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The use of isotopically enriched tin tracers to follow the transformation of organotin compounds in landfill leachate

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ABSTRACT

Landfill leachates are an important pool of organotin compounds (OTCs). Several studies have been performed on the occurrence of OTCs in landfill leachates, but only a few of them report degradation and biomethylation processes by bacteria. In the present study transformation of OTCs in landfill leachate was investigated under simulated landfill conditions over a time span of six months. The degradation and biomethylation processes of OTCs were followed by the use of isotopically enriched tin tracers, namely ^{117}Sn-enriched tributyltin (TBT), ^{119}Sn-enriched dibutyltin (DBT), ^{117}Sn-enriched $SnCl_2$, ^{117}Sn-enriched $SnCl_4$ and a ^{119}Sn-enriched butyltin mix containing TBT, DBT and monobutyltin (MBT). Transformation of OTCs in spiked leachates was followed at *m/z* of the enriched spikes and at *m/z* 120, which allowed simultaneous observation of the transformation of OTCs in the leachate itself and of the added spike. In parallel, these processes were also monitored in a non-spiked leachate sample at *m/z* 120. Quantification of OTCs was performed by gas chromatography – inductively coupled plasma mass spectrometry (GC-ICP-MS). To discriminate the biotic and abiotic transformations of OTCs and inorganic tin species, sterilization of leachate was also performed and data compared to non-sterilized samples. During the course of the experiment the microbial degradation of TBT was clearly manifested in Sn-enriched spiked leachate samples, while abiotic pathway of degradation was observed for DBT. Biomethylation process was also observed in the leachate spiked with Sn-enriched Sn^{2+} or Sn^{4+}, in concentrations close to those found for total tin in landfill leachates. Monomethyltin (MMeT) was formed first. Stepwise alkylation resulted in dimethyltin (DMeT) and trimethyltin (TMeT) species formation. Hydrolysis of Sn^{2+} and Sn^{4+} species was found to be a limiting factor which controlled the extent of methyltin formation. The results of the present investigation importantly contribute to a better understanding of the processes that OTCs undergo in leachates, and provide useful information to managers of landfills in taking measures necessary to prevent the release of toxic methyltin species to the nearby environment.

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1. Introduction

Organotin compounds (OTCs) have a wide spectrum of physical, chemical and biological properties. The element tin has the largest number of known organometallic derivatives. The most important commercial applications of OTCs are their use as biocides in agriculture, textiles, antifouling paints and in timber treatment, or as heat and light stabilizers for PVC. Because of the tremendous growth of its industrial production and applications, considerable amounts of OTCs have entered various ecosystems (Hoch, 2001; Gallina et al., 2000; de Carvalho Oliveira and Santelli, 2010; Zuliani et al., 2006, 2008, 2012; Ščančar et al., 2007; Furdek et al., 2012). OTCs are among the most hazardous pollutants known so far ever to have been introduced into aquatic ecosystems by man (Fent, 2004; Chou and Lee, 2005). They are highly toxic even at ng L^{-1} concentration levels and with a high bioacummulation potential. In the marine environment imposex in dog whelk populations was observed, while in mammals including humans, OTCs are neurotoxic and endocrine disrupters (Yamada et al., 1997; Gumy et al., 2008). Because of its widespread use as a biocide in antifouling paints on ships, tributyltin (TBT) is of particular concern in the aquatic environment (Díez et al., 2002; Ščančar et al., 2007; Milivojevič Nemanič et al., 2009; Vahčič et al., 2011a; Furdek et al., 2012). To prevent environmental pollution various legislative restrictions on the use of TBT were issued. The European Commission prohibited the use of OTC-containing antifouling paints on the hulls of boats of less than 25 m and vessels of any length used predominantly on inland waters (Commission Directive, 2002). According to the International Convention on the control of harmful anti-fouling systems on ships, from 1 January 2008 any TBT should be either removed from the surfaces of ships, or efficient sealing should be performed to prevent TBT leaching into the water (Regulation (EC) No. 782, 2003). TBT is also included to the list of priority pollutants in the field of water policy in the EU Water Framework Directive (WFD) – integrated river basin management for Europe (Commission Directive, 2000). The legislative ban on TBT has led to subsequent control of its content in surface and marine waters at very low concentration levels. According to the WFD environmental quality standard (EQS) the highest allowed concentration of TBT in waters is 0.2 ng L^{-1} of TBT expressed as a cation (Directive, 2008/105/EC, 2008). In addition to its presence in different environmental samples, OTCs were also found at detectable levels in household products, such as fungicides, pesticides or treatment against dust-mites in carpets and textiles (Greenpeace Research Laboratories, 2003).

The collection of municipal waste on landfill sites is one of the most commonly employed waste management systems worldwide. Thus, a landfill can be considered to be an important pool of OTCs as a result of their presence in plastic materials, manufactured household products and cans for food packing. Both OTCs and inorganic tin can be mobilised and likely released to the environment by percolation of water through the waste pile. To prevent the water that percolates through the waste from coming into contact with surface or groundwater, a pond is constructed to collect landfill leachate. The environments in landfills generate conditions for the chemical and biological modification of inorganic tin and OTCs, which can be transformed by hydridation, methylation, ethylation, dealkylation or transalkylation reactions (Amouroux et al., 2000; Pinel-Raffaitin et al., 2008). These result in the formation of new tin compounds in landfill leachates and biogases (Pinel-Raffaitin et al., 2008; Ilgen et al., 2008; Vahčič et al., 2011b). The release of OTCs from landfill leachates into the aquatic ecosystem or atmosphere is still scarcely documented. In order to prevent environmental pollution, there is a need for estimation of the ecological impact of OTCs, since tin was found as one of the main leachate contaminants among the metals and metalloids (Pinel-Raffaitin et al., 2008). The use of enriched isotopes can provide comprehensive information in investigations of the transformation of OTCs in environmental samples. Nevertheless, they were rarely applied in studies of the fate of OTCs in landfill leachates and were only used for the quantification of alkyltin species in these samples via the isotope dilution technique (ID)-GC-ICP-MS by addition of a ^{119}Sn-enriched butyltin mix spike containing MBT, DBT and TBT (Pinel-Raffaitin et al., 2007).

Microorganisms may significantly influence the transformation processes of OTCs in landfill leachates, so it is important to study the pathways of their degradation and/or the formation of newly formed OTCs. In our previous work the occurrence of OTCs in leachates from the Barje landfill, Slovenia, was investigated (Vahčič et al., 2011b). The data revealed that the prevailing OTCs found in leachates were methyltin and butyltin species. To better understand the processes that OTCs undergo in leachates the emphasis of the present work was to follow the degradation and biomethylation of these OTCs in leachate by the use of isotopically enriched tin tracers, namely ^{117}Sn-enriched $SnCl_2$, ^{117}Sn-enriched $SnCl_4$, ^{117}Sn-enriched TBT, ^{119}Sn-enriched DBT, and a ^{119}Sn-enriched butyltin mix containing TBT, DBT and MBT. In parallel, processes in the leachate itself were followed in a non-spiked sample. Quantification of OTCs was performed by GC-ICP-MS.

2. Materials and methods

2.1. Instruments

The analysis of OTCs was carried out on an Agilent 6890 gas chromatograph (GC) (Agilent Technologies, Santa Clara, CA, USA) equipped with an Agilent 6890 Series Autosampler Injector. GC was coupled to an Agilent 7700× ICP-MS via a heated transfer line and fitted with a 15 m × 0.25 mm DB-5MS capillary column (film thickness 0.25 μm) coated with 5% phenylmethylpolysiloxane (Agilent J&W Scientific, Palo Alto, CA, USA). Control and operation of the coupled system was performed using Agilent MassHunter software.

For the separation of OTCs on the 15 m column, the following GC temperature programme was applied: at the start the column temperature was held at 50 °C for 0.8 min, then raised to 200 °C at a heating rate of 20 °C min^{-1} and held there for 2 min, then raised to 220 °C at a heating rate of 40 °C min^{-1} and held there for 0.5 min and, in a final step,