



Behaviour of butyltin compounds in the sediment pore waters of a contaminated marina (Port Camargue, South of France)



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H I G H L I G H T S

- Study of OTs distribution in pore waters of sediments by peeper samplers.
- TBT released into pore water.
- Released attributed to the mineralization of the sedimentary organic matter.
- Possible stabilization of TBT into pore water by complexation with sulphides.
- Lower debutylation rates in anoxic than in oxic conditions.

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Despite the ban on tributyltin (TBT) in marine paints, harbour sediments are still highly contaminated by this antifouling agent. Concentrations of TBT and its dealkylated products dibutyltin (DBT) and monobutyltin (MBT) were determined in the pore waters of Port Camargue, a large marina located on the French Mediterranean coast. Pore waters were sampled in the field using peepers deployed in summer 2012 and 2013 and in winter 2012–2013. The winter surveys were characterized by the presence of sulphides in pore waters from a depth of 5 cm, which was not the case in winter. In summer 2013, TBT was shown to be released into pore waters below the sediment–water interface (SWI) at concentrations of up to 70 ngSn L⁻¹. This release was also observed in sediment anaerobic incubations and was attributed to the mineralization of the sedimentary organic matter, possible stabilization of TBT by complexation with sulphides, and lower debutylation rates in anoxic than in oxic conditions. In summer 2012, a comparatively lower concentration of TBT (around 20 ngSn L⁻¹ below the SWI) was measured and the presence of methyltin species was detected. We hypothesize that the differences between the two surveys reflect different microbial activity. In winter 2012–2013, marked by Fe-reducing conditions in the sediments, TBT was released into solution at the SWI at concentrations of up to 40 ngSn L⁻¹. Sediments are thus a continuing source of TBT for the overlying waters despite the ban on its use for boats in France.

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1. Introduction

Between the 1960s and the 2000s large quantities of organotin (OTs) were released into seawater due to the intensive use of TBT (tributyltin) as a biocide in antifouling paints for boats. In the 1980s, a concentration of less than 2 ng L⁻¹ of TBT was shown to cause

deformities and to affect the reproduction (imposex) of oysters (Alzieu et al., 1986). This led to restrictions on the use of TBT in France and in several industrialized countries and finally to a ban on its use in antifouling paints in 2008 (International Maritime Organization, 2001). Despite the ban, today TBT and its degradation compounds MBT (monobutyltin) and DBT (dibutyltin) are still present in sediments (Díez et al., 2002; Kim et al., 2011; Briant et al., 2013) in water (Berto et al., 2007; Garg et al., 2011) and in marine organisms (Belfroid et al., 2000; de Mora et al., 2003; Antizar-Ladislao, 2008).

TBT associates strongly with natural sorbents (Maguire, 1987)

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and accumulates in sediments. Understanding the processes that control the fate of TBT in sediments is crucial to assessing the long-term impacts of past pollution on marine and coastal waters. To date, these processes have mainly been studied in laboratory experiments, which showed that TBT was more adsorbed by organic phases than by mineral phases such as aluminosilicates, Fe oxides and clay (Randall and Weber, 1986; Weidenhaupt et al., 1997; Arnold et al., 1998; Berg et al., 2001; Hoch and Schwesig, 2004). The experiments also revealed the impact of salinity, pH and organic carbon concentration on the sorption of TBT (Burton et al., 2006; Bangkedphol et al., 2009). Maximum TBT sorption was observed at pH 8. In seawater, sorption coefficients decreased with increasing salinity and varied by a factor of 2 over a range of salinity from 0 to 34‰ (Unger et al., 1988). TBT sorption on sediment has been shown to increase with the contact time between the TBT in solution and the sediments (aging effect) (Burton et al., 2006).

In the aquatic environment, TBT is degraded through dealkylation and forms DBT, MBT and finally Sn^{4+} . In the water column, the half-life of TBT is a few days to several months (Cruz et al., 2015). In sediments, TBT has a much longer half-life ranging from one to several years (Stewart and De Mora, 1990). TBT degradation is slower in anaerobic than in aerobic conditions (Dowson et al., 1996) and also when the concentrations of TBT are high (Hoch, 2001).

Methylation of TBT can also take place in estuarine and coastal sediments (Amouroux et al., 2000; Vella and Adami, 2001). Using anaerobic incubation of sediment spiked with TBT (Yonezawa et al., 1994) showed that both dealkylation and methylation in sediments were mediated by different microbial communities: nitrate-reducing and sulphate-reducing bacteria, respectively.

Only a few studies have examined the mobility and transformation of OTs in sediment pore waters and their exchanges at the sediment–water interface (SWI). In those studies, different techniques were used to sample pore waters and contradictory results were obtained. Using dialysis tubes filled with hexane to collect pore waters, Stuer-Lauridsen and Dahl (1995) only detected DBT in the pore waters of a TBT-polluted sediment. Using sediment centrifugation to collect pore waters, Berg et al. (2001) demonstrated that the diffusion of OTs from deeper sediments to the surface was rather slow, and that major release of OTs from undisturbed sediments was unlikely, whereas using the same technique, Burton et al. (2005) concluded that TBT, DBT and MBT could be released into the water column through diffusion in pore waters. Using a sediment nitrogen-pressurized squeezer to sample pore waters, Viglino et al. (2004) showed that diffusion of TBT from pore waters to the water column was slow and that TBT was efficiently buried and preserved in the sediments of the Saguenay fjord. More recently, butyl- and phenyltin degradation processes in sediments and pore waters were studied using species-specific, isotopically enriched tin tracers (Furdek et al. (2016)). Results from sediment and pore water separate incubations for three days highlighted that a limiting step in OTs degradation in marine sediments is their desorption into pore waters. In oxic pore waters, TBT degradation occurs notably fast (half-life 9.2 days). For DBT, half-lives of 2.9 ± 0.1 and 9.1 ± 0.9 days were obtained in oxic and anoxic pore waters, respectively.

Point et al. (2007) using a benthic chamber, emphasized the importance of microalga activity on the benthic flux of TBT in a Mediterranean lagoon.

The aim of the present study was to investigate the mobility of TBT and its degradation products MBT and DBT in the sediments of a Mediterranean harbour, Port Camargue marina, where serious TBT contamination has been reported (Briant et al., 2013).

Peeper samplers deployed in the sediment were used to collect pore waters. To the best of our knowledge, this is the first time

peeper samplers have been used to study OT distribution in pore waters, although they have already been used for the assessment of concentrations of trace elements in pore waters (Hesslin, 1976; Teasdale, 1995; Mason et al., 1998; Elbaz-Poulichet et al., 2005; Briant et al., 2016).

Butyltin (TBT, DBT and MBT) concentrations in pore waters were determined by solid-phase microextraction (SPME) as a pre-concentration technique before analysis of the OT species to compensate for the small volume of pore water recovered in the peeper samplers. The high SPME pre-concentration combined with GC-ICP-MS allows very low limits of detection (pgSn L^{-1}) to be reached (Aguerre et al., 2001). To better characterize the chemistry of the pore waters, concentrations of dissolved organic carbon (DOC) were also determined.

In parallel to field studies, experiments involving the incubation of harbour sediments in anaerobic conditions were performed in the laboratory.

2. Material and method

2.1. Study area

Port Camargue (South of France, Fig. 1) has a capacity of 5000 moorings and is among the biggest marinas in Europe. The marina was built between 1960 and 1985. The characteristics and the pollution of the <63 μm fraction of the sediment core are detailed in Briant et al. (2013). That study revealed high metal and OT pollution near the boat maintenance area, with maximum concentrations of butyltins ($45,861 \text{ ngSn g}^{-1}$ for ΣBT and $21,769 \text{ ngSn g}^{-1}$ for TBT) observed at a depth of 23 cm in the sediments. The authors concluded that the distribution of total butyltins (ΣBT) and TBT in the sediment column reflected the history of TBT use in the harbour.

2.2. Sampling

Three surveys corresponding to different redox conditions in the sediments were conducted in summer 2012 (September 9 to October 8), winter 2012–2013 (January 10 to February 12) and summer 2013 (September 18 to October 16). In summer, salinity was 35 and water temperatures ranged from 19 to 21 °C. In winter, salinity decreased to around 30 and the water temperature was around 10 °C. Samples of pore waters were collected at site 19, located in the boat carenage zone (Fig. 1) where TBT concentrations of up to $10,000 \text{ ngSn g}^{-1}$ in the sediments have been recorded (Briant et al., 2013). Dialysis peeper samplers (Hesslin, 1976), 65 cm in height and 18 cm in width with 1.8 cm-thick methacrylate casing, were used. The device consisted of two columns of 50 horizontal cells (4.6 mL) with a 1 cm vertical resolution.

Prior to sampling, the peepers were acid-cleaned with HCl (Merck Suprapur) and then rinsed with Milli-Q water. The dialysis cells were filled with Milli-Q water and covered with a 0.22 μm Millipore filtration membrane. The peepers were prepared inside a Class 100, laminar airflow clean bench cabinet in a clean room. They were stored in Milli-Q water and degassed with N_2 for a period of two weeks before sampling.

In the field, peepers were placed in pairs within the sediment by divers. The peepers were not completely immersed in the sediment. The position of the SWI in the peepers was determined visually by the change in colour of the peepers. The precision of the determination of the position of the SWI was ± 1 cm. One peeper was reserved for organotin analysis (this study) and metals (Briant et al., 2016). The second peeper was used for DOC (this study) and sulphide analyses (Briant et al., 2016). Exposure duration was four weeks, one week more than the minimum duration necessary to

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