in seawater and up to 260 days in sediments (Okamura et al., 2002; Zhou, 2008; Thomas and Brooks, 2010; Sapozhnikova et al., 2013). The available data for M1 toxicity is limited but M1 was reported might be less toxic than its parent compound, Irgarol 1051 (Zhang et al., 2008).

In the effort to reduce the widespread of these persistent and toxic alternative biocides, several countries have already banned the use of Diuron and Irgarol 1051 since the early 2000s (Lamoree et al., 2002; Gatidou et al., 2007; Sapozhnikova et al., 2008). In addition, Omae (2006) has suggested and explored an approach in using natural products antifouling substances, i.e., terpenes, nitrogen-containing compounds, phenols, steroids, and others that showed no or very low toxicity, and are biodegradable in marine environment to prevent aquatic environment from toxicity of OTs and NEW.

Due to the persistence of TBT and several alternative antifouling biocides, they are still detected over the world despite the international regulations. High concentration of TBT is found in coastal areas in many countries (Bigatti et al., 2009; Langston et al., 2015; Paz-Villarraga et al., 2015; Batista et al., 2016). High contamination levels of NEW have also been reported in both water and/or sediment from various coastal areas in England (Zhou, 2008), California marinas, USA (Sapozhnikova et al., 2013), Korea (Lee et al., 2011; Kim et al., 2015; Lee et al., 2015). In Korea, an extremely high concentration of TBT (55,264 ng/g) has recently been reported for a sediment sample from a large shipyard (Kim et al., 2015) and no significant change for TBT contamination levels was found for sediments from a bay utilized for fish boat harbors, small and large-scale shipyards, and naval bases, even 7 years after the total TBT ban on all oceangoing vessels in the country (Kim et al., 2014b). The investigation on alternative antifouling biocides in Korean coastal areas is still limited and it's needed to carry out more continued monitoring for Diuron in Korean coastal water since its concentration was greatly exceeded worldwide guideline values (Kim et al., 2014a). In addition, higher level of toxicity of the mixture of OTs and/or NEW than the individual compounds in marine phytoplankton and algal communities caused by was reported (Arrhenius et al., 2006; Delorenzo and Serrano, 2006). Following these reasons, it is concluded that simultaneous monitoring study on OTs and NEW in Korean is necessary. The main purpose of this study was to investigate concentration and spatial distribution of organotin (butyltins and phenyltins) and alternative antifouling biocides (Irgarol 1051, Diuron, Sea-Nine 211 and M1) in seawater and sediment from the three Special Management Sea Areas operated by Korean government including Gwangyang, Busan and Ulsan Bay areas where have high-density shipping activities and be surrounded by various industrial facilities, shipyards, commercial and fishery ports. The contamination levels of TBT and alternative biocides in seawater and sediments were compared with water quality and sediment quality standards and quality guidelines to evaluate the probable toxic effects on aquatic organisms.

2. Materials and methods

2.1. Chemical and reagents

HPLC grade water, acetonitrile, methanol, ethanol were obtained from J.T. Baker (Center Valley, PA, USA). Other chemicals and reagents were obtained from several companies: tropolone, benzene, ethyl acetate, supelclean ENVI-Carb SPE tube (250 mg, 3 mL), florisil (60–100 mesh), anhydrous sodium from Sigma-Aldrich (Bellefonte, PA, USA), silica gel 60 mesh from Merk (Darmstadt, Germany), propylmagnesium bromide from Tokyo Chemical Industry Co. (Kita-ku, Tokyo, Japan), hydrobromic acid from Wako Pure Chemical Industry Inc. (Japan), n-hexane from Kanto Chemical Co., Inc. (Japan) and hydrochloric acid from Junsei Chemical (Chuo-ku, Tokyo, Japan). The organometallic butyltin and phenyltin chloride standards of OMT-001 including monobutyltin (MBT) trichloride, dibutyltin (DBT) dichloride, tributyltin (TBT) chloride and OMT-002 including monophenyltin (MPT) trichloride, diphenyltin (DPT) dichloride, triphenyltin (TPT) chloride were obtained from AccuStandard (New Haven, CT, USA). The surrogate material of tripentyltin chloride and internal standard of tetrapentyltin was also obtained from AccuStandard (New Haven, CT, USA). Diuron, Sea-Nine 211 and M1 were purchased from Sigma-Aldrich and Irgarol 1051 was purchased from AccuStandard. The internal material of Atrazine-$^{13}C_3$ for NEW was purchased from Cambridge Isotope Laboratories, Inc. (Andover, MA, USA).

2.2. Sample collection

Forty-four samples of water and corresponding sediments were collected during August 2014–April 2015. Details with regard to the sampling location and the types of environmental samples collected are shown in Fig. 1 and Table 1. A total of forty four sampling sites in this study is located in Gwangyang, Busan and Ulsan Bays where are designated as Special Management Sea-Areas in the Korean Marine Environment Control Act Section 5 and Section 8, paragraph 1 due to the arising of pollution concerns from the development of surrounding industrial facilities and commercials activities from the past decades. These areas are mainly utilized for commercial and fishery ports, small and large scale shipyards, and leisure ship and coast guard harbors. In details, the areas of investigating regions in this study located in the southern and southeastern part of Korea peninsula are approximately 70 km^2 for Ulsan Bay, 60 km^2 for Busan Bay, and 250 km^2 for Gwangyang Bay. The Busan Bay area, which is the largest commercial port areas which are accounted for 34% of marine export cargo and 75% of containerized cargo of Korea, has low water exchange and be