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Butyltin accumulation in marine bivalves under field conditions in Taiwan

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ABSTRACT

This study aimed to characterize the butyltin bioaccumulation in a simple food chain under varied conditions. Significant trophic level magnification factors of tributyltin (21.5–1546) were observed in two filter-feeders, oysters (*Crassostrea gigas*) and mussels (*Perna viridis*), in an environment with low tributyltin pollution levels (0.4–13.1 ng L^{-1} as tin). Both of these bivalve species showed higher bioaccumulation factors (BAFs) of tributyltin under low pollution levels, while smaller magnification factors (5.4–6.4), an up-regulated tributyltin metabolism and smaller BAFs of tributyltin were found in oysters at higher tributyltin pollution levels (39.6–99.3 ng L^{-1} as tin). Unlike oysters, mussels cannot up-regulate their tributyltin metabolism, which caused a dramatic change in butyltin accumulation between oysters and mussels as tributyltin pollution levels increased. In addition, higher BAF values of tributyltin were also obtained under the water summer conditions when higher temperatures and phytoplankton contents, and lower tributyltin pollution levels were observed.

1. Introduction

Organotin compounds are used extensively in the manufacturing and agricultural industries as stabilizers for PVC, fungicides, pesticides, and biocide additives in antifouling paints. Tri-organotins, such as tributyltin (TBT), directly and continuously enter watersheds through runoff from sources such as antifouling paints on ships and channel facilities, which often causes significant quantities of organotins to collect in the ambient environment (Hoch, 2001). Tributyltin has been shown to cause deleterious effects in a variety of non-target organisms, even at extremely low concentrations. These effects can include the generally known reproductive impairment of imposex-affected in dogwhelk and other gastropod species (Omae, 2003), which have also been confirmed by an investigation into the mechanism of induction in recent studies (Nishikawa et al., 2004; Shi et al., 2005). In addition, decreased fishery resources due to TBT-induced effects of shell thickening and reduced growth in oysters have been observed (Alzieu, 1991), as well as an increased mortality rate of larval fish (Fent and Meier, 1992). These studies indicated that butyltins are extensively distribution butyltins in marine organisms at high trophic levels such as marine mammals, birds and tuna, and that the accumulated load of butyltins in these animals are at or above the threshold levels for adverse effects (Kannan and Tanabe, 2009; Murata et al., 2008; Ueno et al., 2004). Considerable potential threats to human health resulting from exposure to TBT via seafood ingestion have also been proposed (Chien et al., 2002).

Legislation restricting the use of TBT on ships worldwide was first introduced in developed nations during the 1980s. The effects of this legislation were reflected in the decreased TBT concentrations in the water sources. However, considerable TBT levels are still present in some coastal areas decades after TBT regulations were initiated. In these cases, TBT pollution may be derived from the slow degrading butyltins in sediments (Diez et al., 2002). Today, TBT pollution is still a serious problem in some marine environments around the word, especially in places where the use of TBT is unregulated, such as in developing Asian countries (Sudaryanto et al., 2002). The International Maritime Organisation has continually promoted restricting the use of paints containing TBT on ships, and has imposed further regulations in many countries.

Filter-feeders such as mussels and oysters usually show high TBT accumulation, since their efficient pump activity readily transfers TBT into their tissues (Laughlin et al., 1986), and because the low efficiency of metabolic system causes TBT to be degraded slowly (Lee, 1991). Programs for monitoring TBT pollution, such as International Mussel Watch, have considered these characteristics, as well as other advantages unique to mussels and oysters, such as their resistance to stress, wide geographical distribution, and

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sessility, in order to provide baseline data on TBT contaminants and to compare contaminant levels between different marine environments worldwide (Sudaryanto et al., 2002). The bioaccumulation factor (BAF) for TBT shows a high degree of variation ranging from 16 000 to 4 025 000 and from 52 000 to 1 456 000 (dry wt. basis) in oysters and mussels, respectively (Suzuki et al., 1998; Shim et al., 1998, 2005a). The differences in TBT bioaccumulation can be caused by the effects of environmental factors in which it influence the accumulation process in organisms. The accumulation processes involved include uptake, distribution, metabolism, elimination and accumulation (Gomez-Ariza et al., 1999). For example, several water condition factors (e.g., pH value and salinity) are known to alter the bioavailability of TBT (Fent and Looser, 1995; Arnold et al., 1997). The inhibition of the metabolic system caused by TBT may lead to changes in the bioaccumulation of butyltin (Morcillo and Porte, 1998). Thus, more studies of TBT accumulation using oysters and mussels as bioindicators are needed to understand the process of bioaccumulation butyltin and to determine appropriate pollution control strategies.

In the present study, our goal was to characterize butyltin accumulation in a simple food chain under different ambient conditions. We conducted a field survey measuring the butyltin content in water, suspended particles, green mussels (*Perna viridis*) and Pacific oysters (*Crassostrea gigas*) at different TBT pollution levels. Further, we examined the probability of trophic level magnification of TBT in these two filter-feeders (green mussels and Pacific oysters), which represent the lowest order of consumers available in the study area and also the shortest path by which waterborne TBT can be transferred to humans.

2. Materials and methods

2.1. Reagents and chemicals

Analytical reagent grade hydrochloric acid (37%), acetic acid (99.7%), phosphoric acid (86.7%), nitric acid (69.0–70.0%), and potassium hydroxide (>86.0%) were obtained from J.T. Baker (Phillipsburg, NJ, USA). Analytical reagent grade hydrobromic acid (48%) was obtained from Lancaster Synthesis (Morecambe, England). Isooctane (analytical reagent grade) was purchased from R.D.H. (Seelze, Germany). Ethylmagnesium bromide (39% w/v solution in ethyl ether) was supplied by T.C.I. (Tokyo, Japan). Sodium tetraethylborate ($NaBEt_4$, >98%) was manufactured by Strem Chemical (Bischheim, France). Dibutyltin dichloride (97%) and monobutyltin trichloride (95%) were purchased from Aldrich (Milwaukee, WI, USA). Tripropyltin chloride (98%), tributyltin chloride (98%), hexane, acetone and methanol (analytical reagent grade) were purchased from Merck (Darmstadt, Germany). Pure chlorophyll *a* (>96%) was supplied by Sigma (St. Louis, MO, USA). Ethylated organotin standards were prepared in hexane by direct Grignard ethylation of the corresponding organotin chlorides, according to the method described earlier (Nagase et al., 1995). Reagent water was obtained with a Millipore Milli-Q ultra-purification system (Bedford, MA, USA).

2.2. Sampling

The location of the study area and the distribution of sampling stations are shown in Fig. 1. Eight sampling stations were set up along a suspected butyltin pollution gradient, from a fishing port to the upstream area of the Luermen Stream estuary in southwestern Taiwan. The fishing port is located on the southern bank of the mouth of Luermen Stream (23°, 01′ N, 120°, 06′ E) and serves a local fishery. Samples of water, suspended particles, green mussels and Pacific oysters were collected at each station during the summer (July 2003) and winter (February 2004). Wild oysters and mussels were sampled from hard substrate on the ebb tide. Water samples were collected during flood and ebb tide periods and were filtered through a 1.0-μm glass fiber filter (Whatman GF/B, 55 mm Ø). The water samples were acidified with 1.5 mL of nitric acid per litre of sample and stored in dark glass bottles at 4 °C prior to analysis. The glass fiber filter that collected suspended particles was stored on ice in the short term and submitted for chlorophyll *a* analysis immediately thereafter. In addition, each water sample (5–8 L) was filtered through the pre-weighed 1.0-μm glass fiber filter (Whatman GF/B, 125 mm Ø) which collected the suspended particles for organotin analysis. The residual salinity in the filter was washed by reagent water (100 mL × 3), and the filter was stored in the dark at −20 °C prior to analysis. At the time of water sampling, the salinity, pH value and temperature of each sampling station were also measured *in situ*.

2.3. Organotin analysis

Analyses of butyltins in individual bivalve samples were performed following a procedure published elsewhere (Tang and

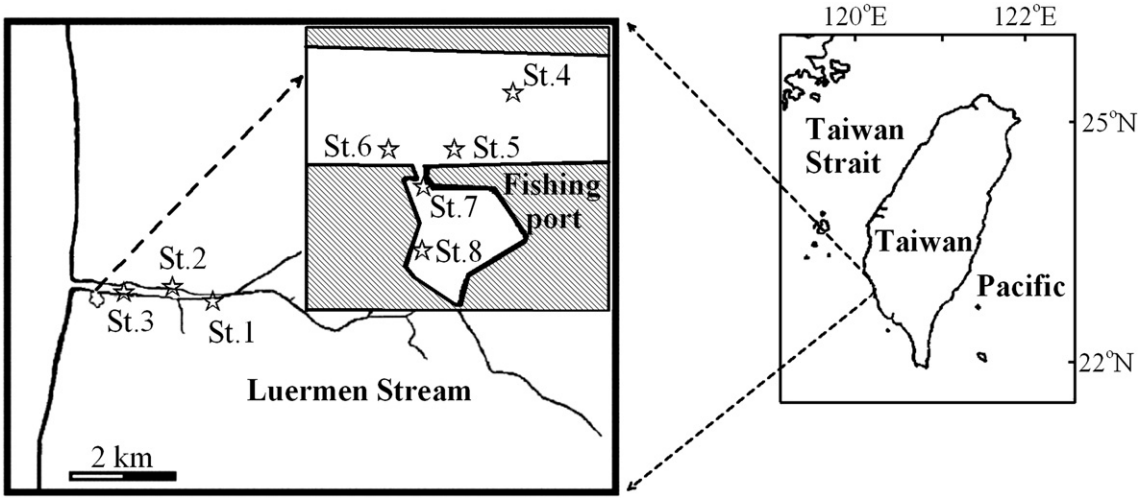

Fig. 1. Map of the Luermen Stream showing the locations of the sampling stations.