

## ABSTRACT

Organotin compounds (OTCs) are among the most toxic substances that were ever introduced into the environment by man. They are common pollutants in the marine ecosystems, but are also present in the terrestrial environment. Studies showed that detectable levels of OTCs can also be found in household products, which are disposed on landfills at the end of their life cycle. OTCs are then leached out of the wastes. Hence, landfill leachates can be considered as an important pool of OTCs.

In the investigations of the degradation and methylation processes of OTCs in environmental samples, the use of enriched isotopic tracers represents a powerful analytical tool. Sn-enriched OTCs are also necessary in the application of the isotope dilution (ID) mass spectrometry technique due to their accurate quantification. Since Sn-enriched monobutyltin (MBT), dibutyltin (DBT) and tributyltin (TBT) are not commercially available as single species, “in house” synthesis of the individual butyltin-enriched species is necessary. The preparation of the most toxic butyltin, namely TBT, was performed via a simple synthetic path, starting with bromination of metallic Sn, followed by butylation with butyl lithium. The formed tetrabutyltin (TeBT) was transformed to tributyltin chloride (TBTCl) using concentrated hydrochloric acid (HCl). The purity of the synthesised TBT was verified by speciation analysis using the techniques of gas chromatography coupled to inductively coupled plasma mass spectrometry (GC-ICPMS) and nuclear magnetic resonance (NMR). The results showed that TBT had a purity of more than 97 %. The remaining 3 % corresponded to DBT. The concentration of Sn in the synthesized  $^{117}\text{Sn}$ -enriched TBT was determined by reverse ID-GC-ICPMS. The synthesis yield was around 60 %. The advantage of this procedure over those previously reported lies in its possibility to be applied on a micro-scale (starting with 10 mg of metallic Sn). This feature is of crucial importance, since enriched metallic Sn is extremely expensive. The procedure is simple and repeatable, and was successfully applied for the preparation of  $^{117}\text{Sn}$ -enriched TBTCl from  $^{117}\text{Sn}$ -enriched metal.

Since landfill leachates are an important pool of OTCs, 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  $^{117}\text{Sn}$ -enriched TBT,  $^{119}\text{Sn}$ -enriched DBT,  $^{117}\text{Sn}$ -enriched  $\text{SnCl}_2$ ,  $^{117}\text{Sn}$ -enriched  $\text{SnCl}_4$  and a  $^{119}\text{Sn}$ -enriched butyltin mix containing TBT, DBT and MBT. Transformation of OTCs in spiked leachates was followed at  $m/z$  of the enriched

isotope 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 GC-ICPMS. To discriminate between the biotic and abiotic transformations of OTCs and inorganic tin species, sterilization of the leachate was also performed and the data compared with non-sterilized samples. During the course of the experiment the microbial degradation of TBT was clearly manifested in Sn-enriched spiked leachate samples, while the abiotic pathway of degradation was observed for DBT. Biomethylation process was also observed in the leachate spiked with Sn-enriched  $\text{Sn}^{2+}$  or  $\text{Sn}^{4+}$ , in concentrations close to those found for total tin in landfill leachates. Monomethyl tin (MMeT) was formed first. Stepwise alkylation resulted in dimethyltin (DMeT) and trimethyl tin (TMeT) species formation. The hydrolysis of  $\text{Sn}^{2+}$  and  $\text{Sn}^{4+}$  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 for taking necessary measures to prevent the release of toxic methyltin species into the nearby environment.

The biotic and abiotic degradation of toxic OTCs in landfill leachates is usually not complete. Therefore, adsorption and degradation processes of TBT and TMeT in leachate samples treated with different iron nanoparticles (FeNPs): nanozerovalent iron (nZVI), iron oxide nanoparticles (FeONPs) and magnetite nanoparticles ( $\text{Fe}_3\text{O}_4$ NPs) were investigated to find conditions for their efficient removal. One sample aliquot was kept untreated (pH 8), while to the others (pH 8), FeNPs dispersed with tetramethyl ammonium hydroxide (TMAH) or by mixing were added. The samples were shaken under aerated conditions for 7 days. The same experiments were done in leachates in which the pH was adjusted to 3 with citric acid. The size distribution of TBT and TMeT between particles  $> 5000$  nm, 450 - 5000 nm, 2.5 - 450 nm, and  $< 2.5$  nm was determined by sequential filtration and their concentrations in a given fraction by GC-ICPMS. Results revealed that most of the TBT or TMeT were present in the fractions with particles  $> 2.5$  or  $< 2.5$  nm, respectively. At pH 8, the adsorption of TBT to FeNPs prevailed, while at pH 3, the Fenton reaction provoked degradation of TBT by hydroxyl radicals. TBT was the most effectively removed (96 %) when a sequential treatment of the leachate with nZVI (dispersed by mixing) was applied, first at pH 8, followed by a nZVI treatment of the aqueous phase, previously acidified to pH 3 with citric acid.

Such a treatment removed less effectively TMeT (about 40 %). It was proven that TMAH provoked methylation of ionic tin, so mixing was recommended for the dispersion of nZVI.

FeNPs are used for environmental water remediation. The NPs which persist in solution after the treatment may cause hazardous effects to the environment. To evaluate the potential environmental threat, the time dependent size distribution of iron particles was investigated in different aqueous samples after the FeNPs treatment. The efficiency of metal removal by FeNPs was also examined. Concentrations of metals in aqueous samples were determined, before and after the nanoremediation, by ICPMS. The data revealed that settling and removal of FeNPs after the treatment of environmental waters was related to the sample characteristics and the ways of NPs dispersion. The dispersion with TMAH was more effective than by mixing. When mixing was used for dispersion, nZVI, FeONPs and Fe<sub>3</sub>O<sub>4</sub>NPs were quickly settled in Milli Q water, forest spring water and in landfill leachate. The dispersion with TMAH resulted in a slower iron particles settling. In Milli Q and forest spring waters treated with FeONPs, a double layer of oleic acid and TMAH was formed around NPs, which prevented the formation of iron corrosion products. So, nanosized iron, which persisted in solution for at least 24 h after the treatment, represented a potential environmental threat. The removal of elements from environmental waters depended on the type of used FeNPs and the dispersion efficiency. The contaminant concentration and sample characteristics like the pH, the ionic strength, the content of organic matter, the presence of complexing ligands and the interactions of FeNPs with the sample matrix, as well as the chemical speciation of elements, contributed also considerably to the remediation efficiency. If the surface of FeNPs is contaminated by a particular metal, this contaminant may be during the NPs treatment released into the water, which is being remediated.