

Organotin compounds in marine sediment: Detection and concerns

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Abstract

The determination of organotin compounds (OTCs) in environmental matrices has been subject to great scientific attention during last years, as the accuracy and sensitivity of analytical methods need to be improved in order to be able to detect the compounds of interest in a complex matrix such as sediment. The European Union Water Framework Directive (2013/39/EU) sets very restrictive environmental quality standards for 45 priority substances and other pollutants, including OTCs. Therefore, it is necessary to develop analytical methods in compliance with the environmental quality standard (EQSs) proposed to protect the aquatic environment and human beings. So far various analytical procedures have been used, including gas chromatographic analyses. Most of these methods comprise different steps such as extraction, derivatisation, clean up and the use of several sophisticated instrumentations, as well. Among them the conversion of tributyltin into Sn to allow its determination by Atomic Absorption Spectrometry or Anodic Stripping Voltammetry (AVS) has also been attempted. A great number of studies have been performed on OTCs analysis in marine sediment. However, the only review available in literature discussing the upgrades of analytical methods is dated back to 1997. We reviewed the analytical procedures and discussed them comparatively in order to identify the current state-of-the-art in OTCs detection. Finally, environmental concerns about OTCs were discussed.

Keywords: OTCs, TBT, antifouling paint, marine sediment, analytical methods

1. Introduction

Organotin compounds (OTCs) have been used extensively worldwide as biocides in marine antifouling paints. As a result, they have become one of the major categories of pollutants entering the marine environment and finally accumulating in sediment being characterized by high toxicity, high stability in the environment and high lipophilicity (Diez *et al.*, 2005; Gomez-Ariza *et al.*, 2006; Libralato *et al.*, 2008, 2010; Mamindy-Pajany *et al.*, 2010;

Lofrano *et al.*, 2016a). Tributyltin compounds (TBT) occur at high concentrations in water, sediment, and biota associated with harbour locations whereas dibutyltin (DBT) and monobutyltin (MBT) contamination is believed to result from tributyltin degradation rather than from direct input. TBT can cause chronic and acute toxic effects to algae, zooplankton, molluscs, and some fish species even at very low concentrations. Moreover, Tributyltin (TBT) is associated to imposex phenomena (Fernandez *et al.*, 2005). Triphenyltin (TPHT) is less toxic than TBT, but can also be of high risk to aquatic life. The high level of BT contamination and their adverse health effects resulted in the restriction of the use of tributyltin (TBT) in antifouling paints. As a result, BT levels in coastal environments have been decreasing worldwide (Sousa *et al.*, 2007; Rato *et al.*, 2009). However, high levels of BTs are still detected in a variety of aquatic organisms and are found in water and sediment from estuaries and harbours (Leung *et al.*, 2006; Berto *et al.*, 2007; Lofrano *et al.*, 2016; Lofrano *et al.*, 2017). Thus, the environmental occurrence and adverse health effects of BTs on marine organisms are still of concern.

The first regulatory actions and legislative management of tributyltin were adopted in France in 1982. The UK followed suit in 1985 (Terlizzi *et al.*, 2001). However it was only with the AFS Convention, which was signed in 2003 but came in force only since January 2008, that any OTC was completely banned. The United Nations Environment Programme (UNEP) and Food and Agriculture Organization of the United Nations (FAO) added the pesticide TBT to a global trade "watch list" after the Rotterdam Convention in November 2008. Despite these bans, high concentrations of OTCs continue to be detected in marine sediment (Lofrano *et al.*, 2016). Their widespread use has introduced high levels of contamination into the environment and raised concerns about their toxic effects on marine communities.

The scientific interest in the quality of marine sediment has increased remarkably in the past 30 years and especially in relation to application of the European Union Water Framework Directive (WFD 2000/60/EC). Since 1980, when

the ecological impact of OT-based antifouling paints on marine biota became evident, the negative effects of such biocides have been studied with increasing intensity. Using the website www.sciencedirect.com as a research tool, in the period from 1980 to 2016 we found 1811 scientific papers dealing with marine sediment related to OTCs. According to Figure 1 literature studies significantly increased until 2000 as consequence of the severe restrictions on the use of TBT.

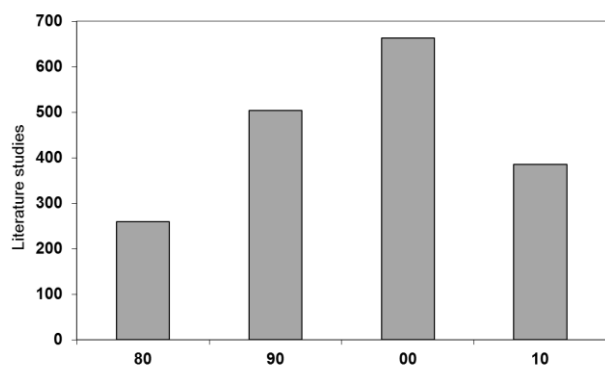


Figure 1. Distribution of literature studies on OTCs in the period from 1980 to 2016

To evaluate the environmental distribution and fate of these compounds and to determine the efficiency of legal provisions adopted by a number of countries, a variety of analytical methods have been developed for OT determination in the environment. (Ochsenkühn *et al.*, 2001; Szpunar-Lobinska *et al.*, 1995). However, the only

review available in literature discussing the upgrading of analytical methods is dated 1997 (Abalos, 1997).

2. OTCs: Sink, source, and final fate

OTCs comprise a group of organo-metallic moieties characterized by the presence of one or more covalent bonds between atoms of tin (Sn) and one or more organic substituents (methyl, ethyl, butyl, propyl, phenyl). The physical and chemical properties of OTs vary widely, according to the number and type of organic and inorganic moieties bonded to the tin atom. The persistence and fate of OTs in the aquatic environment are functions of such factors as aqueous solubility and vapour pressure of the compound, adsorption to suspended matter and sediment, and abiotic and biotic methylation and demethylation. Water solubility typically range from 5 to 50 mg L⁻¹ and are inversely proportional to the number and molecular weight of the organic groups attached to the tin atom (NRCC 1985). Most commercially used OTs have low mobility in aquatic environments as a result of low aqueous solubility, low vapour pressure, and a high affinity for aquatic sediment (Blundin and Chapman, 1982). Table 1 presents the basic physical and chemical characteristics for the OTCs most frequently detected in environmental matrices.

Among OT species, tributyltin (TBT), triphenyltin (TPHT) and their derivatives have been of particular concern because they were usually used as paint additives to prevent bio-fouling on ship hulls, marine platforms and fishing nets resulting in a world-wide pollution of aquatic environments (de Carvalho Oliveira *et al.*, 2010). Table 2 gives an overview of OT product use patterns.

Table 1. Physical and chemical characteristics of selected OTCs (Adopted from Hoch, 2001).

OTCs	Melting temperature (°C)	Boiling Point (°C)	Density (g cm ⁻³)	Solubility (mg dm ⁻³)
Bu ₄ Sn	-97	145/1.3 kPa	1.06	n.i
Bu ₃ SnCl	-16	172/3.3 kPa	1.21	50 ^b
Bu ₂ SnCl ₂	39-41	135/1.3 kPa	- ^d	5-17 ^c
BuSnCl ₃	n.i. ^a	93/1.3 kPa	1.69	4-50 ^b
Me ₃ SnCl	37-39	154	-	92 ⁺
Me ₂ SnCl ₂	106-108	188-190	-	n.i.
MeSnCl ₃	48-51	171	-	n.i.

^a n.i. no information, ^b solubility in sea water, ^c solubility in distilled water, ^d no data

Table 2. Main industrial applications of OTCs (Piver, 1973; Hoch *et al.*, 2001; de Carvalho Oliveira, 2010)

OTCs production	Industrial applications	OTCs
Heat stabilizers	Transformer oils stabilizers	tetraphenyl tin
	PVC stabilizer	dibutyltin dilaurate; dibutyltin maleate; dibutyltin laureate-maleate; dibutyltin bis (lauryl mercaptide); dibutyltin S, S-bis (isooctyl thioglycolate); dibutyltin β- mercaptopropionate; di-n-octyltin maleate; di-n-octyltin S, S-bis (isooctyl thioglycolate); di-n-octyltin β- mercaptopropionate.
Catalysts	Curing agent for silicone rubbers	dibutyltin dioctoate; dibutyltin dilaureate
	Urethane and esterification catalysts	dibutyltin diacetate; dibutyltin dioctoate; dibutyltin dilaureate; dibutyltin dilchloride; dibutyltin dilauryl mercaptide; dimethyltin dichloride; diethyltin dioctoate; stannous octoate
Biocides	Rodent repellent, molluscicide, fungicide, algicide and insecticide	tributyltin chloride; tributyltin acetate; triphenyltin chloride; triphenyltin hydroxide; dibutyltin dilaurate
	Preservatives for food, textile, paper, leather and glass	bis(tributyltin) oxide; TBT0; tributyltin linoleate

Table 3. Same analytical methods for GC reported by different researchers for OTCs in marine-sediment samples (2005 – 2013). a) Homogenization, b) Extraction, c) Clean up.

Derivatization	Sample treatment	Detector	LOD (ng/g)	Recovery (%)	References
Methylation	a) 0.05% w/v tropolone solution in methanol – ultrasonic bath for 15 min and centrifugation at 4000 rpm for 10 min (repeated three times).	MS	MBT	-	Berto <i>et al.</i> (2007)
	b) dichlorometane		DBT	82	
	c) n-hexane.		TBT	81	
Ethylation	b) 20% HCl/methanol solution (1:1) - ultrasonic bath for 1h – centrifugation at 3000 rpm for 5 min – adding of solution sodium acetate and heating at 40 °C for 15 min.	FPD	MBT	116	Wang <i>et al.</i> (2008)
			DBT	93	
	c) SPME		TBT	122	
	a) ascorbic acid with ethyl acetate – homogenization with 1N HBr-methanol/ethyl acetate (1:1) – centrifugation.	MS	MBT	38	Sousa <i>et al.</i> (2007)
	b) ethyl acetate/hexane (3:2), adding of hexane to separate water phase - concentration near to dryness – solved into ethanol and mixed with 1M acetate buffer (pH 5.0).		DBT	38 – 123	
	c) Florisil Sep – Pak column – eluent: -.		TBT	38 – 123	
	b) mixture of methanol, hexane and glacial acid.	AED	MBT	-	Verslycke <i>et al.</i> (2005)
	c) de-activated aluminum oxide and C18 material – eluent n-hexane.		DBT	-	
			TBT	-	
	b) acetic acid/methanol solution (3:1) – microwave 90W for 4 min	ICP-MS	MBT	-	Üveges <i>et al.</i> (2007)
			DBT	-	
			TBT	-	
	b) glacial acetic acid in methanol – mechanical stirring for 12 h.	FPD	MBT	-	Mzoughi <i>et al.</i> (2005)
			DBT	-	
			TBT	-	
	b) acetone +1 M HCl-methanol/ethyl acetate (1:1) shaken for 10 min	MS	MBT	107	Harino <i>et al.</i> (2007)
	c) hexane + water shaken for 10 min - Florisil Sep-Pack column – eluent: diethyletherhexane		DBT	108	
			TBT	109	
Propylation	a) HCl/methanol (1:20, v/v) solution – vortex for 1 min – sonication for 20 min – centrifuged at 3000 rpm for 5 min. (repeated once)	FPD	MBT	85.8	Zhang <i>et al.</i> (2013)
	b) Adding a buffer (HAc/NaAc, pH 5)		DBT	94.2	
	c) SPME to the headspace of solution, stirred at 750 r min ⁻¹ under 25° C for 15 min		TBT	91.7	
	a) 0.1% tropolone–benzene and 2N HCl – centrifugation	FPD	MBT	85	Sudaryanto <i>et al.</i> (2005)
	b) 0.1% tropolone–benzene and dried with Na ₂ SO ₄ .		DBT	94	
	c) Florisil-packed glass column – eluent: n-hexane.		TBT	92	
	b) tropolone/benzene solution	FPD	MBT	85.6	Liu <i>et al.</i> (2011)
			DBT	93.5	
			TBT	92.4	
Pentylation	b) toluene/HOAC (10:4) – sonication for 5 min - centrifugation at 2000 rpm for 3 min - (repeated twice).	FPD	MBT	-	Diez <i>et al.</i> (2005)
			DBT	-	
	c) Neutral alumina column (3 g) with anhydrous Na ₂ SO ₄ – eluent: n-hexane		TBT	-	

Derivatization	Sample treatment	Detector	LOD (ng/g)	Recovery (%)	References
	b) toluene/acido acetico (10:4) solution – ultrasonic bath 125 W for 15 min - 0.05% ammonium pyrrolidinedithiocarbamate APDC aqueous solution. (repeated three times).	PFPD	MBT	4.5	Fernandez <i>et al.</i> (2005)
			DBT	4.5	
	c) 2% de-activated allumina and anhydrous Na ₂ SO ₄ eluent: n-hexane.		TBT	5.9	
	a) water/HBr (1:1)	FPD	MBT	0.8	Gomez-Ariza <i>et al.</i> (2006)
	b) 0.04% w/v tropolone solution in dichloromethane		DBT	0.8	
	c) Florisil column – eluent: penthane		TBT	0.8	
	a) 0.03% solution of tropolone in methanol and HCl – vortex for 1 h.	MS	MBT	0.2	Jadhav <i>et al.</i> (2009)
	b) dichloromethane (repeated twice)		DBT	0.2	
	c) Activated silica gel – eluent:		TBT	0.2	
Hexylation	a) extraction cell with n-hexane 1 mL min ⁻¹ – heating to 60° C.	MS	MBT	-	Lee <i>et al.</i> (2006)
	b) 100° C and 100 atm for 10 min (repeated three times)		DBT	-	
			TBT	1.8	
				80.2 – 106.7	

Under favorable conditions, OTCs may degrade through successive dealkylation producing dibutyltin or diphenyltin (DBT or DPhT), monobutyltin or monophenyltin (MBT or MPhT), and, ultimately, inorganic tin and becoming progressively less toxic in the process (NRCC, 1985).

3. Analytical methods for OTCs in marine sediment

In Fig. 2, the typical procedures used for the determination of OTCs in marine sediment are presented. In the first studies carried out on sediment, the butyltin concentrations were measured by hydride derivatization and atomic absorption (Stallard *et al.*, 1987; Dowson *et al.*, 1992).

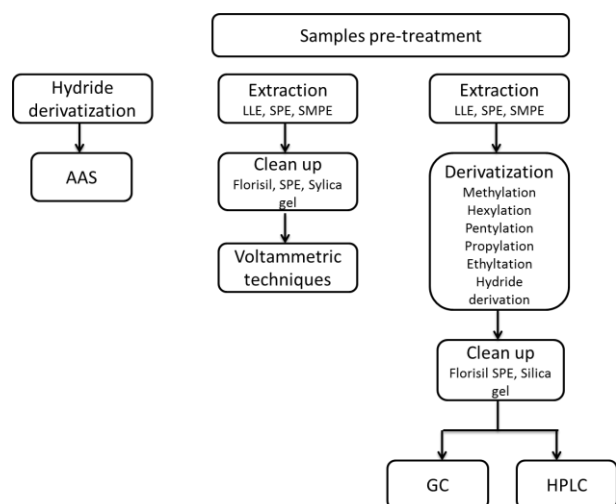


Figure 2. Typical procedures followed for the analysis of OTCs in marine sediment.

Nowadays species selective analysis of OTs is performed by coupled techniques based on the combination of chromatography separation with a sensitive and element selective detection method. The most common technique is gas chromatography (GC) coupled with element specific detection. Despite the need for thermally stable and volatile analytes GC has become the preferred sample introduction technique for the time resolved introduction of analytes into an atomic spectrometer because of the high resolution and sensitivity, the latter due to quasi - 100% sample introduction efficiency and virtually no energy losses for the vaporization and desolvation of the mobile phases.

Table 3 provides summary information on the analytical methods applied by different researchers from 2005 up to the present and the analytical conditions used in each case as well as method validation results (recoveries and detection limits) obtained through GC analysis of marine sediment samples. Gas chromatography with mass spectrometry detection (GC–MS) in full scan and selective ion monitoring (SIM) modes has become a useful tool in organometallic compounds analysis because it offers simultaneous identification and quantitation of a large number of these compounds, including OTCs (Moscoso-Pérez *et al.*, 2015).

The OTCs extraction is carried out with multi-step procedures such as liquid/liquid extraction (LLE), cryogenic trapping, supercritical fluid extraction or solid phase micro extraction (SPME) (Ochsenkühn *et al.*, 2001). The SPME sampling can be carried out either in the direct mode (immersed in the liquid) or in the headspace (HS) mode (Moscoso-Pérez *et al.*, 2015). Due the high volatility of OTCs in their alkylated forms, HS mode is the technique usually selected. Other procedures, also included in the group of green analytical pre-concentration procedures like SPME, have been applied to determine OTCs, e.g. stir bar sorptive extraction (SBSE) or liquid phase micro-extraction (LPME) (Moreda-Piñeiro *et al.*, 2013). For most of the above-mentioned techniques usually an additional step, the derivatization of the OTCs to more volatile compounds are required, such as Grignard alkylation (Szpunar-Lobinska *et al.*, 1995). Clean-up procedures are applied by many researchers in order to increase the sensitivity of the methods, usually by silica and florisil columns. In order to overcome the derivatization step, OTs can be converted into inorganic tin making possible the use of all techniques usually applied for metal determination as AAS, AVS, Inductive Coupled Plasma – Optical Emission Spectrometry (ICP – OES) and Inductive Coupled Plasma – Mass Spectrometry (ICP – MS). Nevertheless in some cases AAS technique not allow to assess low tin concentrations, due to the complexity of the sediment matrix. Therefore, various voltammetric techniques have been attempted in the last years giving results accurate and reproducible (Ochsenkühn *et al.*, 2001). Although in some cases no differentiation of OTs can be achieved, the polarographic determination of the interfering species DPT and MPT, as well as DBT and TPT is possible through a double peak evaluation and a prior chromatographic separation and the detection limits for the determination of TBT, DBT, MPT, DPT and TPT can be improved to lower concentrations, when using ASV at a hanging mercury drop electrode (HMDE). By comparing the different techniques use to detect OTCs in sediment no significant difference could be observed in LOD. Dowson *et al.*, (1992) used a modified version of the “purge and trap” boiling point separation method. OTs hydrides generated by the adding of NaBH₄ to the sample were cryogenic trapped using liquid nitrogen. Hydride species were sequentially desorbed in relation to their specific boiling point after heating of the trap and were carried by helium flow into the quartz cell of AAS. TBT, DBT and MBT detection limits were reported around 1 ng g⁻¹. According to Table 3, some GC methods present LOD higher than these values. The lowest LOD for TBT corresponding to 0.08 ng g⁻¹ has been reported by Wang *et al.*, (2008). On the other hand, no comparison could be carried out between “old” and “new” techniques in terms of recovery due to missing of data in papers published around 1980 applying hydride generation. Although traditional methods are considered time-consuming, also the sample preparation for GC analysis is an often-tedious step, involving much time and efforts in order to obtain a clear extract for low-levels OTCs analysis, and this is due to the complexity of sample matrix. Ultrasonic extraction appears to be the mostly preferred sample preparation

method currently. The problem associated with GC include: i) the need for the extra equipment, e.g. a GC oven for temperature programmed runs and ii) the duration of analytical runs for OTCs detection (15-20 min); the draw of large amount of solvents for the preparation and derivatization of the samples. Following the ongoing technological evolution in the laboratory equipment and consumables, the aim of tracing the OTCs residues in the marine sediment with higher precision and accuracy is being approached.

4. Environmental concern

The global concern about the environmental impact of OTCs on coastal ecosystems has been intensified after the first negative effects were reported in numerous studies (de Mora and Pelletier, 1997; Evans and Nicholson, 2000). Tributyltin is recognized worldwide as an endocrine disruptor, being associated with the imposex phenomenon on female dogwhelks and shell thickening on oysters during the 1980s (Lintelmann *et al.*, 2003). Several scientists around the world are wondering if the total ban has been successful (Anastasiou *et al.*, 2016; Batista *et al.*, 2016; Filipkowska *et al.*, 2016). Nevertheless, sixty-two years following their first application and 9 years after the complete ban on their use as biocides in 2003 (EC No. 782/2003), the negative impact of OTC seems still evident. In vitro studies suggest that TBT may cause immunotoxicity, teratotoxicity and neurotoxicity in mammals, including humans. Choi *et al.*, (2013) measured the concentrations of butyltin compounds (BTs) in the livers of finless porpoises (*Neophocaena asiaeorientalis*) caught off the Korean coast in 2003 and 2010, to assess the effectiveness of legislative action against BTs. The concentrations of BTs ranged from 65.1 to 1432 (average: 370) ng/g wet weight, within the ranges reported by previous studies. More recently, Anastasiou *et al.*, (2016) reported high imposex frequency in *Hexaplex trunculus* and *Nassarius nitidus* collected from the ports of Cagliari (Italy), El Kantaoui (Tunisia) and Olhão and Faro (Portugal), showing as in ports of Atlantic Ocean and Mediterranean Sea the contamination is still active. Imposex in gastropods (*Acanthina monodon*, *Oliva peruviana* and *Xanthochorus cassidiformis*) has been reported by Batista *et al.*, (2016) in three areas along the central Chilean coast.

Filipkowska *et al.*, (2016) analysed muscle and liver tissues of nine fish species reporting maximum total concentrations of butyltin compounds (BTs) of 715 and 1132 ng g⁻¹ d.w. of Sn, respectively. Results demonstrate that butyltins are still present in fish from the Polish coast of the Baltic Sea.

Finally, the contamination related to disposal of tributyltin (TBT) by contaminated harbour sediment, sewage sludge and/or biocide products has been raising concerns also for terrestrial environment and it may pose a risk to soil invertebrates and plants.

5. Conclusions

Marine sediment is a complex matrix where OTCs occur in concentration levels of ng/g, exhibiting toxic effects. In order to accurately quantify such levels of OTCs, increased analytical efforts and optimizations have been reported in the literature, regarding AAS, GC and HPLC. In conclusion, the increase of sensitivity and recovery of analytical methods for the determination of OTCs in marine sediment, still consists a challenge for researchers worldwide, although there has been a great progress regarding the capabilities of the analytical instrumentation available nowadays. Although TBT-based antifouling paints had been banned worldwide TBT pollution remains a serious environmental issue. The recent use and inputs associated to the lack of restrictions in some countries such as South America, where only Brazil and Uruguay are signatories of the IMO antifouling systems convention are contributing to this scenario.

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