

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 $<1\text{ ng L}^{-1}$) 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, hepatotoxins, immunotoxins, neurotoxins and obesogens [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 ng L^{-1} (allowable annual average) and 1.5 ng L^{-1} (maximum allowable concentration). In order to attain these concentrations, the limit of detection (LOD) for TBT by compliant laboratories is 50 pg 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 ($<63\text{ }\mu\text{m}$) [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.* $\text{TBT} \rightarrow \text{DBT} \rightarrow \text{MBT} \rightarrow \text{Sn(IV)}$).

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 3 shows 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 (ng g^{-1} and ng 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 ng g^{-1} or ng L^{-1} range, with only a few reports at sub ng 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.

Table 1
International regulatory limits and guideline quality standards for tributyltin (TBT).

Country/region	Guideline publication/ legislation	Matrix				Ref.
		Salt water	Fresh water	Sediment	Biota	
European Union	EU WFD surface water limits for TBT	0.2 ng L ⁻¹ annual average and 1.5 ng L ⁻¹ maximum allowable concentration		–	–	[11]
OSPAR Region	OSPAR CEMP assessment reports/EACs	0.1 ng L ⁻¹ water concentration		0.02 µg kg ⁻¹ sediment dry weight	12 µg kg ⁻¹ mussels dry weight	[12]
United States of America	US EPA	One-hour average concentration not exceeding 0.42 µg L ⁻¹ more than once every three years (acute criterion). Four-day average concentration does not exceed 0.0074 µg L ⁻¹ more than once every three years (chronic criterion)	One-hour average concentration does not exceed 0.46 µg L ⁻¹ more than once every three years (acute criterion). Four-day average does not exceed 0.072 µg L ⁻¹ more than once every three years (chronic criterion)	–	–	[13]
Australia	Toxicant Guidelines for the Protection of Aquaculture Species (under review). Australian Sediment Quality Guidelines for TBT	Salt water production: <0.01 µg L ⁻¹	Fresh water production: <0.026 µg L ⁻¹	Low value: 5 ng g ⁻¹ , Trigger value: 70 ng g ⁻¹	–	[14]
Canada	Canadian Water Quality Guidelines of Organotins for the Protection of Aquatic Life	0.001 µg L ⁻¹	0.008 µg L ⁻¹ (and 0.022 µg L ⁻¹ for triphenyltin)	–	–	[15]
Italy	Italian Parliament (Legislative Decree 219/2010) for Priority and Priority Hazardous Substances in Sediments	–	–	0.5 µg kg ⁻¹	–	[16,17]
Norway	Norwegian Sediment and Marine Water Quality Guideline Values for TBT	Group 1—background (0 ng L ⁻¹) Group 2—good (0 ng L ⁻¹) Group 3—moderate (0.2 ng L ⁻¹) Group 4—polluted (1.5 ng L ⁻¹) Group 5—severely polluted (3 ng L ⁻¹)	–	Group 1—background (0 µg kg ⁻¹) Group 2—good (1 µg kg ⁻¹) Group 3—moderate (5 µg kg ⁻¹) Group 4—polluted (20 µg kg ⁻¹) Group 5—severely polluted (100 µg kg ⁻¹)	–	[17]

First TBT biocide applications.
Introduction of TBT self-polishing paints.

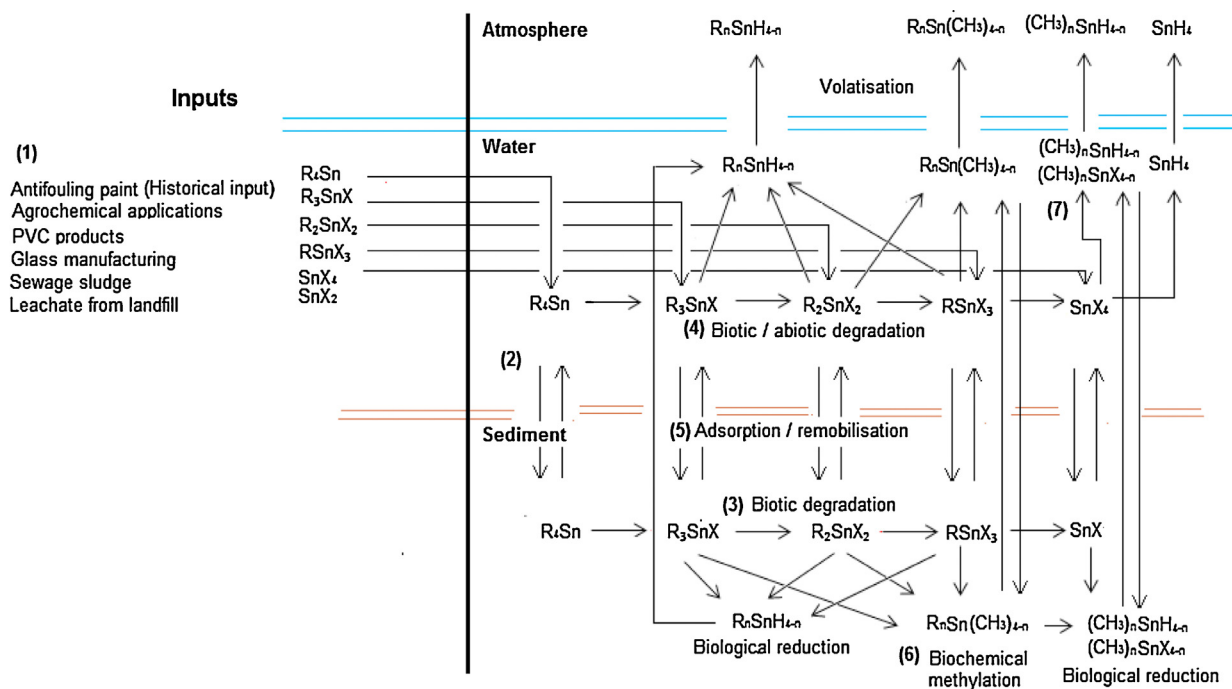


Fig. 1. Biogeochemical cycle of organotin compounds in the aquatic environment, adapted from Refs. [20,28] (with permission).

3.1. Extraction of organotins

3.1.1. Reagents

Extraction of organotins is complicated by the dualistic binding mechanism associated with hydrophobic partitioning and the possession of counter ions and associated bound ligands [32]. From the studies presented in Table 3, extraction can be broadly categorised under: (1) co-solvent (leaching with a medium-polar solvent and weak acid (e.g. methanol:acetic acid)), (2) leaching under acidic conditions exclusively (often acetic acid or HCl only) [33,34]. Due to their lipophilic nature, TBT and TPhT require extractions using medium-to-low polarity solvents (e.g. dichloromethane, *n*-hexane, pentane, or tetrahydrofuran). For less organically substituted compounds, such as MBT, the influence of electrostatic binding is more typical of a trace metal [34], so extraction is often undertaken with an acidic constituent (acetic acid, HCl) followed by the extraction into a non-polar solvent [9] (e.g. dichloromethane, *n*-hexane, toluene). Complexing agents (commonly carbamates or tropolone) can be added to the organic solvent to increase the extraction yields for more polar, lesser substituted compounds [32] (e.g. MBT); although these cannot be applied in low pH conditions [33]. Alkaline digestion with hydroxide solutions, or by the addition of enzymes, can be used for the decomposition and extraction of organotin within biological materials [32].

3.1.2. Techniques

The extraction methods used for organotins have undergone a significant evolution from the conventional liquid-liquid extraction (LLE), Soxhlet and solid-liquid extraction (SLE) procedures; where extraction can be time consuming, expensive and use high volumes of toxic solvents. Microwave assisted extraction (MAE) and accelerated sample extraction (ASE) (also known as pressurised liquid extraction) are more prevalent methods, providing benefits of autonomous rapid extraction times, high sample throughput and often reduced solvent consumption [35]. SPE is used widely owing to its general

availability, often yielding a higher pre-concentration factor relative to the other conventional techniques [36]. Octadecylsilyl (C_{18}) (either as cartridges, columns or bound disks) is the most commonly used sorbent (Table 3). Other sorbents such as Carboxypack, C_2 , C_8 , C_{60} -fullerenes and cation-exchange phases are used to a lesser extent [32,36–38]. On-line SPE coupled to LC is an attractive option, offering benefits in the reduction of analysis time, labour costs and a reduction in matrix effects. LODs of 20 ng L^{-1} in water (3.0 mL sample) using a C_{18} pre-column and LC-MS have been reported [38]. Off-line SPE applications have also received attention. Methods include the *in-situ* extraction of organotins from water samples using dispersive molecularly imprinted polymers (MIPs), with isolation of TBT from water samples achieved using Fe_3O_4 and molecularly imprinted templates [39,40]. SPME and liquid-phase microextraction (LPME) have received much interest [41], owing to their sensitivity, the reduction/elimination of harmful solvents and incorporation of simultaneous *in-situ* on-line extraction and derivatisation. SPME can be used either with direct immersion (DI-SPME) or headspace sampling (HS-SPME), typically using polydimethylsiloxane (PDMS) as the pre-concentration phase (although alternative phases are emerging [42]). pH, temperature and stirring/agitation of the extractant need to be optimised for efficient adsorption of organotins on to the SPME fibre; which with investment into auto-sampling equipment, can be undertaken autonomously (with on-line extraction, derivatisation and desorption of analytes into the GC injector). For LC, a special desorption chamber is required to allow mobile phase access to the SPME fibre [43]. SPME can suffer from sample matrix interferences (reduced using HS-SPME), increased sample carry over as well as significant costs associated with PDMS fibres. Despite these relative disadvantages, low LODs (0.025 ng L^{-1} for TBT) have been reported [6]. LPME is an adaption of liquid-liquid extraction (LLE) and is receiving attention owing to benefits in solvent reduction and the subsequent high pre-concentration factors from a decreased volumetric ratio of the solvent acceptor-donor phase [41]. LPME can achieve high sample throughputs with rapid extraction times, as well as

Table 2
Concentrations of organotin in sewage sludge, landfill leachate and landfill gas.

Sample type	Study	MMT	DMT	TMT	DMDET	TEMT	TPHT	Unit (cation)	Ref.
Sewage sludge	Data from review of micro-pollutants in sludge (3 studies)	-	-	-	ND-6000	ND-7500	ND-6000	ng g ⁻¹	[22]
Sewage sludge	GC-PPPD method for organotins in sewage sludge	-	-	-	265	376	100	ng g ⁻¹	[23]
Landfill leachate	Transformation of organotin compounds in landfill leachate. Municipal non-hazardous waste landfill, Ljubljana, Slovenia	99	188	289	149	16	23	ng L ⁻¹	[24]
Landfill leachate	Municipal non-hazardous waste landfill, Barje, Ljubljana, Slovenia (excluding hazardous landfill)	144–258	54–198	167–469	161–195	57–141	9.7–51	ng L ⁻¹	[25]
Landfill leachate	Municipal landfill, South of France (2005–2006)	ND–169	38–1002	165–8958	ND–458	ND–215	195–3314	ng L ⁻¹	[26]
Landfill leachate	Municipal landfill (excluding hazardous landfill), Bavaria, Germany	ND–27	ND–1227	37–2894	ND–843	ND–411	ND–37	ng L ⁻¹ , as reported median(s)	[27]

Sample type	Study	TeMT	TMET	DMDET	TEMT	TBMET	TeET	TPHT	Unit (cation)	Ref.
Landfill gas										
Landfill gas (volatile organotin species)	Municipal landfill (excluding hazardous landfill), Bavaria, Germany	6468-->240,000	-	-	-	-	-	-	ng m ⁻³	[27]
Landfill gas (volatile organotin species)	Municipal landfill, South of France (2005–2006)	2106-->34,000	196–1467	948–6322	282–1392	ND	ND–24		ng m ⁻³	[26]

DMDET: dimethyldiethyltin; DMT: dimethyltin; GC: gas chromatography; ND: not detected/below detection limit; PFPD: pulsed flame photometric detector; TBMET: tributylmethyltin; TeET: tetraethyltin; TEMT: methyltriethyltin; TeMT: tetramethyltin; TMT: trimethyltin; TMET: trimethylethyltin.

increased selectivity using either a single solvent (α,α,α -trifluorotoluene) [44] or a mixture of solvents (e.g. methanol/tetrachloromethane) [45]. Analysis of the resultant extracted organotins is by conventional GC injection. The most recent LPME procedures used with organotins include dispersive liquid–liquid microextraction (DLLME) [46], headspace–single drop micro-extraction (HS-SDME) [47] and direct immersion–single drop microextraction (DI-SDME) [44]; with LODs using tandem mass spectrometry (MS–MS) and inductively coupled plasma–mass spectrometry (ICP–MS) ranging between 0.4 and 3.0 ng L⁻¹ [44,47]. Stir-bar sorptive extraction (SBSE) is similar to SPME with both solvent less direct immersion or headspace sampling applications [7,48,49]. SBSE provides an increased pre-concentration capacity of 50–250 times over SPME [47], however, uptake and elution conditions (e.g. sample pH, stirring speed, and temperature) must also be optimised for the target analytes. Recovery of extracted organotins is by liquid desorption [48] or on-line thermal desorption [49] (using a specialised unit). Using PDMS stir bars and 2D gas chromatography–tandem mass-spectrometry (GC–GC–MS–MS) or LC–MS–MS, LODs of 0.01–0.8 ng L⁻¹ for butyltins in sea water have been reported [7,50]. Commercially available SBSE sorbent coatings were previously limited to PDMS; however, bespoke adaptations (e.g. C₁₈) are emerging [48].

3.2. Derivatisation

Derivatisation is fundamental to the analysis of organometallics by GC; with a review of *in-situ* borate methods by Zachariadis [51]. Derivatisation strategies for organotins include alkylation using Grignard reagents or alkylborates (commonly NaBEt₄) or conversion using borohydride species (e.g. sodium borohydride–NaBH₄). NaBEt₄ is the most popular reagent (Table 3), due to its application within aqueous matrices, its functionality in on-line and off-line simultaneous derivatisation and extraction and its extended range to phenyltin compounds [47]. Grignard reagents (e.g. ethyl-, pentyl- or hexyl-magnesium bromides) are used post extraction within a non-polar phase and can be used to manipulate GC retention times for organotin derivatives. Although high derivatisation yields are possible with most sample matrices [52], Grignard reagent is less favoured due to the requirement of expert handling techniques together with dry conditions to avoid reactions with water, acids ketones and alcohols [52]. Derivatisation with NaBEt₄ is simpler; undertaken in the aqueous phase converting organotins into their ethyl derivatives. The pH must be regulated (pH 4–6) to allow for nucleophilic substitution of ethyl groups to the organotin cation. NaBEt₄ is made-up at concentrations 1–5% within deionised water or methanol, having a short shelf life (~3–4 days at 4 °C). Reagent life-times can be extended by freezing, although most methods use a fresh solution for each batch of extractions [34]. NaBH₄ can be used with aqueous matrices for simultaneous derivatisation and extraction, however, due to the volatility of these organotin derivatives losses can occur. NaBH₄ can suffer from interferences with complex matrices (e.g. biota and sediments); mainly from interactions with metals and the subsequent production of metal borides (inhibiting the formation Sn–H bonds on organotin compounds) [52]. Due to the robustness of the above procedures, investigations for alternative reagents have received little attention, however, there is interest in developing automated on-line methods to promote consistency and reduce labour costs.

3.3. Separation

3.3.1. Gas chromatography

Capillary GC is the most common technique used for the separation of organotins, owing to its high resolving power and the

Table 3
Selected extraction and analytical procedures for the analysis of organotin from 2004.

Extraction method	Matrix	Method	Extraction and derivatisation	Instrument	Method detection limits (MDL)						Units (as cation)	Ref.	
					TBT	DBT	MBT	TPhT	DPhT	MPhT			
Accelerated solvent extraction (ASE)	Marine sediment ^a artificial sea water ^b	ASE at 100 °C at 1500 psi	1:1 (v/v) MeOH:0.5 M acetic acid	LC–MS–MS	3.7 ^a , 244 ^b						ng g ^{-1a} ng L ^{-1b}	[53]	
	Marine sediment	ASE at 50 °C at 13,790 kPa	750 mL MeOH, 250 mL of H ₂ O, 1 mol of acetic acid, 1 mol anhydrous sodium acetate and 0.6 g tropolone. Derivatised using NaBEt ₄ .	GC–FPD								[54]	
	Marine sediment	ASE at 100 °C at 1500 psi	1 M sodium acetate, 1 M acetic acid:MeOH (1:1). Derivatised using 5% NaBEt ₄ .	GC–MS	1.0	1.0	1.0				ng g ⁻¹	[55]	
	Marine sediment	ASE at 125 °C at 14 MPa	0.01 M HCl Grignard reagents (pentyl magnesium bromide). Extracted into hexane/tropolone	GC–MS	3.7						ng g ⁻¹	[35]	
	Marine sediment	ASE at 50 °C at 13,790 kPa	750 mL MeOH, 250 mL of H ₂ O, 1 mol of acetic acid, 1 mol anhydrous sodium acetate and 0.6 g tropolone. Derivatised using NaBEt ₄ .	GC–FPD	19	3.7	10	14	18	13	ng g ⁻¹	[56]	
	Mammalian liver	ASE at 125 °C at 800 psi	1 M acetic acid and 1 dm ⁻³ of MeOH–water. Derivatised using 2% NaBEt ₄ . Extracted into <i>n</i> -hexane.	GC–FPD	15	14	15	38	17	28	ng g ⁻¹	[57]	
Liquid phase microextraction (LPME)	Estuarine water	DLLME	780 µL of MeOH and 20 µL of CCl ₄ . Derivatised using 2% NaBEt ₄ .	GC–MS	1.7	2.5	5.9				ng L ⁻¹	[45]	
	Sea water	HS–SDME	Sample pH adjusted to 5. NaBEt ₄ ^a and NaBH ₄ ^b derivatisation. Extracted into <i>n</i> -decane.	GC–ICP–MS	0.80 ^a , 20 ^b	1.8 ^a , 60 ^b	1.4 ^a , 480 ^b				ng L ⁻¹	[47]	
	Mussel tissue, PACS-2 sediment Sea water	HS–SDME and UAE DI–SDME into α,α,α-trifluorotoluene	5 mL HCl:MeOH (0.12 mol L ⁻¹). Optimal derivatisation with NaBEt ₄ . pH adjusted to 3. Tetrakis(4-fluorophenyl) borate ^a and NaBEt ₄ ^b derivatisation.	GC–ICP–MS GC–MS–MS	0.36 ^a , 6.3 ^b			2.9 ^a , 0.85 ^b			ng L ⁻¹	[44]	
Solid phase microextraction (SPME)	Mussel tissue	UAE HS–SPME with PDMS fibre	10% NaOH:MeOH. Derivatised using 2% NaBEt ₄ .	GC–MS–MS	7.3	5.9	4.4				ng g ⁻¹	[58]	
	Fresh water	HS–SPME with PDMS fibre	Sodium acetate to buffer to pH 4.0. Derivatised using 4% NaBEt ₄ .	GC–MS	4.1	2.4	1.4	6.7	5.0	3.6	ng L ⁻¹	[59]	
	Marine sediment	UAE and HS–SPME with PDMS fibre	HCl:MeOH (1:20 v/v). Derivatised using 2% NaBEt ₄ .	GC–FPD	1.7	4.5	5.3	20	17	8.4	ng g ⁻¹	[60]	
	Sea water, effluents	HS–SPME PDMS fibre investigated	NaCl added to sample, sodium acetate buffer to pH 5. Derivatised using 2% NaBEt ₄ .	GC–FID ^a GC–MS ^b	100 ^a 0.025 ^b			1000 ^a 0.5 ^b	100 ^a 0.025 ^b			ng L ⁻¹	[6]
	Fresh water and sea water	HS–SPME with DVB/CAR/PDMS	1 mL buffer solution 5 mL sample. 200 µL of 2% NaBEt ₄ added. SPME for 15 min ⁻¹ at 40 °C.	GC–MS ^a GC–MS–MS ^b	27 ^a 9.0 ^b	17 ^a 33 ^b	28 ^a 4.0 ^b				ng L ⁻¹	[61]	
	Sea water	SWCN using HS–SPME	Sodium acetate buffer to pH 5.3. Solution magnetically stirred at 45 °C and derivatised with NaBEt ₄ .	GC–MS					2–5 for butyltins		ng L ⁻¹	[42]	
	Fresh water and sea water	DI–SPME. PDMS/DVB ^a and CW/TPR ^b investigated. TMT and TPrT included in study	NaCl added to 75 g L ⁻¹ . Sample magnetically stirred during SPME immersion.	LC–ICP–MS	449 ^a				32 ^a			ng L ⁻¹	[43]
Microwave assisted extraction (MAE)	Marine sediment	ID spiking. Samples microwaved at 100 °C for 4 min at 200 W	Acetic acid ^a and tartaric acid ^b . pH adjusted to pH 5. Derivatised using 2% NaBEt ₄ . Extracted into <i>iso</i> -octane.	GC–MS	126 ^a , 133 ^b	82 ^a , 70 ^b	63 ^a , 32 ^b				ng L ⁻¹	[62]	
	NMIJ CRM 7306-a marine sediment	MAE at 120 °C in 10 min then held for 10 min. ID spiking used for quantification	Toluene with 0.1% tropolone, 10 mL 1 mol L ⁻¹ acetic acid:MeOH. Derivatised with NaBEt ₄ . Extracted into toluene.	GC–ICP–MS								[63]	

Solid phase extraction (SPE)	Mineral water	Strata C ₁₈ -E ^a , SCX, and Chromabond [®] aminopropyl phases (NH ₂ /C ₁₈). ID spiking for quantification	Adjusted to pH 5. Derivatisation using 0.5% NaBEt ₄ (H ₂ O) and 10% NaBEt ₄ in THF. DCM, ethyl acetate, THF, MeOH investigated for C ₁₈ elution.	GC-ICP-MS	0.50 ^a			ng L ⁻¹	[2]
	Marine sediment	Post extraction purification undertaken on florisil and silica columns	10 mL tetrahydrofuran solution (containing 0.6 M HCl). Extracted into 20 mL of 0.01% tropolone-hexane (m/v). Derivatisation using Grignard's reagent.	GC-MS-MS	0.4–1.5			ng g ⁻¹	[64]
	Sea water	C ₁₈ cartridges	C ₁₈ pre-treated with 5 mL MeOH and 10 mL of 10 ⁻² M HCl. Eluted using 2 mL MeOH.	LC-MS	20–80			ng L ⁻¹	[65]
	Fresh water and sea water	Online SPE (C ₁₈) coupled with LC electrospray ionisation mass spectrometry	Adjusted to pH 2.7. 3 mL of sample introduced on to C ₁₈ pre-column. Elution by 0.1% (v/v) formic acid and 5 mM ammonium formate.	LC-MS	20		20	ng L ⁻¹	[38]
	Marine sediment and water assays	Development of a multi-method on-line derivatisation sequence incorporating SPE Envi [™] 18 cartridges	SPE conditioned using 3 mL ethyl acetate, 3 mL MeOH, 3 mL H ₂ O and 3 mL 5% HCl. Elution by 3 × 0.5 mL ethyl acetate. Derivatisation using NaBH ₄ .	GC-MS					[66]
SPE-molecularly imprinted polymer solid-phase extraction (MISPE)	Mussel tissue	Fe ₃ O ₄ nanospheres with MIP poly (ethyleneglycol dimethacrylate) layer with a TBT template. Supplemented with UAE.	MeOH:acetic acid (1:1 v/v). Washed with 6 mL of 4:1 MeOH:CH ₂ Cl ₂ . Final elution 6 mL of 0.1 M formic acid in MeOH; reconstituted in formic acid and H ₂ O (1:9 v/v).	LC-MS-MS	1.0–2.8			ng g ⁻¹	[39]
Soxhlet extraction	Sea water	Passive sampling. Deployment (7 weeks) of silicone rubber sheets within sea water	200 mL acetonitrile:3 mL acetic acid. 20% NaBEt ₄ in ethanol. LLE = <i>n</i> -hexane.	GC-MS			0.04–0.1 (freely dissolved concentrations).	ng L ⁻¹	[67]
Stir-bar sorptive extraction (SBSE)	Fresh water, sea water, fresh water sediments and marine sediment	100 μm silica C ₁₈ particles, fixed with PDMS. Stir bar pre-treated with methanol. Optimised to pH 4 for 30 min at 600 rpm	Desorption undertaken with formic acid (10% v/v) triethylamine (5%) oxalic acid (10 mmol L ⁻¹) and 40% (v/v) methanol.	LC-ICP-MS	16	16	29	ng L ⁻¹	[48]
	Sea water, tap water	HSSE-TD. PDMS stir bar.	pH adjusted to 4.8. Derivatisation using 2% NaBEt ₄ .	GC-MS		3.9	4.4	ng L ⁻¹	[49]
	Sea water	Method for SBSE (PDMS) using <i>in-situ</i> derivatisation and LVI	MeOH added to 40% in 30 mL sample. Extracted into <i>n</i> -pentane Derivatisation using NaBH ₄ .	GC-MS	23			ng L ⁻¹	[68]
	Sea water	Method development of SBSE with PDMS stir bar	Sample adjusted to pH 2. Elution by ultrasonication with acetonitrile and formic acid (0.1% v/v).	LC-MS-MS	0.80			ng L ⁻¹	[50]
	LC-MS, sea, industrial effluent, tap and mineral water	SBSE with PDMS stir bar. Use of deuterated (TBT-d ₂₇) internal standard. 2 h stirring at 750 rpm	1% NaBEt ₄ solution.	GC-GC-MS-MS	0.01			ng L ⁻¹	[7]
	Estuarine water ^a , marine sediment ^b and biota ^c	(HSSE-TD) PDMS stir bar	Sediments extract = 2 mol L ⁻¹ HCl with anion exchange resin and ultrasonication. Biota samples = 10% KOH-MeOH. Derivatised using 0.1–2% NaBEt ₄ .	GC-MS	0.8 ^a , 0.04 ^b , 0.03 ^c	0.4 ^a , 0.04 ^b , 0.01 ^c	2.0 ^a , 0.03 ^b , 0.02 ^c	ng L ^{-1a} ng g ^{-1b,c}	[69]
Supercritical fluid extraction (SFE)	Clam tissue	SFE and SPME. SFE = 45 °C at 30 MPa, 1.2 L min ⁻¹	CO ₂ modified with 5% MeOH. Derivatised using 2% NaBEt ₄ .	GC-MS					[70]

CCl₄: tetrachloromethane; CW/TPR: Carbowax/templated resin; DCM: dichloromethane; DI-SDME: direct immersion-single drop microextraction; DLLME: dispersive liquid-liquid microextraction; DVB: divinylbenzene; DVB/CAR/PDMS: divinylbenzene/Carboxen/polydimethylsiloxane; FPD: flame photometric detector; GC: gas chromatography; GFAAS: graphite furnace atomic absorption spectrometry; HS-SDME: headspace-single drop microextraction; HSSE-TD: headspace sorptive extraction-thermal desorption; HS-SPME: headspace-solid-phase microextraction; ICP-MS: inductively coupled plasma-mass spectrometry; ID: isotope dilution; LC: liquid chromatography; LLE: liquid-liquid extraction; LVI: large volume injection; MAE: microwave assisted extraction; MIP: molecularly imprinted polymer; MQL: method quantification limit; MS: mass spectrometry; MS-MS: tandem mass spectrometry; NaBEt₄: sodium tetraethylborate; NaBH₄: sodium borohydride; PDMS: polydimethylsiloxane; PFPD: pulse flame photometric detector; SWCN: single walled carbon nanotubes; THF: tetrahydrofuran; UAE: ultrasonic assisted extraction; a,b,c: experimental variables.

variety of sensitive and selective detectors available. Modern methods can separate differing organic moieties (butyl, phenyl, propyl) in one run [32] using a non-polar column (e.g. 5% phenyl-methylpolysiloxane stationary phase). Typically, columns are 25–30 m long, with inner diameters of 0.25 mm and stationary phase film thicknesses of 0.1–0.3 μm [33]. Analysis is undertaken using splitless injection (1–5 μL , 250–280 °C) initially with the oven temperature held just below the boiling point of the extractant solvent, then increased ~40–280 °C over a cycle. Other injection techniques such as on-column and programmed temperature vaporisation-large volume injection (PTV-LVI) can be used to improve LODs [68]. PTV-LVI is an on-line solvent evaporation technique, where larger injection volumes (10–100 μL) are evaporated within the inlet. Loss of early eluting compounds (e.g. ethylated MBT and TPrT) can be problematic and the method needs careful optimisation. Cryo-apparatus for cooling the inlet <20 °C can improve the retention of early eluting compounds. Sample run times range from 10 to 40 min, and are dependent on the mass range of analytes separated and the type of organic species produced in the derivatisation step.

3.3.2. Liquid chromatography

Derivatisation is not required for LC allowing faster analytical procedures and eliminating a potential source of cross-contamination. Limitations include sensitivity and the types of detectors, as well a limited range of organic moieties separated with one analytical sequence. Commonly used detectors are MS, MS–MS, ICP–MS [71], with fluorimetry now reported less. A variety of mobile and stationary phase combinations are used. The latter include ion-exchange, reversed phase, normal phase, ion-pair, size exclusion, micelle and vesicle-mediated and supercritical fluid systems [32]. Stationary phases can broadly be categorised by either ion-exchange or reversed phase chromatography [32,72]. Ion-exchange stationary phases are typically based on styrene divinylbenzene resin or silica, where cationic organotin species compete with the mobile phase counter ions for ionic sites [32,72]. Styrene divinylbenzene resins swell causing compression effects. Cross-linking overcomes this but causes a decrease in the mass transfer process [32,72]. Silica groups are more stable allowing faster elution and use of high column pressures. Silica columns are pH sensitive and stable at pH 2–8, therefore, buffer solutions are used to reduce peak tailing [32,72]. With ion-exchange chromatography, strong retention of mono-substituted organotins is problematic, and complexing agents and pH gradient elution are often needed [71]. For silica-based columns, mobile phases use methanol (50–90% v/v) with an added salt (e.g. ammonium acetate or citrate at 0.005–0.2 mol L⁻¹) [32,72]. With reversed phase chromatography, the mobile phase is typically water with an organic modifier where the elution strength is increased over time [29,32].

3.4. Detection

The most sensitive detection methods are coupled with GC, where tin-specific element detection (ICP–MS, PFPD, and microwave induced plasma-atomic emission detection (MIP–AED)) provides instrument detection limits (IDL) at sub pg (Table 4). Method detection limits (MDLs) are dependent on the sample concentration in the analytical procedure, as well as the capacity of the chromatographic procedure [33]. In terms of meeting the analytical compliance for the EU WFD for TBT (50 pg L⁻¹), IDLs of detectors achieving sub pg detection (ICP–MS, PFPD, MS–MS) can theoretically attain the required sensitivity, when using large sample volumes (~1 L), and a pre-concentration stage. Consideration must be given to achieving very low procedural blanks. In routine laboratories these optimal

Table 4

Instrumental detection limits (IDL) of butyl- and phenyl-tin compounds using gas chromatographic and liquid chromatographic separation with various detection systems.

Instrument	IDL (pg)	Ref.
GC–AAS	40–95	[75]
GC–FPD	0.2–18	[75]
GC–PFPD	0.07–0.48	[74]
GC–QF–AAS	10–100	[75]
GC–MS	01–10	[75]
GC–MS–MS	0.20–0.35 (as Sn)	[76]
GC–ICP–MS	0.0125–0.17	[75,77]
GC–MIP–AED	0.01–0.03	[75]
LC–MS (ESI ^a , APCI ^b)	12–700 ^a , 30–1800 ^b (as Sn)	[71]
LC–MS–MS	10 (as Sn)	[53]
LCMS–IT–TOF	13–45 (as Sn)	[78]
LC–ICP–MS	3.0 (as Sn using TBT)	[77]

AAS: atomic adsorption spectrometry; APCI: atmospheric pressure chemical ionisation; ESI: electrospray ionisation; IT-TOF: ion trap-time of flight; MIP-AED: microwave-induced plasma atomic emission detector; a,b: detector configuration.

procedures are rarely found, being impaired by day-to-day changes in the instrument sensitivity, high procedural blanks and complications related to field sampling (see Section 4).

Hyphenation of sensitive detection systems (e.g. ICP–MS) to GC and LC is complex to set-up and expensive to operate. For example, LC–ICP–MS requires additional oxygen to the nebuliser argon gas flow (for higher temperature combustion of organic solvents), increased power to the plasma, de-solvating equipment and a refrigerated spray chamber to avoid blockages of the interface [48]. LC applications can suffer reduced sensitivity (Table 4); typically being two orders of magnitude higher than GC–ICP–MS. The sensitivity of GC–ICP–MS is enhanced by using oxygen/nitrogen/argon plasma gas mixtures, which give an efficient breakdown and transmission of ethylated tin compounds [73] and permit higher tolerances to impurities in the sample matrix [51]. With ICP–MS detection, additional cleaning and maintenance of interface cones is required due to carbon deposition from solvents used in GC and LC applications. Conventional MS detection is more widely used, with IDLs (in selected ion monitoring (SIM) mode) being adequate for measuring organotins in biota and sediment samples (typically $\mu\text{g g}^{-1}$ to ng g^{-1} ranges) [34]. MS–MS methods using ion trap [7] and triple quadrupole techniques [64] have been described recently; allowing for greater sensitivity and selectivity over single MS detection methods at sub pg concentrations. Flame photometric detectors (FPD) (and the more recent pulsed flame photometric detector) have a slightly reduced selectivity in comparison to mass selective detectors and can suffer matrix interferences (in particular from sulphur compounds sometimes found in sediment samples) [56]. Despite the requirement for increased sample clean-up, photometric methods have LODs in the sub pg range [74].

3.5. Quantification

Quantification can be undertaken by external calibration or using isotopically enriched organotin compounds in ID procedures. When using derivatisation, the use of internal standards (typically tripropyltin) is important to correct for the efficiency of this step and the extraction yield. Pre-derivatised standards (as ethylated tin compounds) are available commercially, but are expensive to purchase in comparison to their non-derivatised analogues. Non-derivatised standards can be obtained either as pre-made stock solutions (within a miscible solvent for ethylation), or as alkyl-tin liquids and salts. Non-derivatised standards should be made up as matrix-matched equivalents to the sample(s) being analysed. Quantification using ID is the main technique for measuring butyltins. ID uses ¹¹⁹Sn enriched MBT, DBT and TBT

spiked into the sample. The concentration of each organotin in the sample is then calculated as a ratio from the known isotopic abundances of both the spike and sample [79]. ID reduces sample and standard processing and accounts for interactions and conversions by the different organotin species in the sample [80]. High sensitivity can be achieved, with LODs ~ 0.18 – 0.25 ng L⁻¹ in 100 mL of water [81]. Commercially available isotopically enriched standards are expensive, but this can be offset from the reduction of analysis time compared with external quantification methods.

4. Monitoring of organotins

Sampling organotins in water and sediment needs special precautions. Usually amber shaded glass bottles are used, but polycarbonate, PTFE and aluminium materials are alternatives [20]. Polyvinyl chloride (PVC) should be avoided as di-substituted butyltins are used as stabilisers in this material. Short-term storage of sediment samples is optimal at 4 °C (with long-term storage at -20 °C being preferred) [33]. Sampling of organotins in water is problematic as normally large volume samples are needed in order to achieve the sub ng concentrations necessary to fulfil the current EQS requirements for TBT in the WFD. Ultra-clean sampling containers and laboratories are necessary to achieve low background blanks, along with the associated sensitive and robust instrumental methods. An alternative method for monitoring organotin compounds in water is the use of passive sampling, and this technique has received some attention over the past decade.

Passive samplers can effectively reduce LODs of the analytical procedure to within the EQS ranges for TBT, as well as reducing some sources of error inherent with spot water sampling methods. The devices can be used to sequester the bioavailable fraction of organotins in the water column, and depending on their mode of operation, allow for estimation of time-weighted average (TWA) concentrations of pollutants over their deployment [67]. Samplers also allow the detection of intermittent pollutant events that can be potentially missed using low frequency spot sampling methods. Organotin compounds detected in the aquatic environment have range of log octanol/water partition coefficients ($\log K_{ow}$), with TBT having reported $\log K_{ow} = 3.49$ – 5.07 , depending on the associated anionic ligands [82]. Table 5 shows the types of passive sampler used to monitor organotins in the aquatic environment, which can be broadly considered as non-polar types of device. The organotin Chemcatcher[®] uses a 47 mm C₁₈ 3M Empore[®] solid-phase extraction disk as the receiving phase overlain with a thin cellulose acetate diffusion-limiting membrane. Both are contained in PTFE housing. Aguilar-Martinez et al. [83] using a laboratory calibration tank with varying water temperatures and turbulences, determined the sampler uptake rates of different organotins as MBT = 6–18 mL d⁻¹, DBT = 41–204 mL d⁻¹, TBT = 29–202 mL d⁻¹ and 26–173 mL d⁻¹ for TPhT. Limits of detection ranged from 0.2 to 7.5 ng L⁻¹. Due to the small active sampling area (17.4 cm²) of the Chemcatcher[®] (and hence lower uptake rates compared with other methods) lower LODs (at sub ng L⁻¹ for TBT) have been achieved using large silicone rubber sheets (active sampling area = 300 cm²) [67] (Fig. 2). The more hydrophobic compounds with the higher $\log K_{ow}$ gave the largest sampling rates with MBT = ~ 1.0 L d⁻¹, DBT = ~ 1.8 L d⁻¹ and TBT = ~ 2 L d⁻¹. Smedes and Beeltje [67] found that diffusion coefficients of organotins were relatively slow, with di-substituted organotins having the lowest diffusion coefficients. The diffusion coefficients for ionic species were also found to be much lower than neutrally associated organotins [67]. LODs of <0.1 ng L⁻¹ for TBT were anticipated using this technique.

Biofouling of samplers and the influence of the diffusive boundary layer at the water-sampler interface (as a function of

Table 5
Passive sampling devices used to monitor organotins in water.

Passive sampling device	Deployment and location	Compounds detected	Receiving phase, extraction techniques and analytical procedure	Limits of detection (as cation)	Ref.
Chemcatcher [®]	Municipal water and sea water; 14 days—Alicante Harbour, Spain	MBT, DBT, TBT, TPhT	C ₁₈ 47 mm 3M Empore [™] disk (overlain with a cellulose acetate diffusive layer), Methanol:acetic acid (1:3 v/v) into 1 mL <i>n</i> -hexane. Derivatised using NaBEt ₄ . Analysed by GC-ICP-MS/GC-FPD.	0.2–7.5 ng L ⁻¹	[83,84]
SPMD	Sea water; 15 days—4 week deployment in Oslo Fjord Harbour, Norway	DBT, TBT	Triolein 1st: cyclohexane-DCM. 2nd: concentrated to 0.5 mL then extracted into 10 mL methanol. 3rd: Extracted into 10 mL <i>n</i> -hexane with simultaneous derivatisation using NaBEt ₄ . Analysed by GC-AED. LDPE tubing containing triolein	—	[85]
SPMD	Municipal water supply (flow through tank experiment) with other organic pollutants, 28 days	DBT, TBT, TPhT	25 mL of acetate buffer (pH 4.5) added along with 25 mL of <i>n</i> -hexane. 0.5 mL of NaBEt ₄ added for derivatisation. Extracts analysed using GC-MS.	—	[86]
Silicone rubber (30 mm × 30 mm × 0.5 mm)	Bottle exposure on deionised and saline water; 6 weeks shaking. Field trials in Ijmuiden Harbour, The Netherlands	TeBT, TBT, DBT, MBT, TPhT, DPPhT, MPhT, TeOT, TOT, DOT, MOT, TeOT, TcHT	Silicone rubber Dosing of organotins on to sheets investigated along with 26 extraction techniques. Soxhlet extraction with acetonitrile; 1% acetic acid and a polar solvent (followed by <i>n</i> -hexane pre-concentration). Analysed by GC-MS.	<0.1 ng L ⁻¹	[87]

MOT: monoocetyl tin; TcHT: tetracyclohexyltin; TCN: tetrachloronaphthalene; TeBT: tetrabutyltin; TeOT: tetraoctyltin; TOT: trioctyltin; LDPE: low density polyethylene; SPMD: semi-permeable membrane device.

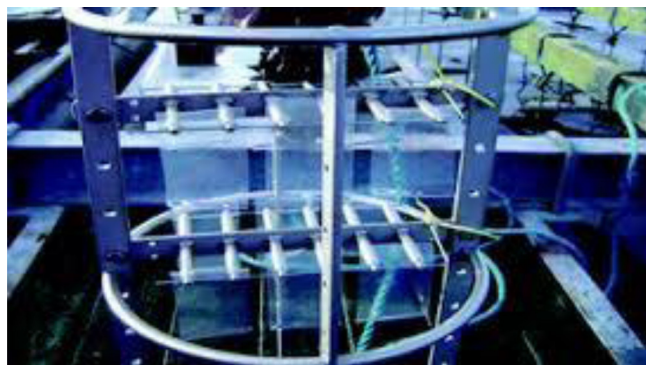


Fig. 2. Silicone rubber passive sampler sheets attached to deployment frame (reproduced with permission from Ref. [88]).

flow rate variations) can cause inaccuracies with the measurement of TWA concentrations. These factors need to be considered as part of the overall validation procedure when using passive samplers. As samplers sequester the freely dissolved concentrations of target analytes, their direct use can be problematic within the WFD and other statutory regulations, where the determination of 'total' concentrations is mandated. However, the measurement of the freely dissolved (sometimes referred to as the 'bioavailable fraction') concentration may more accurately reflect environmental risk and this aspect is presently under discussion with scientists, policy makers and regulators

5. Conclusions

Due to its ubiquitous presence, persistence, and high toxicity at low concentrations, TBT will remain on the regulatory agenda for some time. Current monitoring and analytical methods are able to meet sediment and biota EQS requirements for TBT. These, however, cannot routinely achieve those stipulated for surface waters within the WFD. It is challenging to achieve these low concentrations for TBT, requiring dedicated laboratories and a high capital investment in instrumentation. The use of isotopically enriched organotin standards help in allowing more sensitive analyses and these can be readily incorporated into mass spectrometric assays. Despite these advancements in quantification, analysis of organotins is still comparably complex and time consuming, with extraction and derivatisation procedures accounting for the highest sources of analytical error. In terms of autonomy, miniaturisation, and the reduction in labour; on-line SPME and LPME show potential as sample extraction and pre-concentration procedures; although these still may not be seen as routine methods and require significant investment in equipment for large sample throughputs. *In-situ* long-term deployment of silicone rubber passive samplers, used in conjunction with highly sensitive analytical methods may offer a path forward to attain the measurement of the low aqueous concentrations of organotins as required in many international directives.

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