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Organotins (TBT and DBT) in water, sediments, and gastropods of the southern Venice lagoon (Italy)

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Abstract

The release of tributyltin (TBT) from maritime traffic represents one of the main problems of direct, diffuse, and continued contamination of the marine environment.

In the present survey, the concentrations of TBT and dibultytin (DBT) in brackish waters, sediments, and the gastropods *Nassarius nitidus* were evaluated in order to estimate the contamination of the southern part of the Venice lagoon.

TBT and DBT were determined by GC–MS/MS. Recent contamination of TBT was found in brackish waters near marinas, whereas the highest concentrations of TBT and DBT were observed in surface sediments at dockyards and harbours. High content of organotin in the gastropods sampled near the dockyards, harbours, and marinas showed a mobilisation from the sediments through the food web.

The present study allowed assessment of whether, despite the ban on the use of TBT paints, waters, sediments, and biota were still being contaminated by organotin compounds in the southern Venice lagoon.

Keywords: TBT; DBT; Organotin; Antifouling paints; Venice lagoon

1. Introduction

Butyltins, including tributyltin (TBT), are widely used as biocides in antifouling paints. Evidence of the damaging effect of organotin compounds (BTs) on the reproduction and growth of various marine organisms has prompted action by many countries to regulate or ban their use in antifouling products. The widespread use of BTs as stabilizers in the manufacture of polyvinylchloride (Blunden et al., 1984), as a biocide in agriculture (Champ and Seligman, 1996), as a fungicidal in wood preserve (Bennett, 1996), and as a biocide in antifouling paints for vessels (Hoch, 2001; Yebra et al., 2004) and for cooling pipes of thermoelectric power (Bacci and Gacci, 1989; Bressa et al., 1999) has provided several points of entry for these compounds into aquatic and terrestrial environments.

TBT gained widespread application as an effective antifouling paint biocide on pleasure boats, large ships, and docks in the 1970s and 1980s (Fent, 1996).

At present, the use of antifouling paints containing TBT is restricted in many countries. In October 2001, MEPC/IMO adopted a new International Convention on the Control of Harmful Antifouling Systems on Ships which will prohibit the use of harmful organotins in antifouling paints used on ships, and will establish a mechanism to prevent the potential future use of other harmful substances in antifouling systems. The resolution called for a global prohibition on the application of BTs, which act as biocides in antifouling systems on ships, by January 2003, and a complete prohibition by January 2008 (Reg. EC 782/2003).

Despite such restrictions, TBT persists in many areas at levels considered to be chronically toxic to the most

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susceptible organisms (Stäb et al., 1995). The release of BTs into terrestrial and aquatic environments has decreased, but inputs still occur, and previously contaminated sites continue to act as sources (Ritsema, 1994; Stäb et al., 1995). The BTs compounds have been routinely found in both estuarine and marine waters, sediments, and biota (Tas et al., 1996).

TBT is characterised by high toxicity, environmental mobility, and a tendency to accumulate in living systems (Fent, 1996). Chronic toxic effects on oysters (shell deformation; Alzieu, 1998, 2000), and in neogastropods and mesogastropods (imposex; e.g., Ellis and Pattisina, 1990; Gibbs et al., 1991; Stewart et al., 1992; Horiguchi et al., 1994) occur at aqueous concentrations of a few ng L^{-1}, and most susceptible marine algae and zooplankton species are negatively affected at a few hundred ng L^{-1} (Huang et al., 1996). It is widely recognised that TBT, as an endocrine disruptor, compromises reproductive capacity and sexual development, increasing incidence of masculinisation, in numerous fish species (Meador, 1997; McAllister and Kime, 2003; Shimasaki et al., 2003). The phenomenon of imposex, a superimposition of male sexual organs (penis and vas deferens) on female gastropods, is reported to occur in more than 150 species belonging to 63 genera of prosobranch gastropods (Schulte-Oehlmann et al., 2000), and is positively correlated to TBT concentrations (Gibbs et al., 1987). Despite the high concentrations of toxic BTs found in aquatic invertebrates, little is known about the accumulation and toxic effects of BTs in higher trophic vertebrate predators, which may be exposed to these pollutants via food ingestion (Hoch, 2001). In general, coastal species exhibit higher butyltins accumulations than their relatives from off-shore areas (Hoch, 2001). Despite this, Borghi and Porte (2002) showed that organotin pollution in the NW Mediterranean is not limited to circumscribed coastal areas, but rather reaches the deep-sea environment and inhabiting organisms (1000–1800 m depth).

At present, scarce information on organotin contamination in Italian waters, sediments, and biota, collected simultaneously, is available; most studies report data on organotin compounds in a selected environmental matrix: seawater (Bacci and Gacci, 1989; Caricchia et al., 1993; Terlizzi et al., 1998), sediments (Cicero et al., 2004; Chiavarini et al., 2003), or gastropods (Terlizzi et al., 1998). Contamination of BTs compounds in the lagoon of Venice was reported by a few papers, focusing either on sediments (Bortoli et al., 2003) or molluscs (Binato et al., 1998; Boscolo et al., 2004; Pellizzato et al., 2004).

The Venice lagoon is subject to intense ship traffic due to the presence of the harbours of Venice (2.32×10^6 t yr^{-1}) and of the port of Chioggia (1.0×10^6 t yr^{-1}). Small ferries, a fleet of 800 fishing boats (APAT, 2005), and the presence of many marinas, dockyards and shipyards contributed to the increase in maritime traffic, mainly in the central and southern part of the lagoon, during the last decades. In recent years, relevant dredging activities were carried out in order to create a new commercial harbour in Chioggia, and to construct the "MOSE" barriers against the flooding at Chioggia inlet (1.4×10^6 m^3 of estimated dredging materials).

The present paper aims to evaluate the TBT and dibultytin (DBT) contamination in the brackish waters, sediments, and gastropods – *Nassarius nitidus* – in the southern part of the Venice lagoon, subjected in the last decades to an increase in dockyards, shipping, and fishing activities.

2. Materials and methods

2.1. Study area and sampling

The Venice lagoon is a transitional coastal environment covering a surface area of 549 km^2, and it is characterised by low average water depth (≈1 m) and tidal range (<1 m). The lagoon is connected to the sea through three inlets (Lido, Malamocco and Chioggia), and water exchange with the Adriatic Sea is controlled by tidal fluxes.

Waters, sediments and gastropods (*N. nitidus*) were collected in late spring–summer 2003 in the southern part of the Venice lagoon, near the town of Chioggia (53,470 inhabitants). The sampling stations were defined as dockyards, harbours, marinas, centre town, and lagoon channels on the basis of their location and the activities undertaken therein (Fig. 1). Water samples were collected using Niskin water samplers (5 L capacity) at a depth of approximately 1 m in navigable areas with a minimum bottom depth of 1.5–2 m. The samples were filtered with GF/F filters, and acidified to pH 2 with concentrated ultrapure HCl.

Bottom sediments were sampled by an Ekman grab in 25 stations. The upper 2 cm were recovered and placed in acid-cleaned glass containers, then homogenised in mortar porcelain, sieved on a 200 μm mesh nylon screen, and stored at −20 °C.

A pool of 25 specimens of dogwhelk (*N. nitidus*), scavenger gastropods feeding on dead or decaying animals, were caught by wire basket in 18 of the sediment sampling sites. The shell length and the maximum diameter were measured.

The mean length of the collected specimens was 25.5 ± 1.8 mm, and the mean width was 12.0 ± 0.7 mm. All the specimens were sexually mature and were therefore presumably at least 4 years old, according to Tallmark (1980). The soft tissues of the molluscs were excised with stainless-steel scalpel blades, thoroughly rinsed with MilliQ water to remove extraneous impurities, and homogenised using a blender (Ultraturrax). The homogenised samples were stored at −20 °C. All samples were lyophilised for 72 h before analysis.

2.2. Reagents and standards

Dibutyltin chloride, tributyltin chloride, and tetrabutyltin chloride (96%, 97%, and 96% purity, respectively) were