



REVIEW

Sources, Environmental Levels and Toxicity of Organotin in Marine Environment-A Review

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Organotin compounds are highly versatile group of organometallic chemicals used in industrial and agricultural applications. The growing use of organotin containing compounds such as agricultural pesticides contaminates the aquatic environment by leaching and runoff. The presence of organotin compounds in environmental samples suggest to the vast increase in the use of organotin made products which affects all facets of the ecosystems and thus lead to the global ban on its application. A lot of work has been done on the presence of organotin compounds in environmental samples. The sources, human health risk and speciation of organotin compounds are discussed in this paper. The use of organotin compounds as biocides in antifouling paints has been the major believe for the sources but a large diversity of this compound can be detected in various environmental samples. The uses of organotin compounds as fungicide, glass coating, catalyst, PVC thermo stabilizer are the important sources of these contaminants. The accumulation of organotin compounds in the sea sediment or marine organisms such as fish, shells and squids are the possible ways of exposure to human, if it is consumed. The predominance of parent compounds (tributyltin and triphenyltin) is commonly found and this may indicate their slow degradation in sediment, biota and sea water samples and when recent inputs occur. The detection level of organotin compounds such as methyl butyltin, dibutyltin, tributyltin and triphenyltin are low in developed countries because organotin health risks are under control unlike the developing countries where their use is not controlled. Thus, there is need to monitor organotin contamination from large shipping vessels.

Key Words: Marine water, Organotins compounds, Sediments, Analysis, Speciation, Antifouling paints, Biota.

INTRODUCTION

Organotin compounds are highly versatile groups of organometallic chemicals used for various purposes. Dibutyltin (DBT) compounds are mainly used as stabilizers in polyvinyl-chloride plastics. Tributyltin (TBT) compounds and triphenyltin (TPT) compounds are used as biocides, fungicides, antifouling agents for ship bottoms and fishery (farm nets)^{1,2}. Organotin (OT) compounds have been extensively used in boat paints since 1960 because of their excellent and long lasting anti-fouling properties. In the 1980s, malformation of American oyster shells was caused by tributyltin (TBT) compounds and led to a decrease in fishery resources³.

Over the past few decades, a considerable number of studies have been conducted on the effects of organotins on aquatic organisms, their concentration and their distributions in aquatic environments. As a result, TBT has been demonstrated to have

high toxicity towards aquatic organisms acting as an endocrine disruptor with effects such as imposex in gastropods at very low water concentrations, causing an increase in the proportion of females in aquatic organisms^{4,5}. Moreover, once it is released from an antifouling coating, TBT is rapidly absorbed by organic materials such as bacteria and algae or adsorbed onto suspended particles in the water⁶⁻⁸.

Furthermore, organotin compounds is readily incorporated into the tissues of filter-feeding zooplankton, grazing invertebrates and eventually, higher organisms such as fish, water birds and mammals where it accumulates⁹⁻¹². Persistence of organotin compounds, wide distribution and their hydrophobicity have raised much concern about bioaccumulation and biomagnification of organotin compounds in the food webs and more so, their adverse effects to human health and the environment¹³⁻¹⁶.

In spite of the regulation of TBT in various countries between the late 1980s and early 1990s, it continues to be detected in the aquatic environment. The contamination of organotin is widespread especially in coastal environment.

In Japan, the use of tributyltin oxide agent was prohibited in January 1990 and the recommendation has also been made that the use of organotin compounds should be also reduced. Also the International Maritime Organization (IMO) called for a global retreat that led to the bans of the application of TBT-based paints starting from January 2003 and total prohibition by 1 January (2008)^{17,18}. In general, a wide and detail review of worldwide organotin regulatory strategies can be obtained from Champ¹⁹. However, marine pollution by organotin has still continued, because contaminated fish and shellfish have been found. Since the Japanese eat relatively large amount of raw fish and shellfish, effects of manmade chemicals such as PCBs and DDT has caused great concern²⁰.

Takahashi *et al.*¹⁵ observed butyltin (BT) compound accumulation in organisms collected at depths of 135-980 m in Suruga bay and reported butyltin concentrations in deep-sea fish, crustaceans, cephalopods, echinoderms and gastropods of up to 980, 460, 460, 130 and 21 ngg⁻¹ wet wt, respectively. Since a French scientists reported marine pollution by organotin compounds²¹, many studies have since been done. France was the first country to prohibit the use of antifouling paints containing TBT on boats shorter than 25 m in 1982. Later, several advanced countries regulated the use of organotin²². However, the use of antifouling paints containing TBT for large vessels is not yet internationally regulated.

In recent years, many reviews have been reported on TBT environmental levels²³⁻²⁶ and toxicity^{27,28} and most review focuses on possible endocrine disrupting effects of organotin compounds^{14,29-31}.

In spite of the knowledge of contamination of organotin compounds, only developed countries have taken step to prohibit the use of organotin compounds and follow the guidelines to date³². As a result of lack of enforcement on the control of organotin compounds, especially in Africa, there is a need to carry out detailed environmental assessment of organotin compounds in sediments and marine water samples.

There is need also to know the environmental impact of these compounds on living organisms. Since enforcement is still a problem in Africa, we would be able to draw the attention of the government and the individuals on the toxicity and environmental impact of organotin compounds. Presently, there are only few studies that have been conducted to investigate the environmental impacts and human health risk of this contaminant in Africa. Thus, it remains necessary to monitor the sources through which these contaminants get into environmental samples.

This review paper, aims to provide a general overview on the sources and industrial applications, environmental levels, toxicity and chemical analysis of organotin compounds.

Occurrence of organotin compounds: Organotin compounds or stannous occurred in nature as chemical compounds based on tin with hydrocarbon substituents. Organotin chemistry is part of the wider field of organometallic chemistry³³. The first organotin compound was diethylindioxide, discovered

by Edward Frankland in 1849. An organotin compound is commercially applied as a hydrochloric acid scavenger or heat stabilizers in polyvinylchloride (PVC) and as a biocide. Tributyltin oxide [or tributyltin for short] has been extensively used as a wood preservative. Tributyltin compounds are used as marine anti-fouling agents. Concerns over the toxicity of these compounds have led to a worldwide ban by the International Maritime Organization (IMO) on its use. Butyltin trichloride is used in the production of tin oxide layers or glass bottles by chemical vapour deposition³³.

Classification of organotin compound: Organotin compounds are classified into Aliphatic and Aromatic organotins.

Organic tins: These are thus classified as R₄Sn, R₃SnX, R₂SnX₂ and RSnX₃. In compounds of industrial importance, R is usually a butyl, octyl, or phenyl group and X, a chloride, fluoride, oxide, hydroxide, carboxylate or thiolate.

Mono organotin compounds: RSnX₃, are known but so far have found only limited application for example, butyltin sulfide is used as a stabilizer in polyvinylchloride [PVC] film.

Diorganotin compounds: R₂SnX₂ are chemically reactive and most of their applications are based on this property. They are used as stabilizers of PVC, as catalysts in the production of polyurethane foams and in the cold-curing of silicon elastomers³⁴.

Triorganotin compounds: R₃SnX are the most important class of organotin chemicals. They are biologically very active and are widely used as biocides. The chemical nature of the R group has a strong influence on the biological properties of these compounds. The X-group, on the other hand, influence their solubility and volatility (Table-1). The two most important groups of triorganotin compounds are tributyltin and triphenyltin derivatives.

TABLE-1
PHYSICAL PROPERTIES OF SELECTED ORGANOTIN
COMPOUNDS* [Ref. 36,37]

	m.p. (°C)	b.p. (°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 5-17 ^c
Bu ₂ SnCl ₂	39-41	135/1.3 kpa	- ^d	4-50 ^b 92 ⁺
BuSnCl ₃	n.i. ^a	93/1.3 kpa	1.69	
Me ₃ SnCl	37-39	154	-	n.i
Me ₂ SnCl ₂	106-108	188-190	- ^d	20 000 ^b
MeCl ₃	48-51	171	-	n.i

* (Adapted from Ref. 35); ^an.i. = no information; ^bSolubility in seawater; ^cSolubility in distilled water; ^dNo data.

Tetra-alkyl and tetraaryltin: These compounds are primarily used as intermediates in the preparation of other organotin compounds. Tetraalkyltin compounds are colourless and the compounds of lower molecular weight are liquid at room temperature. Tetraorganotin compounds possess typical covalent bonds and are stable in the presence of air and water. Tetra-butyltin, Sn(C₄H₉)₄ is a colourless oily liquid with a distinct odour. Tetra-phenyltin, Sn(C₆H₅)₄ is a white crystalline powder, soluble in organic solvents and insoluble in water. Since 1974, a new class of organotin compounds, called estertins has been developed for use as stabilizers in poly(vinyl chloride) their general structure is (R-O-CO-CH₂CH₂)₂SnX₂

or R-O-CO-CH₂-CH₂SnX₃ where X may be, for example, isooctylmercaptoacetate. They have low volatility and extractability³⁴.

Hypercoordinated stannanes: Unlike their carbon analogues, tin compounds can also be coordinated to five and even six atoms instead of the regular four. These hyper coordinated compounds usually have electronegative substituent for stabilization. Lithium pentaorganostannates were first detected and characterized in solution in 1986 by Reich³⁸. While in the subsequent year a six-coordinated tetraorganotin compound was reported³⁹. In 2007, a crystal structure at room-temperature stable (in argon) all-carbon pentaorganostannane was reported⁴⁰.

Properties and uses: Organotin compounds comprise a group of organometallic moieties characterized by a Sn atom covalently bound to one or more organic substituents (*e.g.*, methyl, ethyl, butyl, propyl and phenyl). Organotin compounds conform to the following general formula: (n-C₄H₉)_nSnX₂, chemically represented as by the formulas RSnX₃, R₂SnX₂, R₃SnX and R₄Sn in which R is any alkyl or aryl group and X is anionic species⁴¹. The nature of X influences the physico-chemical properties, notably the relative solubility in water and non-polar solvent and the vapour pressure. They are reported to be stable at temperature up to 200 °C, thermal decomposition has no significance under environmental conditions, UV-radiation, strong acids and electrophilic agents readily cleave the Sn-C bonds.

The number of Sn -bonds and the length of the alkyltins chains have profound effect on the chemical and physical properties of organotins. Progressive introduction of organotin groups to the tin atom^{42,43} in any number of the R_nSnX_{4-n} series producing maximal biological activity against all species, when n = 3. Tributyltin oxide (TBTO) and tributyltin chloride have been normally used in laboratory experiments to investigate organotin toxicity^{42,43}.

Generally, the solubility of organotin compounds in water decreases with increasing number and length of the organic substances and also depends on the particular X. According to Blunden and Chapman⁴⁴, who experimentally determined aqueous solubility range between 20 g L⁻¹ for the readily soluble Me₂SnCl₂ to less than 1 mg L⁻¹ for sparingly soluble phenyl-, cyclohexyl- and octyltin compounds. Organotin compounds are used as pesticides (TBT in antifouling paints applied to boats and ships and TPT in agricultural formulations) and as a heat stabilizer (DBT) in PVC pipes.

The major commercial use of organotin compounds is as a light and heat stabilizer in the PVC industry, where less toxic monoalkyltin and dialkyltin compounds are used. Organotin compounds were intentionally used as anti-fouling agents, due to their low toxicity to fouling organisms^{45,46}. Shell deformity and carval mortality is also caused by TBT at low concentrations⁴⁷. Many different organotin complexes are being studied in anticancer therapy, observing that their cytotoxicity and selectivity towards cancer cell is higher than that of cisplatin. Tributyltin compounds such as tributyltin oxide (TBTO), tributyltin chloride (TBTCl) are extremely toxic substances belonging to the organotin group.

Tributyltin is used mainly in antifouling paints for ship hulls to inhibit growth of algae, barnacles or mussels, which

are killed upon contact with the paint. In addition, butyltin is used as a catalyst or as a stabilizer in the production of plastics like formica as well as a biocide in wood preservatives and for the conservation of outdoor textiles⁴⁷. Tributyltin compounds are the main active ingredients in biocides used to control a broad spectrum of organisms. Antifungal action on textiles and industrial water system, such as cooling tower and refrigeration water systems, wood pulp and paper mills systems and breweries⁴⁸⁻⁵⁰. Dibutyltin is also increasingly used as binder in water based vanishes⁵¹ in general, various uses and applications of organotins and its derivatives leads to direct and indirect input into the environment.

Environmental chemistry of tin: Sequel to considerably higher toxicity of some organometallic tin compounds compared with inorganic forms of tin, the possibility of biomethylation of tin is obviously of considerable interest. A possible mechanism of such biomethylation has been proposed⁵². Recently, laboratory studies have indicated that the methylation of tin by methylcobalamin (CH₃-B₁₂) requires a one electron oxidation of Sn(II) to a Sn(III) radical, which can take place in the presence of Fe(III), Sn(IV) would of course, require a single electron reduction). The stannyl radical [Sn(III)] can then react with CH₃-B₁₂ [Co(III)] to produce (under conditions of high chloride ion concentration) CH₃-SnCl₂ and reduce cobalamin, containing Co(II)⁵².

The methylation of tin takes place in a strain of *Pseudomonas* bacteria found in Chesapeake bay, USA. Subsequently Brickman *et al.*⁵³ and Hue *et al.*⁵² proposed a "mercury-tin cross over" system, which may have some real basis as indicated by Schvamel who found that mercury and tin accumulated together in some water plants in Bavarian river⁵³.

Industrial application of organotin compounds and its pollution sources: According to Ross⁵⁴, there are three main areas in which organotin compounds have product and process utility; (1) heat stabilizers; (2) catalytic agents; (3) biocidal compounds. Organotin derivatives account for the fourth largest production of organometallics amounting to *ca.* 3-4 million pounds per year as compared with about 485 million pounds per year for organolead compounds. Diorganotins have no antifungal activity, low toxicity and low antibacterial activity except for diphenyltins. They are used in polymer manufacturing, as PVC stabilizers [monoorganotin are mostly used for this since they have no biocidal activity and their toxicity to mammals is very low]. Methyltin, butyltin, octyltin and manostertiss are used as PVC heat stabilizers⁵⁵.

Organotins are remarkably varied in their physical, chemical and biological properties. Therefore, Sn has a large number of its organometallic derivatives in commercial use than any other element. This is reflected in their divergent industrial applications (Table-2) and is mainly restricted to compounds of the types R₄Sn, R₃SnX, R₂SnX₂, RSnX₃. Tetraorganotin compounds do not have any large scale commercial outlets, but are important intermediates in the production of less alkylated derivatives.

Synthesis: Organotin compounds can be synthesized by several methods, namely Grignard route, Wurtz route, alkylaluminium route and direct synthesis. These routes to produce organotin halides involve two reaction steps. The first

TABLE-2
INDUSTRIAL USES OF ORGANOTIN COMPOUNDS

Industrial application	Function	OTC
PVC stabilizers	Stabilization against decomposition by heat and light	R_2SnX_2 and $RSnX_3$
Antifouling paints	Biocide (due to low toxicity to Fouling organisms). It control broad spectrum of organisms	$R = Me, Bu, Oct; R_3SnX$
Agrochemicals	Fungicides, Insecticide, Miticide, Antifeedant	R_3SnX
Wood preservation	Insecticide, Fungicide	$R = Bu, Ph, Cy, Bu_3SnX_2$
Glass treatment	Preursor for tin(IV) oxide films on glass	$Me_2SnX_2; RSnX_3, R = Me, Bu$
Materials protection (stone, leather, paper)	Fungicide, Algicide, Bactericide	Bu_3SnX
Impregnation of textiles	Insecticide, Antifeedant	Ph_3SnX
Poultry farming	Dewormer	Bu_2SnX_2
Industrial water	Cooling water and refrigeration water systems	$C_{12}H_{27}Sn^+, C_8H_{18}Sn^{2+}, C_4H_9Sn^{3+}$

step is a reaction of tin tetrachloride ($SnCl_4$) with suitable reagents to form various tetraalkyltins compounds (R_4Sn). In the second step, R_4Sn reacts with $SnCl_4$ in a redistribution reaction to form less alkylated organotin chlorides, like R_3SnCl , R_2SnCl_2 or $RSnCl_3$ ⁵⁶. From these organotin chlorides, various Sn derivatives can simply be produced. The commercial production of organotin compounds by using the Grignard reagent ($nRMgCl$) began in the USA and the Metal and Thermit corporations plant in Rath way, New Jersey, in the late 1940s⁵⁷.

The process of commercial production of organotin by Grignard reagent gives high yield but the use of high solvent is required while manufacturing of organotin compounds by alkyl aluminium route started in Germany at Schering industrial chemical divisions⁵⁸. Organotin halides can also be directly synthesized by a reaction between Sn metal or Sn alloys and alkyl halides. The order of reactivity of alkylhalides with tin follows $RI > RBr > RCl$. Methyltin stabilizers are produced by direct synthesis in USA while direct synthesis routes using alkylhalides and bromides was developed in Japan in the early 1950s.

PVC stabilizers: About 70 % of the total annual organotin production is applied as derivatives for thermal and heat stabilizer in the plastic industry and as catalysts for polyurethane foams and silicones. PVC decomposes easily upon heating (80-200 °C) or on prolonged exposure to sunlight due to loss of HCl from the polymer. The results are embrittlement and discolouration. To avoid this kind of degradation, certain organotins, mainly mono and dialkylated derivatives, are added to the PVC at a level^{59,60} of 5-20 g kg⁻¹. Organotin-stabilized PVC has numerous applications including packaging materials, foils, piping of potable water, wastewater and drainage water, window frames and coating materials.

Leaching of organotins from PVC pipes with a length of 46 m lead to a concentration of 35 mg (Sn)/m³ in the water after first use and to a subsequent constant release of 1 mg (Sn/m³). Several studies have shown that leaching of organotin ingredients from PVC and related materials lead to the contamination of foodstuffs, beverages, drinking water, municipal water and sewage sludge⁶⁰⁻⁶². An ordinary plastic product produced was also analyzed by Takahashi *et al.*¹⁵, TBT were detected.

Butyltin (BT) from supermarket were detected in 50 % of the plastic product samples including baking parchements made by siliconized paper, gloves made of polymethane, sponges for dish washing and cell phone film for foodstuffs. The transfers of this pollutant to foodstuffs were confirmed

by analyzing the cookies, which were baked on the investigated baking parchment. Methyl butyltin, DBT and TBT were detected by the authors respectively in these cookies. This means that high temperature is not sufficient enough to eliminate butyltin compounds. It is also worth to note that significant amount of butyltin, remained in the baking parchment after cooking in the oven.

Since we have little knowledge especially in Africa about chemical leaching of organotin compounds mobilized by degradation of PVC materials in dumping sites. The ever growing production and use of PVC and its consequent disposal will lead to an accumulation of mono-alkylated organotin derivatives in the environment and possible long term effect on man and biota⁶³.

Agriculture: Until recently, investigations concerning environmental pollution by organotin compounds have focused primarily on TBT used in antifouling paints. Freshwater and soil contamination by organotin compounds has received less attention. However, the agricultural and biocidal application of organotin compounds probably give rise to a significant portion of the pollutants in the environment, due to their direct input into soil, water and air by spraying, leaching and runoff. Since 1960, both triphenyltin hydroxide and triphenyltin acetate has been used to control fungal diseases causing potato blight (leaf spots) on sugar beets, carrots, onions and rice and used also to prevent tropical plant diseases in peanuts, pecants, coffee and cocoa⁶⁴.

In general, the agricultural use of organotin containing pesticides represents also another potential source of environmental pollution. They are mostly applied by spraying, which means that the surrounding can also be contaminated. It is well known that triorganotins are strongly adsorbed onto soil particles. Little knowledge is known about the degradation rates and desorption processes of these compounds under soil conditions. An entrance of organotin compounds into surface water due to runoff has to be taken into account⁶¹.

Antifouling coatings: Organotin (OT) compounds have been used extensively in boat paints since 1960 because of their excellent and longer lasting antifouling properties³. Due to biocide components which are released only at the paint surface, the releasing rate is low and this results in antifouling lifetimes of 5-7 years. Surface treated with modern TBT-based copolymer paints are designed to reach a constant TBT leach rate of 1.6 µg cm⁻² per day (Sn). The leach rate of freshly painted surfaces will be as high as 6 mg cm⁻² per day (Sn) and is reduced in several weeks to the desired constant rate⁶⁵. For

example during a 3 days stay in a harbour, a commercial ship, leaching TBT at the constant leach rate, can release more than 200 g TBT into water. If freshly painted, this can be resulted in dissolved TBT contamination of the surrounding water ranging between 100 and 200 ng L⁻¹ or *ca.* 600 ng L⁻¹ (Sn), respectively⁶⁵. These are the reason why major harbours or other facilities where ship building, repairing and repainting have been contaminated by TBT pollution. This acute toxic chemicals (TBT) compound which is the active ingredient in antifouling paints thus affects the aquatic organisms ever introduced into the water.

Toxicity of organotin compounds: Tributyltin compounds are extremely toxic substances belonging to the organotin group. Besides, the toxicity evaluation of commercially important organotin stabilizers found in PVC medical devices, there have been many investigations concerned with the toxicity of all types of organotin compounds. The toxicity of alkyl and aryltin derivatives has been recognized for a long time and is primarily due to the solubility of these organotin fluids. Triethyltin derivatives were indentified as the toxic contaminant in stalinon which resulted in neurological symptoms in many of the afflicted patients. Triethyltin appeared to be the work active, producing muscular weakness followed by some recovery⁶⁶.

Tributyltin is extremely toxic to aquatic organisms. It may cause imposex and calafication abnormalities in mollusk⁶⁷.

Toxic lesions among laboratory and process workers handling di- and tributyltin compounds were typical acute skin burns, caused by the colourless di- or tributyltin dichloride⁶⁸. Ingestion of fruit juices containing high concentrations of tin. The major symptoms and signs are nausea, vomiting, diarrhoea fatigue and headache⁶⁹. Inhalation of triphenyltin caused acute intoxication in man. Tetraalkyltin also caused muscular weakness and paralysis followed by respiratory failure⁷⁰.

Tetraorganotins are very stable molecules with low toxicity and low biological activity. They can be metabolized to toxic triorganotin compounds. Triorganotin are also very toxic, Tri-*n*-alkyltins are phytotoxic and therefore cannot be used in agriculture. Depending on the organic groups, they can be powerful bactericides and fungicides. Both Diorganotins and monoorganotins have low toxicity to mammals^{55,71}.

Despite the toxicity and lots of environmental effects of organotin compounds. There are comparatively few clinical observations and epidermiological data concerning the effects of inorganic tin compounds on man and even fewer on the effects of organotin compounds. Therefore the EC, banned, TBT-containing paints due to the evidence of their extremely hazardous nature Bottom-dwelling organisms in particular are exposed to this contamination. Tin in its inorganic form is generally acceptable as being non toxic, but the toxicological pattern of organotin is very complex.

However, the biological effects of the substances depend on both the nature and the number of the organic groups bound to the Sn cation. Tributyltin is an agent showing a high toxic effect to aquatic life. Even at low nanomolar aqueous concentrations (1-2 ng L⁻¹) TBT causes chronic and acute poisoning of the most sensitive aquatic organisms, such as algae, Zeroplankton, mollusks and the larval stage of some fish⁷².

Lethal concentrations are in the range of 0.04-16 µg L⁻¹ for short term exposure, depending on the aquatic species⁷³.

Organotins: Levels of contamination: Despite the global ban on the application of organotin compounds as biocides as it was shedulled by IMO to begin in January 2003. The convention has however, not yet been enforced and the use of the compounds continues in several countries especially in Africa where increase in usage of organotin products still continuing to date. Since the first reports on the environmental contamination of organotin compounds in the early 1970s, considerable amount of research has been performed worldwide on organotin compounds in the environment. However, only a handfull of studies on organotin contamination has been carried out in the gulf region⁷⁴.

The biological effects of organotin compounds have been described in many areas of the Brazilian coasts. It has been always related that organotin compounds present in many centers where maritime activity such as harbours, shipyards and marinas are carried out. Relative high concentrations of organotin compounds have been detected in sediments and organisms in the two most important areas of maritime activity in Brazil⁷⁵⁻⁷⁸. This situation shows the need to assess the possible health risks for human populations, arising from ingestion of contaminated sea foods.

In the NIN Mediterranean Borghi *et al.*¹⁰ worked on organotin compounds present in deep sea fish. It was shown that organotin compounds are even present in deep sea marine organisms^{10,79}. They found that the concentraion of TBT in different tissues of several deep sea fish species collected between 1000 and 1800 m depth in the NW Mediterranean are comparable to levels found in coastal fish. In addition, deep-sea fish contained much higher levels of phenyltins, particularly TPT, than previously reported concentrations in shallow water organisms⁷⁹. Their results established the long-range transport of organotin compounds to the deep-sea environment and the subsequent exposure of fish inhabiting non-point source areas. They attributed the high residual levels of TPT detected in deep-sea organisms to the use of TPT in agriculture or as an anti-fouling agent, its transport to the deep-sea environment associated with particulate matter and the non-biodegradable nature of TPT in the food chain⁷⁹.

In France, Ruiz *et al.*⁸⁰ found that the oyster farming industry at Arcachon bay nearly collapsed due to the effects of TBT on the reproductive cycle of oysters. France is the first country⁸⁰ to introduce legislation prohibiting the application of tributyltin (TBT) paints to small (L 25 meter) vessels in 1982 after establishing the link between TBT and the fall of oyster production at Arcachon bay from 10,000-15,000 tons per year in the mid seventies to 30,000 tons in 1981.

Donard *et al.*⁸¹ pointed out that organotin compounds affect all facets of the ecosystem and that they should be listed as global pollutants similar to polychlorinated biphenyl. Mercury and polychlorinated dibenzodioxins owing to their efficiency as endocrine disrupters, even at very low concentrations. Donard *et al.*⁸¹ suggested that trisubstituted organotin compounds should be at the top of the list of priority pollutants.

Sentosal *et al.*⁸², recently noted the usage of ion pair reversed phase chromatography (IP-RP) techniques for the

speciation of dibutyltin (DBT), tributyltin (TBT) and triphenyltin (TPT). Organotin compounds were detected and the capacity factors (k_1) for DBT, TBT and TPT species were 0.27, 2.54 and 5.92, respectively. While the selectivity for DBT-TBT and TBT-TPT were 9.76 and 3.50, respectively.

Federico *et al.*⁸³ reported levels of organotin pollution. They carried out systemic measurements of both tributyltin (TBT) and dibutyltin (DBT), in sediments along different locations in the inner zone of Bahia Blanca Estuary. Two samples were taken near the main dry dock facility, at Peutro Belgrano naval base, in Argentina. Tributyltin concentrations from non-detected to 170.3 ng g⁻¹ Sn were measured in the inner region of the estuary and higher one of 3.288 ng g⁻¹ Sn near the dry dock at Peuto Belgrano. DBT values ranging between non-detected and 7.52 ng g⁻¹ Sn were obtained along the principal channel, but extreme concentration of 1.645 ng g⁻¹ was measured at Puerto Balgrano. These values show that this estuary is affected by organotin pollution, mainly in areas of heavy shipyard activities.

Jiayang *et al.*⁸⁴ reported field studies on trophic magnification factors (TMF) of TBT and TPT in a marine foodweb. TBT, TPT and their metabolites in plankton five benthic invertebrate species and six fish species collected from Bohai bay, North China were determined and was found that the concentration of TPT in marine fish were unexpectedly higher than those of TBT. A positive relationship was found between trophic levels and concentration of TPT indicates trophic magnification of TPT in this foodweb. Analysis of organotin in the

water and surface sediment from Bohai bay revealed low inputs of TPT to the environment, which indicated that the high concentrations of TPT found in fish Bohai bay, were done to the food web magnification of TPT. However, exhaustive information on the level of contamination by these pollutants can be seen in Tables 3-5. This information may be useful to know the level of distribution and to evaluate the harm caused by these pollutants.

Analytical methods: Sample preparation techniques for speciation analyses generally consist of several steps¹²². The necessary steps depend on the physico-chemical properties of the analytes to be determined and of matrix (water, sediment and biological materials) to be analyzed. However, the suitability of the sample preparation steps with the chosen determination technique must also be assured. Each analytical step needed in such determinations (*e.g.*, derivatization, extraction, separation and detection) can affect the accuracy and precision of the final quantitative speciation results¹²³⁻¹²⁵.

To provide time-resolved introduction of the analytes into the detector, a selective and sensitive detector coupled with some chromatographic separation step *i.e.* high performance liquid chromatography (HPLC), gas chromatography (GC), gel electrophoresis (GE) are required¹²⁶. A significant number of various instrumental techniques are reviewed in the literature for the determination of organotin compounds¹²⁶⁻¹²⁹. The most commonly applied techniques over the past year have been based on gas and liquid chromatographic separation followed by different types of detectors¹³⁰.

TABLE-3
BUTYLtin COMPOUNDS IN SEDIMENTS (ng Sn (g dw)⁻¹ UNLESS INDICATED OTHERWISE)
REPORTED FOR SEVERAL REGIONS IN THE WORLD

Sampling location	Year	MBT	DBT	TBT	Ref.
American harbours and marinas					
West and east coast, Canada	1995	< d.l-330	< d.l-1100	< d.l-5100	85
Crystal Lake, US	2001-2003	21.3-320 ^a	59-350 ^a	1.5-14,000 ^a	86
Asian and Oceanian harbour and marinas					
Port of Osaka, Japan	1995-1996	< d.l	< d.l	10-2100	87
Coast, Malaysia	1997-1998	5.0-360 ^{a,b}	3.8-310 ^{a,b}	2.8-1100 ^{a,b}	88
Great Barrier Reef World Heritage Area, Australia	1999	< d.l-1.61	< d.l-7.1	< d.l-1275	89
Alexandra harbour, Egypt	1999	< 0.1-186	< 0.1-379	1-2076	90
Kochi harbour, India	2000-2001	< d.l-470 ^b	n.a	16.4-16,816 ^b	91
Mumbai harbour, India	2000-2001	< d.l-131 ^b	n.a	4.5-1193 ^b	91
Fishing harbours, Taiwan	2001-2004	n.a	n.a	2.4-8548 ^b	20
West coast, India	2002-2003	n.a	< d.l-469	5-2384 ^b	92
North coast of Kyoto, Japan	2003	4.3-22	2.3-23	1.2-19	12
Coast, Vietnam	2003	3.9-30	8.1-42.7	8.3-51	25
Sanricu coast, Japan	2005	< d.l-3300	< d.l-3400	2-14,000	93
European harbours and marinas					
West coast, France	1993	25-74	9-29	7-30	94
River Thames, UK	1994	12-172	12-219	1-60	95
South west coast	1998	2.5-95	2.1-284	1.2-130	96
Tagus Estuary, Portugal	1998-1999	n.a	n.a	5.4-35 ^b	97
Danish harbours and marinas, Demark	1998	n.a	n.a	100-5000 ^b	98
North west Sicilian coast, Italy	1999-2000	< d.l	< d.l	3-27	99
North east coast, Spain	1995-2000	5-1131	47-3519	51-7673	100
Coast, Portugal	1999-2000	< 5.2-78	< 5.3-65	< 3.8 -12.4	24
North coast, Spain	2000	860-2870 ^a	150-710 ^a	50-5480	101
South west, France	2001	1.0-125	< d.l-8.7	< d.l-89	102
Barcelona harbour, Spain	2002	35-440	67-2607	98-4702	103
North west coast, Spain	2005	0.7-3.8	0.5-357	0.6-303	104

MBT = monobutyltin; DBT = Dibutyltin; TBT = tributyltin; < d.l = below detection limit; n.a = no data available

^aWet weight; ^bng organotin instead of Sn; ^cIt is not specified whether concentration is given on basis of dry or wet weight

TABLE-4
BUTYLTIN COMPOUND IN SEAWATER (ng S nl⁻¹) REPORTED FOR SEVERAL REGIONS IN THE WORLD

Sampling location	Year	MBT	DBT	TBT	Ref.
American harbours and marinas					
West and east coast, Canada	1995	< d.1, -460	< d.1,-270	< d.1,-500	85
Asian and Oceanian harbour and marinas					
Coast, Korea	1997-1998	< d.1-13.4	< d.1-22.3	< d.1,-4.5	105
North coast of Kyoto, Japan	2003	2.5-23	2.1-13	3.9-27	12
European harbours and marinas					
South west coast, Spain	1993	< d.1.-51	6.8-20	9.1-79	96
South east coast, France	1998	-	-	< 0.015-0.12	106
Coastal waters, Greece	1998-1999	< d.1.-19	< d.1.-159	< d.1.-70	107
North west coast, Spain	Not provide	0.8-11.6	0.3-33.7	0.4-196.6	108

MBT = Monobutyltin; DBT = Dibutyltin; TBT = Tributyltin; < d.1 = below detection limit.

TABLE-5
BUTYLTIN COMPOUNDS IN BIOLOGICAL TISSUES (ng Sn (g dw)⁻¹ UNLESS INDICATED OTHERWISE

Sampling location	Year	Biological sample	MBT	DBT	TBT	Ref.
American harbours and marinas						
Coast, Canada	1995	Mussel	< d.1. -708	< d.1, -1062	20-1198	85
	1996	Mussel	-	-	< 1440 ^{a,b}	109
Asian an ocean harbour and marinas						
Japan sea, Japan	1991	Walley pollock	< 3 ^a	< 2.5 ^a	2.2-6.4 ^a	110
Bangladesh	1994	Fish	< 5.6-170 ^{a,b}	< 0.36-15 ^{a,b}	0.47-3 ^{a,b}	111
Aomori, Japan	1996	Fish	< d.1,-20 ^{a,b}	< d.1, -50 ^{a,b}	< d.1, -240 ^{a,b}	112
Coast, Korea	1997-1998	Vivalves	< d.1, -461	23-699	16-1610	105
Coast, Korea	1997-1998	Starfish	51-2860	8-139	7-323	105
Coast, Malaysia	1998	Fish	2.3-7.4 ^{a,b}	< 1.3-13 ^{a,b}	2.4-190 ^{a,b}	113
Aqua culture area, Taiwan	2002	Oyster	< 3.3- 407 ^{a,b}	< 3.9-281 ^{a,b}	< 3.8-417 ^{a,b}	114
North coast of Kyoto, Japan	2003	Mussel	0.8-2.9 ^a	0.8-3.1 ^a	0.8-11 ^a	12
Coast, Vietnam	2003	Clam	2.8-18	4.4-27	3.8-15	25
Coastline of Hong Kong, China	2004	<i>T. clavigera</i>	< d.1,-336	< d.1,-19.7	< d.1,-18	115
Coastline of Hong Kong, China	2004	<i>T. luteostoma</i>	< d.1, -51	< d.1. -8.5	3.8 -170	115
Sanrieu coast, Japan	2005	Mussel	4-32	3-92	3-287	93
European harbours and marinas						
Northwestern Mediterranean, Spain	1996	Deep sea fish	< d.1-54 ^a	4.0 -67 ^a	1.0-52 ^a	116
River Elbe and North Sea	1993	Fish	< d.1.89 ^{a,b}	< d.1, -55 ^{a,b}	66-490 ^{a,b}	117
The Netherlands	1993	Fish	23-41 ^{a,b}	13-183 ^{a,b}	9.2-67 ^{a,b}	118
South west Coast, Spain	1993-1994	Oyster		59.3±21.3	269±96	96
Strait between Denmark and Sweden	1997	Vivalve	2.5-15 ^b	-	200-300 ^{a,b}	119
Baltic Sea, Poland	1998	Mussel	< 1.4-4.7 ^a	< 1.4-24 ^a	2.2-39 ^a	120
South west coast, Spain	1999	<i>H. trunculus</i>	63	85	48	96
Coast, Portugal	1999-2000	Mussel	< 7.9-41	< 2.5-18	< 5.7-489	119
Northwestern Sicilian coasts, Italy	1999-2000	<i>H. trunculus</i>	< d.1,-167	< d.1, -316	< d.1,-91	120
West coast, Portugal	2000	Mussel	< 10-605	< 10-345	11-789	121
Aegean Sea, Greece	2001-2003	Bivalves	< d.1,151	< < d.1-366	< 5.7-489	24
North west coast, Spain	2005	Oyster	0.4-12.9	7.6-441	74-193	104
North west coast, Spain	2005	Mussel	52.8-96.1	20.2-25.7	52.8-96	104

MBT = Monobutyltin; DBT = Dibutyltin; TBT = Tributyltin; < d.1 = below detection limit; n.a = no data available

^aWet weight; ^bng organotin instead Sn.

Speciation of organotin compounds in sediment and biota may present difficulties during extraction such as the process of isolating the targets chemical compounds from complex cell structures and biomolecules and the number of possible errors is much higher. Generally the applied extraction procedures of organotins in solid samples are Soxhlet, mechanical shaking and use of sonication bath, microwave and pressurized liquid extraction (PLE)¹²⁴. The most frequently adopted methods for organotin extraction from sediment are leaching with acids (acetic acid or hydrochloric acid) or acid polar solvent (methanol) mixtures¹³¹.

Organotin compounds are present in water at ng L⁻¹ levels; their quantification requires highly sensitive techniques and

collection of larger sample volumes together with the application of pre-concentration methods. The high salt content of seawater may pose difficulties in the determination step and the complete validation of organotin analysis in seawater samples is far behind achievement sequel to reproductivity problems¹³². Generally, the applied method for organotin analysis in seawater are (i) direct derivatization with organo-carbonates or hydride in an acidic medium followed by liquid-liquid extraction (LLE) (ii) liquid-liquid extraction with non-polar solvents (toluene, dichloromethane) alone or in mixture and in the presence or not of acidic conditions and subsequent derivatization¹³³.

After derivatization GC separation followed by different detection techniques such as GC-MS, GC-MS-MS, GC-FID,

ICP-MS or flame photometry (GC-FPD) for the determination of the species¹³³⁻¹³⁶. Furthermore, good enhancement is achieved from extraction of organotin from the aqueous to organic phase by the addition of a complexing agent such as tropolone or carbamates^{124,133,137}. In addition, LLE is the less preferred method for solvent extraction because its procedure is time consuming and preconcentration factors achievement is very low. Liquid-liquid extraction can be applied to non-filter samples and does allow transfer of analyte to organic solvent (*e.g.*, hexane, toluene) for subsequent analysis.

Solid-phase extraction involves passing the liquid sample through a solid adsorbent that retains the analytes by mechanism of retention which includes adsorption, chelation, ion-exchange or ion-pair and subsequent recovery upon elution with an appropriate solvent. The advantage of SPE is that, it is fast and sensitive, robust, ease of use, less solvent consumption, possible integration of columns and cartridges in on-line flow injection systems and possible application as species storage device for field sampling. Solid-phase extraction is based on the partition equilibrium of target analytes between a polymeric stationary phase attached onto a fibre and the sample matrix, combining analyte extraction and preconcentration in a single step. The analyte is then desorbed from the fibre at very high temperature into an appropriate separation and detection system.

Presently, SPME application consists in analyte ethylation and headspace extraction. Thus, SPE and SPME meet modern requirements for analysis following point sampling. Following extraction methods for the determination of organotin compounds should provide sufficient sensitivity and selectivity. Most reported techniques so far combine a separation technique such as gas chromatography (GC), coupled to element-specific detection systems including atomic absorption spectrometry (AAS)^{138,139}, flame photometric detection (FPD)^{140,141}, pulsed flame photometric detection (PFPD)¹⁴² or inductively coupled plasma mass spectrometry (ICP-MS)¹⁴³⁻¹⁴⁵.

For GC analysis, a derivatization step is necessary prior to separation, due to the low volatility of the target compounds.

The conversion of ionic alkyltins into species that can be analyzed by gas chromatography can be into two categories, those based on *in situ* hybridization (with sodium borohydride NaBH₄ or alkylation with sodium tetraethyl borate (NaBEt₄)¹³³. *In situ* hydride generation with sodium tetrahydroborate (NaBH₄) as described by Cai *et al.*¹⁴⁶ considers only methyl- and butyltins with appropriate recovery rates. Compounds with higher boiling points such as phenyltins cannot be analyzed after using NaBH₄¹⁴⁷. Sodium tetraethylborate has become very popular as a derivatization reagent during last years.

This method makes the sample preparation faster and easier because it enables an *in situ* derivatization and following extraction of the ethylated organotin compounds into an organic phase (hexane, isooctane) which is subsequently analyzed. The exact method and description of sample preparation is given elsewhere^{148,149}.

Recently, sodium tetra(*n*-propyl)borate (NaBPr₄) was introduced as a derivatization agent¹⁵⁰, a comparison with NaBEt₄ and NaBPr₄ gave similar derivatization reagents¹⁵¹. In general, proper validation of the sample treatment has been the remaining problems for a variety of biological environmental samples due to the lack of matrix that matched certified

reference materials (CRM). Currently, there are six CRM for tin species, one for fresh water sediment (BCR-CRM 646), certified for MBT, DBT, TBT, monophenyltin (MPT) and diphenyltin (DPT), triphenyltin (TPT), one for a coastal sediment (BCR 462) certified for DBT and TPT, one for harbour sediment (NRCC-PACS-2) certified for MBT, DBT and TBT as Sn, one for marine sediment (NIST-SRM 1941b) certified for MBT, DBT and TPT and one for one mussel tissue (BCR-CRM 477) certified for MBT, DBT and TBT^{124,152}.

Recently, Camilla *et al.*⁷⁶ used two analytical methods for the determination of butyltin compounds in mussels. Both methods include extraction with methanol containing tropolone, derivatization, purification on florisil and GC-MS analysis. The main difference between the procedures is in the derivatization step: one employs a Grignard reagent (*n*-pentyl-magnesium bromide) while the other uses sodium tetraethylborate (STEB). Quantitative determinations were carried out in single ion monitoring using tripropyltin as internal standards. The accuracy of the procedures was verified on a certified reference material (ERM 477), providing good results for both methods.

All the considered compounds showed lower detection limits with STEB derivatization; in particular for tributyltin (TBT), the difference between the methods overcame one order of magnitude. An *in vivo* experiment was then performed exposing mussels *Mytilus galloprovincialis* to known amount of TBT for 7 days; control and contaminated tissues were analyzed using the STEB derivatization method. Results showed the accumulation of TBT, especially in the gills. New sampling approaches are required to provide large scale time weighed average data on tin distribution in order to assess long term and diffuse contamination. In Brunori *et al.*¹³², Dietz *et al.*¹³³ and Nemanic *et al.*¹⁵³ wide and full detailed information on organotin sample preparation can be obtained.

Conclusion

The increase percentage of organotin compounds in environmental samples have raised much concerns and unpalatable. Various applications and sources of organotin compounds including environmental levels, toxicity as well as analytical methods of determination have been reviewed. As a result of lack of enforcement on the control of organotin compounds in the marine environment, especially in Africa, there is need to carry out detailed environmental assesment of organotin compounds in both phases of marine water (water and sediment) as well as biota samples so as to know the concentrations levels of these pollutants in marine water samples. This will further breach the information gap identified in this work. Thus, it remains necessary to investigate the environmental impacts as well as human health risks posed by these contaminants.

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