



Organotin persistence in contaminated marine sediments and porewaters: *In situ* degradation study using species-specific stable isotopic tracers



Martina Furdek^a, Nevenka Mikac^a, Maite Bueno^b, Emmanuel Tessier^b, Joana Cavalheiro^b, Mathilde Monperrus^{b,*}

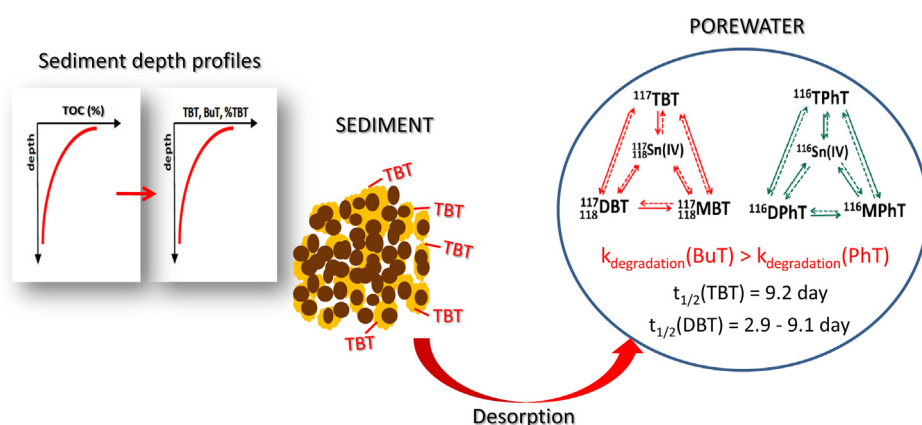
^a Division for Marine and Environmental Research, Rudjer Boskovic Institute, Bijenicka 54, Zagreb, Croatia

^b Laboratoire de Chimie Analytique Bio-inorganique et Environnement, Institut Pluridisciplinaire de Recherche sur l'Environnement et les Matériaux, CNRS UMR 5254, Université de Pau et des Pays de l'Adour, Hélio parc Pau Pyrénées, 2, Av. P. Angot, 64053 Pau Cedex 9, France

HIGHLIGHTS

- Limiting step in OTC degradation in sediments is their desorption into porewater.
- TBT persistence in contaminated sediments increases in sediments rich in organic matter.
- DBT does not accumulate in sediments as degradation product of TBT.
- TBT and DBT degradation in porewaters occurs with half-lives from 2.9 to 9.2 days.
- PhTs degradation is slower than BuTs degradation in oxic porewaters.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 5 September 2015
Received in revised form 1 December 2015
Accepted 20 December 2015
Available online 28 December 2015

Keywords:

Organotin compounds
Tributyltin
Degradation kinetics
Isotopically enriched tracers
Sediments
Organic matter

ABSTRACT

This paper provides a comprehensive study of the persistence of butyltins and phenyltins in contaminated marine sediments and presents the first data on their degradation potentials in porewaters. The study's aim was to explain the different degradation efficiencies of organotin compounds (OTC) in contaminated sediments. The transformation processes of OTC in sediments and porewaters were investigated in a field experiment using species-specific, isotopically enriched organotin tracers. Sediment characteristics (organic carbon content and grain size) were determined to elucidate their influence on the degradation processes. The results of this study strongly suggest that a limiting step in OTC degradation in marine sediments is their desorption into porewaters because their degradation in porewaters occurs notably fast with half-lives of 9.2 days for tributyltin (TBT) in oxic porewaters and 2.9 ± 0.1 and 9.1 ± 0.9 days for dibutyltin (DBT)

* Corresponding author.

E-mail address: mathilde.monperrus@univ-pau.fr (M. Monperrus).

in oxic and anoxic porewaters, respectively. By controlling the desorption process, organic matter influences the TBT degradation efficiency and consequently defines its persistence in contaminated sediments, which thus increases in sediments rich in organic matter.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Tributyltin (TBT), and triphenyltin (TPhT), have found application as biocides in antifouling paints and have therefore been directly introduced into the marine environment. As TPhT is also used as pesticide in agriculture, land run off could additionally contribute to its introduction to the coastal waters. Both compounds, acting as endocrine disruptors, provoke toxic effects to various non-target marine organisms, the most adverse toxic effect being occurrence of imposex in gastropods even at very low concentrations in seawater (1–2 ng/l) [1,2]. Nowadays, TBT is declared as one of the most toxic anthropogenic pollutants in the marine environment [1]. Consequently, the use of TBT-based paints has been banned in many countries worldwide, including all of Europe, and they have been banned in Croatia since 2006. However, an overview of the existing data in recently published papers demonstrates that the marine environment is still polluted with TBT, especially in countries where the usage of TBT-based paints is not yet regulated [3]. Preliminary data on butyltin (BuTs) contamination along the Croatian Adriatic coast also showed widespread pollution with TBT and suggested that those paints are still in use despite their ban [4].

Once introduced into the water column, TBT and TPhT are subjected to biotic (degradation governed by microbial activity) and abiotic degradation with half-lives of several days to weeks [1,2,5,6]. Abiotic degradation includes photodegradation (*i.e.*, degradation by UV irradiation), thermal and chemical degradation. Among all abiotic degradation mechanisms, photolysis has the most important role in BuTs and PhTs degradation in environmental compartments where light is available (water column and the thin surface sediment layer in shallow waters) [7,8]. Both TBT and PhT are stable up to 200 °C [9], and thus are not prone to thermal degradation under environmental conditions, while little is known about chemical degradation of OTC in natural environment, especially aquatic sediments. Because TBT and TPhT have both a high affinity for adsorption onto particulate matter ($\log K_d > 3.5$ [10,11]), they accumulate in sediments where their degradation occurs at considerably slower rates, with half-lives of several years to decades [1,2,12,13]. Due to the persistence of BuTs and PhTs in sediments and their possible desorption back into the water column [10,14,15], contaminated sediments represent a long-term source of pollution. Therefore, TBT and TPhT degradation in sediments can be considered to control the overall persistence of BuTs and PhTs in the marine environment. Since their degradation products (di- and mono-butyl and phenyl derivatives) are far less toxic than initial trisubstituted compounds [16], degradation can be considered as a form of sediment remediation.

During the past decades, numerous papers regarding TBT degradation in the marine environment have been published. Most of them have been macrocosm [17,18] or microcosm [19,20] experiments or other laboratory setups in which complex environmental conditions could never be completely simulated [21,22]. The studies performed *in situ* were primarily based on the modelling of TBT concentration reduction with sediment depth [12,23,24,25]. This approach has several disadvantages because it assumes undisturbed sediment and continuous input, whereas the sedimentation rate has to be known. Additionally, it does not provide the complete interpretation of the degradation mechanisms because the

kinetics of each degradation step cannot be determined. Therefore, more data are required to establish a better understanding of butyltin degradation processes in sediments, especially those that occur under anoxic conditions; meanwhile, the degradation of phenyltins (PhTs) in sediments is rarely experimentally studied and still not well explained.

Sediment characteristics such as organic matter and grain size have been demonstrated many times to have an influence on the adsorption of TBT onto sediment particles [10,11,26], but their role in BuT degradation in the sediment remains unclear. By controlling the adsorption of TBT, organic matter is considered to define its bioavailability because only the TBT present in porewater is believed to be available to microorganisms and actually prone to biodegradation [27]. In spite of this, OTC degradation in porewater has not been studied thus far while only a few papers have reported the levels of BuTs in porewater [13,10,28].

This paper provides a comprehensive study of the persistence of BuTs and PhTs in contaminated marine sediments. The aim was to explain the apparent, different TBT degradation efficiencies in different sediments and to verify whether the degradation of BuTs and PhTs in sediments occurs mainly in porewater. The study was performed as follows: (i) TBT persistence in various types of contaminated sediments was assessed by a determination of butyltin depth profiles in sediment cores; (ii) sediment characteristics (organic carbon and grain size) were determined to study their influence on the TBT degradation efficiency; and (iii) butyltin and PhT degradation processes in sediments and porewaters were studied using species-specific, isotopically enriched tin tracers (^{117}Sn -enriched TBT (^{117}TBT), ^{118}Sn -enriched DBT (^{118}DBT), ^{116}Sn -enriched TPhT ($^{116}\text{TPhT}$)). This multi-isotopic labeling methodology enables any degradation route to be followed individually, despite the simultaneous formation and degradation processes of certain compounds, thereby enabling the determination of the kinetics of each degradation step and consequently helping to characterize the overall degradation mechanism.

2. Materials and methods

2.1. Sediment sampling

The sediment cores were collected in 2011 at 8 locations (M1–M8), mainly marinas, located along the Croatian Adriatic coast, while the incubation experiments were performed in 2012 using sediments from the locations M1, M2 and M6 (Fig. S1, Supplementary information). The marinas differed in size based on the number of berths that varied from 200 to 800 (M1-350; M2-190; M3-800; M4-450; M5-300; M6-city port; M7-200; and M8-630). The depth of the water column at the sampling locations varied between 2 and 35 m (M1-15 m; M2-2 m; M3-35 m; M4-5 m; M5-6 m; M6-14 m; M7-6 m; and M8-3 m). The sampling was performed using a UWITEC gravity corer. The sediment cores (M1–M8) used for the determination of BuTs and sediment characteristics were frozen after sampling, cut in the laboratory into 2 cm layers, freeze-dried and homogenized by milling (except for grain size analysis). The samples were kept at -20°C , and the OTCs were measured within 3 months. The sediment cores used for the incubation experiment were cut into layers, spiked and incubated in the field within 3 h

Download English Version:

<https://daneshyari.com/en/article/6970703>

Download Persian Version:

<https://daneshyari.com/article/6970703>

[Daneshyari.com](https://daneshyari.com)