

Fate and Remediation of Organotin Compounds in Seawaters and Soils

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Abstract: Organotin compounds are chemical compounds based on tin with hydrocarbon substituent used in manufacturing industries, especially the antifouling paint industries. These paints are used to prevent the growth of fouling organisms on marine structures and vessels. They are directed at organisms that settle on solid surfaces after a period of mobility in the sea. Organotin antifouling paints are thus exceptional toxic and they interfere with biological processes in a diverse range of species and as a result been banned in many countries around the world. However, these paints are still applied to large shipping vessels while some third world countries are still utilizing them on smaller vessels. There is therefore a need to prevent a significant part of the introduction of antifouling compounds into the marine ecosystem by treatment of shipyard and antifouling paint industrial wastewaters to about 99% reduction on its concentration before discharge into the marine ecosystem.

Keywords: Seawater and soil, Organotin compounds, Tributyltin chloride, Triphenyltin, Biocides, Antifouling paint, Remediation

Introduction

Organotin compounds (OTC) are chemical compounds based on tin with hydrocarbon substituent¹. OTC are characterized by the presence of a strong carbon-tin bond and have the general formula: $R_x SnL_{(4-x)}$, where R denotes an organic alkyl or aryl group and L denotes one or more organic (or sometimes inorganic) ligands, which may or may not be the same. In general, the properties of OTC vary significantly, depending upon their structure. Thus, while the carbon-tin bond is strong, the association with the ligands is less and so has a tendency to undergo dissociation both in use and in the environment. The first organotin compound was diethyltin diiodide, discovered by Edward Frankland in 1849², other OTC include tetrabutyltin (TTBT), tributyltin (TBT), triphenyltin (TPT), tetraethyltin, trimethyltin *etc.* TTBT is a stable organotin compound, combustible and colourless liquid at room temperature. It is a starting material of TBT and DBT compounds while TBT and DBT are

in turn used for a wide range of OTC used as PVC stabilizers, biocides, fungicides and anti-biofouling agents¹. Concerns over the toxicity of these compounds have led to a worldwide ban by the International Maritime Organization. TBT is considered a severe marine pollutant, Table 1 and 2 shows the physical properties of TBT and some triphenyltin (TPT) compounds while the chemical properties of some organotin chlorides are provided in Table 3.

Table 1. Physical properties of tributyltin compounds

Parameters	Bis(<i>n</i> -tributyltin)oxide	Tributyltinchloride
Solubility	4 mg L ⁻¹ (20 °C, pH 7) ^a 18-19.5 mg L ⁻¹ ^b	17 mg L ⁻¹ ^b 5.7±2.3 mg L ⁻¹ in distilled water with varying temperature ^c
Partition coefficient octanol/ water (log K _{ow})	3.7 in 32% seawater ^d	3.54 in seawater ^f
Vapour pressure (20 °C)	4.1 at pH 7 ^e 0.1 mPa at 20 °C ^a	4.2 at pH>7.4, 18% salinity ^c <1 Pa at 20 °C ^g
Organic carbon-water partition coefficient (K _{oc})	90 800	N/A

^aNLM³, ^bBlunden *et al.*⁴, ^cTas⁵, ^dLaughlin *et al.*⁵⁶, ^eWeidenhaupt *et al.*⁶, ^fWHO⁷, ^gThe Merck Chemical Databases⁸

Table 2. Physical and chemical properties of some triphenyltin compounds^a

	Triphenyltin hydroxide	Triphenyltin acetate	Triphenyltin chloride
Synonyms	Fentin hydroxides; TPTH	Fentin acetate; TPTA	Fentin Chloride; TPTC
Chemical Abstract Service (CAS) Registry No	76-87-9	900-95-8	639-58-7
Molecular formula	C ₁₈ H ₁₆ OSn	C ₂₀ H ₁₈ O ₂ Sn	C ₁₈ H ₁₅ ClSn
Molecular weight	367.0	409.1	385.5
Melting point	122-123.5 °C	122-124 °C	106 °C
Solubility in water (20 °C)	1 mg L ⁻¹ at pH 7	9 mgL ⁻¹ at pH 5	40 mgL ⁻¹ (pH not given)
Solubility in other solvents (20 °C)	Greater at lower pH 10 g L ⁻¹ (ethanol)	22 g L ⁻¹ (ethanol)	moderately soluble in organic solvents
	171 g L ⁻¹ (dichloromethane)	82 g L ⁻¹ (ethyl acetate)	
	28 g L ⁻¹ (diethyl ether)	5 g L ⁻¹ (hexane)	
	50 g L ⁻¹ (acetone)	460 g L ⁻¹ (dichloromethane)	
Vapour pressure	0.047 mPa (50 °C)	1.9 mPa (60 °C)	0.021 mPa
Log K _{ow}	3.43	3.43	-

^aTomlin⁹; NLM³

Table 3. Chemical properties of some organotin chlorides

	MMTC	DMTC	MBTC	DBTC	MOTC	DOTC
Chemical formula	CH ₃ Cl ₃ Sn	(CH ₃) ₂ Cl ₂ Sn	C ₄ H ₉ Cl ₃ Sn	(C ₄ H ₉) ₂ Cl ₂ Sn	C ₈ H ₁₇ Cl ₃ Sn	(C ₈ H ₁₇)Cl ₂ Sn
CAS No.	993-16-8	753-73-1	1118-46-3	683-18-1	3091-25-6	3542-36-7
Molecular weight	240.8	219.7	282.2	303.8	338.3	416
Melting point, °C	47	105	-63	40	10	47
Boiling point, °C	173	189	250	250	250	250
Solubility, g/L	1x10 ⁵	1x10 ⁵	8.2	36	0.1	1.0
Vapour pressure						
at 25 °C (Pa)	33.3	30.0	5.84	0.15	0.55	1.35x10 ⁻⁴
LogK _{ow}	-2.15	-2.18 to -3.1	0.18	1.89	2.14	5.82
K _{oc} (L/kg)	0.2	0.2; 21 537 ^a	1.76; 75 354 ^b	42.8; 61 664 ^a 223.867 ^b	68.2	65 200; 292 556 ^a
Henry's law constant						
(Pa.m ³ /mol)	0.08	0.066	201	1.27	1420	0.056
Air/water partition						
Coefficient	3.38x10 ⁻⁵	2.78x10 ⁻⁵	8.48x10 ⁻²	4.34x10 ⁻⁴	5.98x10 ⁻¹	2.37x10 ⁻⁵

MMTC – Monomethyltin trichloride; DMTC – Dimethyltin dichloride; MBTC – Monobutyltin trichloride; DBTC – Dibutyltin dichloride; MOTC – Mono-octyltin trichloride; DOTC – Dioctyltin dichloride ^aTerytze et al. ¹⁰; ^bBerg et al. ¹¹

Tin in its inorganic form is accepted as being non-toxic¹², but the toxicological pattern of OTC is very complex. The biological effects of the substances depend on the nature, number and type of organic groups R (alkyl or aryl group) bound to the Sn cation. Inorganic anion plays a secondary role. It has been established that the toxicity of OTC is the highest for triorganotins. Therefore, eco-toxicity increases dramatically in the order MBT < DBT < TBT. It should be noted that TBT is more toxic than TPT.

Tetraorganotins are very stable molecules with low toxicity and low biological activity. They are unusable as biocides, but they can be metabolized to toxic triorganotin compounds. They are used as starting materials for catalysts. Tri-*n*-alkyltins are phytotoxic and therefore cannot be used in agriculture. Depending on the organic groups, they can be powerful bactericides and fungicides. TBTs are used as industrial biocides, *e.g.* as antifungal agents in textiles and paper, wood pulp and paper mill systems, breweries and industrial cooling systems and are also used in marine anti-fouling paint. TPT are used as active components of antifungal paints and agricultural fungicides. Other triorganotins are used as miticides and acaricides. Diorganotins have no antifungal activity, low toxicity and low antibacterial activity, except for diphenyltins. They are used in polymer manufacturing, as PVC heat stabilizers, catalysts, in the manufacturing of polyurethane and silicone curing. DBT is however immunotoxic, and has a link to auto-immune related diseases. Monoorganotins have no biocidal activity and their toxicity to mammals is very low, they are used on glass containers in Hot End Coatings (HEC). Methyltin, butyltin, octyltin and monoestertins are used as PVC heat stabilizers. 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.

Organotin antifouling paints

Organotin-based antifouling paints are highly effective against fouling organisms, and their application results in a large amount of savings for the shipping industry¹³. TBT - based paints are described as the most effective antifouling paints ever devised for use on boat hulls¹⁴, on the contrary, they have been described as the most toxic substance ever introduced into the marine environment, especially since they are directly released into the aquatic environment. These organotin-based antifouling paints are used to prevent the growth of fouling organisms on marine structures and vessels. The paints are directed at organisms, which are essentially any marine organisms that settle on solid surfaces after a period of mobility in the sea. The growth of fouling organisms on the hulls of vessels adversely affects the movement of vessels in water, resulting in increased fuel costs and transit time for the shipping industry. Fouling organisms can also interfere with the operation of submerged equipment and lead to the increased corrosion of marine structures. A consequence of the effectiveness of organotin antifoulants is their exceptional toxicity to 'nontarget' marine organisms¹⁵. They interfere with biological processes in a diverse range of species.

High concentrations of TBT found in marines are associated with growth abnormalities in mussels and oysters and a decline in their abundance. Recent scientific studies have also found high elevations of OTC in the tissues of marine mammals and the presence of organotin has been linked to mass mortalities of marine mammals (seals, dolphins) through the weakening of their immune systems. It causes the superimposition of male genital organs (penis and vas deferens) on female gastropods, this is known as imposex. Imposex is cause-specific and occurs at low concentrations of TBT and TPT. Reproductive failure is known to occur in severely affected stages. Imposex has been reported all over the world for more than 140 species. The main cause of population decline in at least seven of these species is considered to be reproductive failure related to imposex¹⁶. Calcification anomalies in mollusks is also known to be caused by TBT. In human, exposure to seafood is the likely source of TBT¹⁷.

Metabolism of organotin compounds

In general, OTC are more readily absorbed from the gut than inorganic tin compounds; allowance must be made, however, for the great variations found between different compounds and different species. As a rule, tin compounds with a short alkyl chain are more readily absorbed from the intestinal tract. The trialkyltin compounds are usually well absorbed through the skin. As far as distribution is concerned, the highest concentrations in rats, guinea pigs, rabbits, and hamsters have mostly been detected in the liver. Trisubstituted OTC have been found in the brain of various species but the form of tin present in the brain has not been satisfactorily identified.

Many OTC are transformed, to some extent, in the tissues. The dealkylation and dearylation of tetra-, tri- and disubstituted OTC seem to occur in the liver, but the dealkylation of diethyltin compounds appears to take place both in the gut and in tissues of other organs. The mode of excretion of OTC largely depends on the type of the compound. For example, ethyltin trichloride seems to be mainly excreted with the urine, but diethyltin is eliminated with the faeces, urine, and the bile. Triethyltin is not only excreted with the urine, but, at least in lactating sheep, also with the milk. The route of excretion for many compounds is not known. The biological half-time of different OTC varies and many compounds are slow to disappear from the organs. Usually the biological half-time seems to be longer in the brain than in other organs¹⁸.

International controls on organotin antifouling paints

Because of the highly toxic effect on the marine environment, TBT restrictions apply in many countries around the world. The notifiable chemical order in victoria restricts the sale, supply and application of organotin antifouling paints. Countries of the European Union, Canada, Scandinavia and South Africa have banned the use of TBT on vessels less than 25 metres in length. Japan and New Zealand have banned the use of TBT antifouling paints on all vessels. Therefore, the international of marine organization (IMO) prohibited the use of such OTC as antifouling biocides after 1st January 2008¹⁷. This has resulted in highly restricted worldwide application of organotin antifouling paints to vessels less than 25 metres in length. Although tightened controls on the application of organotin antifouling paints to small vessels have been positive in reducing the TBT load to the environment, organotin paints are still applied to large shipping vessels (*e.g.* tankers and container ships) while it is still widely used in third world countries. The release of TBT from these vessels thus remains a significant environmental concern.

Fate of organotin compounds

The persistence of OTC in polluted ecosystems is a function of physical (adsorption of suspended solids and sediment), chemical (chemical and photochemical degradation) and biological (uptake and biological degradation) removal mechanisms. Thus, it is important to study the distribution, remediation and the degradation processes of these pollutants under natural condition.

A sequential removal of the consecutive organic groups from the organotin molecule until reaching a complete metamorphosis into inorganic and non-toxic Sn(IV) can be transcribed as follows¹⁹:



Degradation takes place under the influence of radiation (light, UV, gamma), biological as well as chemical factors. Photolysis is considered the fastest degradation process of OTC in the aquatic environment. It has been established that photolysis is faster in phenyltin derivatives as compared to butyltin compounds. The degradation of OTC may also occur as a result of interactions among molecules of nucleophilic and electrophilic character and the polarized Sn-C bond of an organotin compound.

The most important mechanism of TBT elimination from sediment is biodegradation. It has been established that biochemical degradation due to microbial activity (*i.e.* activity of bacteria, algae and fungi) is faster in the water column as compared to sediment. This results from the higher light intensity and better oxygenation of the water column in comparison to sediment. The half-life of OTC in seawater ranges from a couple of days to a couple of weeks. In the case of TBT, it may reach 15 days, while for DBT and TPT 10 up to 60 days, respectively²⁰.

Organotin degradation can also involve the sequential removal of organic moieties to yield less toxic derivatives, *e.g.* debutylation of TBT compounds to di- and monobutyltins. Such degradation is known to take place in bacteria, algae and fungi and this provides one route for detoxification. Table 4 shows a data on degradation of TBT and TPT compounds. The reverse process to degradation is methylation. Methyltin derivatives form in the marine environment via biomethylation, *e.g.* biomethylation of inorganic tin by sulphur bacteria which results in the presence of mono- and dimethyltin in benthic sediments.

Table 4. Data on degradation of tributyltin and triphenyltin

Compound	Half life	References	
TBT	Half-life water DT ₅₀	days to months	
	Half-life sediment DT ₅₀	> 1 year	
	Half-life soil DT ₅₀	40-70 days	
	Half-life soil DT ₅₀	4 – 40 weeks depending on the type of soil	US EPA ⁵⁴
	Half-life water DT ₅₀	Several days in June and 2-3 weeks in November	Soderquist and Crosby ⁵⁵

Biomethylation

Methyltin compounds are widely found in the environment, although it is usually difficult to ascertain the proportions that arise from anthropogenic sources, abiotic or biotic methylation reactions, or the degradation of complex OTC, including tributyl derivatives. Several biotic and abiotic methylation agents are known. They include methycobalamin and methyl iodide. Methylcobalamin (CH₃B₁₂) is a carbanion donor and is able to convert inorganic Sn(IV) to several methyltin species, methyl iodide (CH₃I) which is produced by certain algae and seaweeds can also methylate inorganic Sn(II) salts in an aqueous medium to produce monomethyltin species while certain *Pseudomonas* bacteria are also able to form various methyltin compounds.

Bioaccumulation and soil/sediments trap of organotin compounds

Most studies on bioaccumulation deals with TBT because of its extremely toxicity to several organisms. Some marine bacteria display a remarkable ability to accumulate OTC. Research on TBT accumulation by aquatic invertebrate has been mostly to mollusks (bivalves) and crustaceans (decapods) because these groups are important seafood resources and are ecologically dominant in many habitats. Marine bivalves are able to accumulate significant amounts of TBT (up to > 5 µg g⁻¹) while crustaceans and fish accumulate much lower amounts of this pollutant because of their possession of efficient enzymatic mechanism that degrade TBT in the body¹. The accumulation of TBT by higher tropic aquatic organisms proceeds through either uptake from solution alone or a combination by diet ingestion. Studies have also shown that marine mammals and birds also accumulate high levels of toxic butyltins in various tissues and organs.

Large proportion of OTC are found to be associated with clay fraction of particulate matter, indicating that adsorption and concentration unto fraction is an important control fraction mechanism. Thus, soil and sediments serve as trap for OTC but to what extent have these compounds accumulated in the sediments over the last decades. The adsorption behavior of organotin species is thus important in determining the transport processes as well as their bioavailability especially to aquatic organisms. Experimental results have also shown that clay minerals and metal oxides bearing a net negative charge are effective adsorbents for OTC under environmentally relevant conditions¹.

Analysis of organotin compounds

Because of the high ecotoxicity depending on the nature of OTC alkyl groups, environmental analysis requires the specific determination of the individual OTC. But also

methods that are sensitive enough for the accurate and simultaneous determination of OTC at extremely low concentrations (low ng Sn/L) in different environmental samples are necessary. Several techniques based on species specific analytical methods have been developed for the determination of OTC in environmental matrices¹².

Hyphenated systems, based on on-line coupling of gas chromatography (GC), liquid chromatography (LC), or supercritical fluid chromatography (SFC), to mass spectrometry (MS)^{21,22}; inductively coupled plasma mass spectrometry (ICP-MS)²³; pulsed flame photometric detection (PFPD)^{24,25}; Quartz Furnace Atomic Absorption Spectroscopy (QFAA)²⁶; atomic absorption spectrometry (AAS)²⁷; tandem mass spectrometry (MS-MS)²⁸; atomic emission detector (AED)²⁹⁻³¹; flame photo detector (FPD)^{15,32} and microwave induced plasma atomic emission spectrometry (MIP-AES)³³ are in current use. Among the different techniques, the coupling of GC to ICP-MS appears to be one of the most popular techniques, due to high sensitivity and multi-elemental and multi-isotopic capabilities.

Remediation of organotin compounds

Studies have shown that the remediation of OTC could be achieved by a number of different processes³⁴ ranging from conventional biological treatment to advanced techniques such as ultrafiltration, reverse osmosis, adsorption and solvent extraction. Different studies have shown that the degradation of TBT during sludge treatment is low^{35,36}. However, microbial degradation appears to be possible, although slow, in water if the concentration of TBT is not too high³⁷. Adsorption processes proved to be the most effective means to reduce TBT concentration because the compound is highly attracted to particles in water. It is suggested that technologies such as dissolved air floatation (DAF) and activated carbon adsorption (ACA) are the best candidate technologies.

The removal of TBT from wastewater using a technology which included DAF (removal of suspended particles), sand filtration (removal of fine particles) and ACA (removal of TBT) was reported to result in a removal rate of 90 to 99.99% TBT³⁸. Weidenhaupt *et al.*⁶ investigated the sorption of triorganotin biocides from aqueous solution to mineral surfaces in batch sorption experiments using homoionic clay minerals. Fletcher and Lewis³⁹ have shown that photocatalysis using visible light and UV/oxidation are effective process for the removal of TBT from shipyard wastes. They reported that the processes produce hydroxyl radicals, which destroy TBT compounds by converting them to much less toxic dibutyl tin, monobutyltin and eventually to inorganic tin compounds. Hoch *et al.*⁴⁰ studied the adsorption and desorption behavior of TBT from aqueous solution to clay-rich sediments under various conditions (pH, salinity) using the batch technique. Sediments containing illite, kaolinite and montmorillonite in different proportions were used as sorbent materials and reported that the adsorption mechanism was controlled by the properties of the clay minerals as well as the aquatic chemistry of TBT.

The removal of TBT from artificial wastewater by dead and live cells of microalgal species (*Chlorella miniata*, *C. sorokiniana*, *Scenedesmus dimorphus* and *S. platydiscus*) was investigated by Tam *et al.*⁴¹. They reported that dead cells were more efficient in removing TBT during three days exposure. More than 90% and 85% TBT were reported to be removed by dead cells of *Scenedesmus* and *Chlorella*, respectively. They reported that the degradation products, DBT and MBT, were recorded mainly inside the cells and intracellular MBT concentrations were significantly higher than DBT. In terms of TBT removal, *Scenedesmus* cells were reported to be more effective than *Chlorella*. However, TBT specific uptake and degradation by *Chlorella* was higher than in *Scenedesmus*. Tam *et al.*⁴²

also investigated the biosorption and biodegradation of TBT by free cells of a resistant microalgal species, *Chlorella sorokiniana* at low and high densities. They reported that TBT in contaminated water was continuously removed by microalgal cells and reached a 54% and 74% removal at the end of 14 days treatment in low and high density cultures, respectively.

Daniel and Alfred⁴³ investigated the sorption behaviour of TBT from reconstituted seawater onto municipal solid waste compost. They investigated the rate of adsorption, the influence of pH and the adsorbate hydrophobicity on the partitioning process and reported that the adsorption capacity for TBT onto compost was highest at pH 6.7 and for other OTC it increased with increasing adsorbate hydrophobicity, following the trend tripropyltin < TBT < tripenyltin.

Ottosen *et al.*⁴⁴ observed a decrease in TBT concentration after coagulation with iron salts (FeCl₃ solution) while Honda and Takahashi⁴⁵ also investigated the treatment of TBT and TPT in liquid using iron oxides. They reported that the addition of iron oxide into a liquid containing an OTC allows the trapping of OTC in the liquid by the iron oxide and reduction of the OTC concentration in the liquid. A removal rate of 76% and 56% were achieved for TBT and TPT respectively.

Song *et al.*⁴⁶ reported the removal of TBT from wastewater by extraction with diesel oil. He reported that the level of TBT decreased from 4 mg L⁻¹ to 0.8 µg L⁻¹ after 5 hours of extraction time. Prasad and Schafran⁴⁷ used a full-scale process train consisting of coagulation–flocculation, dissolved air flotation, sand filtration and a series of two granular activated carbon (GAC) filters for the removal of TBT. About 50% of the TBT was reported to have been removed after the sand filtration step. The GAC filters decreased the TBT concentration further to less than 0.1% of the TBT concentration in the influent.

The performance of electrochemical treatment, coupled with activated carbon adsorption for the elimination of OTC, was evaluated by Arevalo and Calmano⁴⁸. Their results showed that the method is suitable to reduce OTC to concentrations down to the range of 100 ng Sn L⁻¹. Different anode materials were tested to evaluate their suitability to eliminate OTC electrochemically from synthetic and real shipyard water. The capacity of niobium coated with boron-doped diamond (BDD) and titanium coated with iridium dioxide, (Ti/IrO₂) was investigated. Their results showed that electrochemical treatment is suitable to eliminate OTC down to very low concentrations following a stepwise debutylation mechanism. Both anode materials exhibited a similar performance with energy consumption in the range of 7–10 kWhm⁻³ in order to decrease OTC down to 100 ng L⁻¹ (as Sn).

Haug *et al.*⁴⁹ reported the use of hydrogen peroxide (H₂O₂) as a photocatalyst to enhance the rate of photodegradation of TBT. They reported that a sufficiently strong UV source, in combination with H₂O₂ dosing (300 ppm), resulted in a reduction of the TBT concentrations in real wastewater below the discharge criterion of 100 ng L⁻¹ within a 2.5 min treatment period. These conditions are considered realistic for the application in full-scale treatment processes for wastewater streams ranging from 10 to 60 m³/h. Bioassays, however, showed no clear reduction in toxicity after the treatment. The presence of other contaminants in the wastewater stream as well as the formation of intermediates is thought to be responsible for the observed toxicity. Thus, additional treatment steps are required before the treated wastewater can be discharged.

Maes and Vreysen⁵⁰ developed and optimized a sorption-flocculation process for the removal of OTC and heavy metals from shipyard wastewater. They tested a clay-based

sorbent and powered activated carbon with artificial and real dockyard wastewater to reach a discharge limit of 100 ng Sn L⁻¹ to the effluent. They reported that the sorption-flocculation process was economically favorable at relatively low organotin concentrations (<10 mg Sn L⁻¹).

Vreysen *et al.*²⁴ investigated the removal of DBT and TBT from shipyard wastewaters by a one-step adsorption-flocculation method. They reported that the activated carbon adsorbents showed the largest ability to remove OTC from wastewater. They also indicated that OTC are mainly removed from the water by hydrophobic adsorption onto the activated carbon.

Hala *et al.*⁵¹ investigated the biosorption and biodegradation of TBT at its sublethal concentration of unicellular algae *Nannochloropsis oculata* and *Dunaliella parva*. They reported that the initial concentration of TBT in the culture media of *N. oculata* was reduced by 46% within 2 days, while in *D. parva* it decreased stepwise reaching 50% within 6 days. Both algae were reported to adsorb nearly 80% of the initial TBT content at the end of 12 days.

The adsorption of TBT to soot and two charcoals with specific surface area in the range of 62-111 m²/g have been investigated with main focus on pH effects by Fang *et al.*⁵². TBT adsorption was reported to reach a maximum at pH 6-7 for charcoals and at pH > 6 for soot. The charcoals therefore showed up to 17 times higher sorption affinities than soot.

The ability of conventional wastewater treatment processes to remove OTC has been proven in full-scale-wastewater treatment plants but the method is probably not suitable for the high concentrations of a shipyard's effluent because the activated sludge could be deactivated. Therefore, advanced techniques, such as ACA, combined with DAF or coagulation-clarification and filtration, or solvent extraction, photodegradation and electrochemical treatment would be better candidates and should be further optimized in order to meet the regulatory limits³⁷. Treating wastewaters in antifouling paint industries and shipyards by conventional wastewater treatment processes will thus prevent a significant part of the introduction of antifouling compounds into the marine ecosystem.

Conclusion

OTC are the most widely used organometallic compounds with a worldwide production volume estimated at 50000 tons. About 70% of the total amount is used as PVC stabilizers, 23% as agrochemicals and the rest as biocides in a broad application spectrum (*e.g.* antifouling paints, wood and stone treatment, textile preservation, dispersion paints, industrial water systems) and as catalysts and reactants in chemical industry. OTC are released into the environment via several pathways, of which the most important are the use as agrochemicals and antifouling paints. Although the physicochemical properties of antifouling compounds differ significantly and some are rapidly degraded, they will accumulate in marine sediments if introduced as paint particles. It is therefore preferable to dispose OTC wastewaters after treatment with 99% reduction on its concentration. The use of oxides most especially iron oxides for the remediation of OTC usually resulted to between 56-76% OTC removal⁴⁵. Vreysen *et al.*²⁴ reported powdered activated carbon to show high ability in removing OTC. Microbial remediations^{41,51} also appear to be possible but only if the concentration of OTC is not too high. Some of the available organotin remediation techniques take between 1-2 weeks of adsorption processes before notable percentage of OTC could be removed. There is therefore a need for a better form of remediation processes, *viz.*, suitable adsorbent that will bring about 99% reduction on

organotin concentrations in wastewater before discharge into the aquatic environment and in seawaters and soils. We are presently working on the use of composite materials involving activated carbon, fly ash and nano materials for the adsorption of OTC in wastewater, seawaters and in soils. The use of these composites is expected to combine the adsorption characteristics with magnetic and catalytic properties of metal oxides and will thus prove more efficient to the adsorption of OTC as compared to previously reported techniques.

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