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Review

Trends in the analysis and monitoring of organotins in the aquatic environment

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ABSTRACT

Organotin compounds are toxic and have long-term persistence in the environment. Consequently very low environmental quality standards are set internationally for tributyltin, the major of substance of concern in water. The fulfilment of these regulatory demands has necessitated the development of highly sensitive and selective analytical techniques for the measurement of these compounds. These developments have been coupled with novel extraction and pre-concentration methods that have the potential to be used with automated on-line procedures. Quantification using isotopically enriched tin standards in mass spectrometric-based techniques have allowed for improvements in robustness and precision of analytical methods. In parallel to these laboratory techniques, there have also been enhancements in monitoring methods, particularly the use of passive samplers. This review gives an overview of organotin compounds in the aquatic environment and current trends for their analysis and monitoring within the context of meeting the statutory regulatory environmental standards for tributyltin.

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1. Introduction

The use of organotin compounds as a marine antifoulant is banned under the International Convention on the Control of Harmful Anti-fouling Systems on Ships (AFS Convention Annex 1, 2001). This is due to the high toxicity (effects in the aquatic environment seen at $<1\,\text{ng}\,\text{L}^{-1}$) of tri-substituted organotins (R_3SnX), primarily tributyltin (TBT). Such effects are well documented, for example, thickening of oyster shells and imposex in gastropods [1–4]. Organotin compounds have teratogenic properties and can cause disruptions to the reproductive function in mammals, as well as acting as endocrine disruptors, hepatoxins, immunotoxins, neurotoxins and obeseogens [5–7]. Recent studies have shown a significant reduction in pollution by TBT along coastlines, as well as the biological recovery of many marine species [8]. Despite the observed improvements from reduced concentrations of organotin compounds; sediment legacy of TBT is still associated with shipping facilities, *i.e.* ports, docks and maintenance facilities, offshore shipping routes and anchorages. The half-life of TBT within aquatic compartments is somewhat ambiguous and is largely dependent on the composition of the surrounding water and the associated benthic deposits (with anoxic marine sediment demonstrating greatest half-lives of >10 years) [8]. Organotins are lipid soluble and adsorb easily into the fatty tissues of marine biota. As these compounds can move through trophic levels and pose a risk to commercial fish stocks, low regulatory limits are set for these chemicals (Table 1). In the European Union, there is currently no agreed Environmental Quality Standard (EQS) for TBT in sediments; however, the Water Framework Directive (WFD, 2000/60/EC, 2008/105/EC) sets the EQS for TBT in unfiltered water as $0.2\,\text{ng}\,\text{L}^{-1}$ (allowable annual average) and $1.5\,\text{ng}\,\text{L}^{-1}$ (maximum allowable concentration). In order to attain these concentrations, the limit of detection (LOD) for TBT by compliant laboratories is $50\,\text{pg}\,\text{L}^{-1}$ (under 2009/90/EC in Technical Specifications for Chemical Analysis and Monitoring of Water Status). Such low regulatory limits are generally considered unfeasible for routine sampling and analysis; with only a small number of publications reporting LODs at this concentration [9,10]. Currently, trends in the analysis of organotins are focussed on the development of routine, highly sensitive speciation and detection methods, as well as associated enhancements in monitoring techniques that are capable of meeting the requirements of these international directives.

This paper provides a brief summary of the sources and behaviour of organotins within the aquatic environment, followed by a review of the current analytical methods used for their laboratory analysis and monitoring.

2. Organotins in the environment

2.1. Uses, entry and fate of organotins

The biogeochemical cycle of organotins within the aquatic environment is shown in Fig. 1. Discounting the biochemical methylation of tin; organotins are not synthesised *via* natural processes. In terms of their use, organotins are the most heavily used organometallic compound in the world, with global consumption reported in the ranges of 40–80,000 t a year; notably through their use as PVC plastic stabilisers (dibutyltin—DBT), chemical catalysts and as precursors in glass coating (monobutyltin—MBT) [18]. Tri-substituted organotin compounds are used within textiles and in other household commodities as anti-fungal agents. The European Commission Decision 2009/425/EC of 4th June 2009 has restricted the use of DBT, dioctyltin (DOT) and tri-substituted organotin compounds in products exceeding 0.1 % (by weight of tin). The use of triphenyltin (TPhT) as an agricultural pesticide has also been subject to restrictions (following EU Commission Decisions 2002/478/EC and 2002/479/EC) [19]. 'Non-historical' modes of entry of organotins to the environment are by either direct introduction or the contamination of municipal waste water. In terms of studies focussed on 'non-historical' emissions, methyltin and butyltin compounds within landfill leachates and sewage sludge have received most attention (Table 2 and Fig. 1, process (**1**)). 'Historical' or legacy TBT is still the major contributor to pollution in the aquatic environment; being sourced from anti-fouling paints and preservatives (Fig. 1, process (**2**)). TPhT is also linked with its use as a co-toxicant in antifouling paints. TBT associates with finer sediment fractions ($<63\,\mu\text{m}$) [20], with its degradation attributable mainly to biochemical interactions with algae, bacteria, and fungi (Fig. 1, process (**3**)) [21], occurring step-wise by loss of the organic moiety (*e.g.* TBT → DBT → MBT → Sn(IV)).

Within the water column, the highest concentrations of organotins are found at the surface microlayer [29], where abiotic influences (UV degradation) also play a degradative role (Fig. 1, process (**4**)). Adsorption of organotins to the solid-phase is a reversible process, with desorption occurring by the hydrolysis of electrostatic bonds between the organotin cation compound and the solid-phase sediment/particulate bound ligands found on the organic material surface [30] (Fig. 1, process (**5**)). Natural derivatisation of the organotin cation under anoxic conditions is an important fate process; with biological and chemical addition of hydride and methyl groups to the tin atom allowing for more mobile organotin species [31] (Fig. 1, process (**6**)). Methylated organotins have a lower affinity for the sediment phase in comparison to non-methylated species; therefore, these have a higher propensity to desorb to the water column and volatilise into the atmosphere [31] (Fig. 1, process (**7**)).

3. Analysis of organotin compounds

Table 3shows a summary of the main analytical methods reported since 2004 for the analysis of organotin compounds. LOD values have been converted to the same units ($\text{ng}\,\text{g}^{-1}$ and $\text{ng}\,\text{L}^{-1}$ as organotin cation) for comparative purposes. Most methods are multi-step, and for gas chromatographic (GC) applications, involve a derivatisation stage (Section 3.2). Because of this, recent trends have focussed on eliminating potential sources of error, reducing the number of procedural steps and the manual handling involved with samples. For example, more recent methods use on-line techniques that promote high pre-concentration factors; including solid-phase microextraction (SPME), solid-phase extraction (SPE) or stir-bar sorptive extraction (SBSE). For accurate internal quantification, isotope dilution (ID) is preferred due to its easy incorporation and its applicability to biotic, sediment and water matrices (Section 3.5). Modern methods used for the analysis of organotins in biota, sediment and water have LODs at the $\text{ng}\,\text{g}^{-1}$ or $\text{ng}\,\text{L}^{-1}$ range, with only a few reports at sub $\text{ng}\,\text{L}^{-1}$ concentrations.

Amongst the methods reported in Table 3, validation is commonly undertaken using commercially available certified reference materials (CRMs). These include: PACS-2 from the National Research Council Canada for butyltins in marine sediment; BCR-646 from the European Commission Joint Research Centre for organotins (MBT, DBT, TBT, monophenyltin—MPhT, diphenyltin—DPhT, TPhT) in fresh water sediment, ERM-CE 477 for butyltins (MBT, DBT, TBT) in mussels from the Institute for Reference Materials and Measurements (IRMM) and NIES No. 11 from The National Institute for Environmental Studies (NIES) for TBT and TPhT (non-certified) in fish tissue.