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Organotin Compounds and the Environment

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ABSTRACT
Organotin compound that have at least one Sn-C bond have wide commercial applications as PVC stabilizer, antifouling agent in paint and as agrochemicals. The general formula for organotin compounds is R_4SnX_{4-n} where R is normally alkyl or aryl groups and X=Cl^-, OH^-, CH_3COO^-. If n=3, the compound has the highest toxicity, for example Et_3SnOA_C has LD_{50} 4mg/Kg (rats) and this is the most toxic compound. Organotin compounds affect natural killer (NK) on lymphocytes in human. It is known NK lymphocyte is the primary immune defense mechanism against tumor and virtually infected the cell in human bodies. Organotin compounds pollute water and soil that can be transferred to human body through seafood. Despite the ongoing legislative restrictions for the use of Organotin compounds in Western Countries, environmental pollution of these compounds is still a big problem. Therefore the investigation on the analysis and the degradation of these compounds in water and sediments is important. In this paper, we present the challenges in the analysis and the degradation of Organotin compounds.

Keywords: *Antifouling, Fentin, Organotins, Pollutants.*

INTRODUCTION

Organotin compounds (OTC) are compounds that have at least one Sn-C bond.The general formula of OTC is R_4SnX_{4-n}. In this formula R is alkyl such as methyl, ethyl, butyl, octyl also tioalkyl,aryl or tioaryl groups. X may be halide, hydroxide, acetate or other esters of carboxylic acid or ester of fatty acid or mercapto group.The first OTC was prepared in 1852 by Lowing but credit for the first comprehensive study of OTC belongs to Edward Frankland (1825-1899). The first OTC for commercial use was diorganotin as PVC stabilizer in 1940 the use of OTC has increased substantially in the past 30 years. In1957, the world production of OTC was 1,000-2,000 ton and reached 35,000 and 50,000 tons in1989and 1992, respectively. Industrial uses of OTC are shown in table 1.

Antifouling:

Most important uses of tributyl tin (TBT) is as antifouling agent in paint coating on the ships. Growth of micro-organism on the hulls of vessel resulted increased in the weight of the ships also reduce the speed and thus increase the energy consumption (John, 2000)

Table 1. Industrial uses of OTC.

Industrial application	OTC
PVC stabilizers	R_2SnX_2 and$RSnX_3$ R=Me,Bu,Oct
Antifouling paint	R_3SnX R=Bu,Ph,
Agrochemicals	R_3SnX R=Ph,Bu,Cy
Wood preservation	Bu_3SnX
Glass treatment	Me_2SnX_2
Material protection (Stone,leather,paper)	Bu_3SnX
Impregnationof Textile	Ph_3SnX
Poultry farming	Bu_3SnX

Agriculture:

The use of OTC as agriculture biocides resulted in a significant increase of environmental pollutants. Since 1960,s triphenyltin (Fentin) hydroxide or acetate was used to control fungi that attack potato, sugar beets, celery, carrot, onion and rice. Triphenyltin(TPT) also used to prevent tropical disease in peanuts, coffee and cocoa. Annually 300 tons of TPT is used in

Netherland for the protection potato crops.

Toxicity:

In OTC $R_4SnX_{4-n,}$ if n=3 (trialkyl or triaryl tin), they are the most toxic. In this class, $Et_3Sn\ OA_C$ is the most toxic of all OTC for mammals. Oral LD_{50} (rat) is 4 mg/Kg. To decrease the toxicity of OTC, the chain length of n-alkyl should be increased as illustrated in Table 2.

Table 2. Oral toxicity of OTC (rats).

OTC	LD_{50} ($mgKg^{-1}$)
Et_3SnOAc	4
Me_3SnOAc	9
Me_3SnCl	13
Me_3SnOH	540
Me_2SnCl_2	74
$MeSnCl_3$	1370
Ph_3SnOH	125
Hex_3SnOAc	1000
$(Bu_3Sn)_2O$	150-234
Bu_3SnOAC	380
Bu_2SnCl_2	100
$BuSnCl_3$	2140
Bu_4Sn	4000
Oct_4Sn	50,000

Octyl-tin which has LD_{50} of 50, 000, are essentially non-toxic and they are used as PVC stabilizer.Comparison of the toxicity of several OTC is given in table 2. Approximately 91 tons of triorganotin biocides enter the environment each year. Little is known about the effect of OTC in human (Hoch, 1982). In 1954 about 100 deaths was reported in France because of oral treatment of diethyltin that was mixed with linoleic acid for the curing skin disease. The toxicity is due to triethyltin iodid that present as an impurity in this drug. Symptoms of poisioning of trialkyl or triaryltin are vomiting, headache, visual defect and electroencephalog-raphic abnormalities. Thyocyte play an important role in human immunity. 24 hours after exposure in vitro to 500 ng /ml DBT their viability was decreased by 50%MBT. TBT affects natural (NK) lymphocyte in human blood. NK lymphocytes are the primary immune defense against tumor and virtually infected cell in human bodies Some imposex was reported in marine organs such as snails and marine whelks (Gómez-Ariza, 2006; Vishwakiran, 2006). To investigate the environmental problems of OTC, the first step is detection and measurement of these compounds in water, sediments and organs. There are some reports in OTC pollution of drinking water that were transferred through PVC pipes. PVC pipes for the first time usage transfer 35mg/m^3 as Sn (Roberts, 1989).

ANALYSIS

Authors mentioned various methods such as spectroscopic and choromatogr-aphy theniques for analysis of OTC. Most of the analytical procedures developed for OTC analysis are based on chromatographic separation (Gomez –Ariza, 2001). Separation coupled with a specific detector such as AES, AAS, atomic fluorescent, flame photometry and mass spectroscopy. Pretreatments of the samples are needed before chromatography analysis. The pretreatment steps (Compano, 1994; Masahiro Takeuchi 2000) are as follow:

1-Digestion
2-Extraction
3-Derivation
4-Purification

12 methods of extraction of OTC were compared. It was known polar solvent such as MeOHand acidic media increase yield of extraction (Caterina Pellegrino, 2000). For GC analysis required sample to be volatile, the polar OTC extracted from the matrix had to be converted into volatile compounds by alkylation ,which can be separated by this analytical method,as a consequence the OTC firstly need to be extracted into a polar solvent usually by using complexing agent such tropolone or sodiumdie thyldithiocarbamate (NaDDTC). Fig. 1 shows one of the procedures for analysis of OTC in water, sediment and organs. One of the most important steps of analysis of OTC is derivatisation. There are three methods (Roberto Morabito, 2000; Tsunoi, 2002) for this step.

1-Hydride generation by use of $NaBH_4$
2-Ethylation by Na $B(Et)_4$
3-Alkylation by Grignard reagent.

Recently scientist used biomarker as a method for investigation the pollution of OTC. Varian company published a report about the measuring of OTC in liver of fish and bird by using GC-Mass Fig. 2 shows choromatogram of some OTC. Unlabeled peaks show internal standards Stab *et al.*

(1993, 1994).

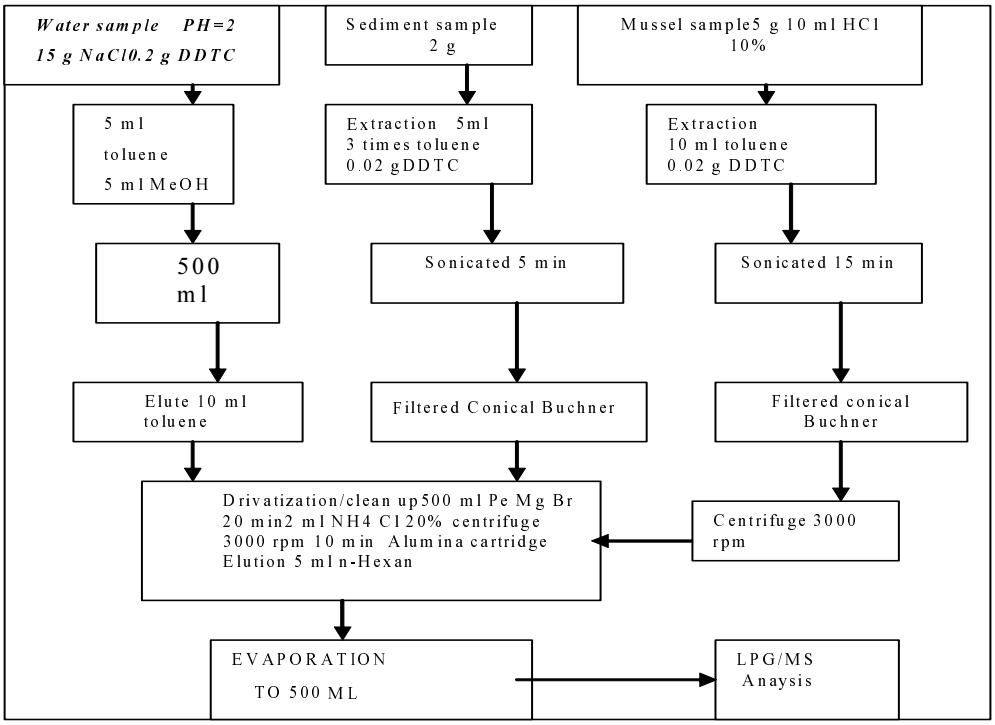

Fig. 1. Analysis of OTC in water, sediments and organs.

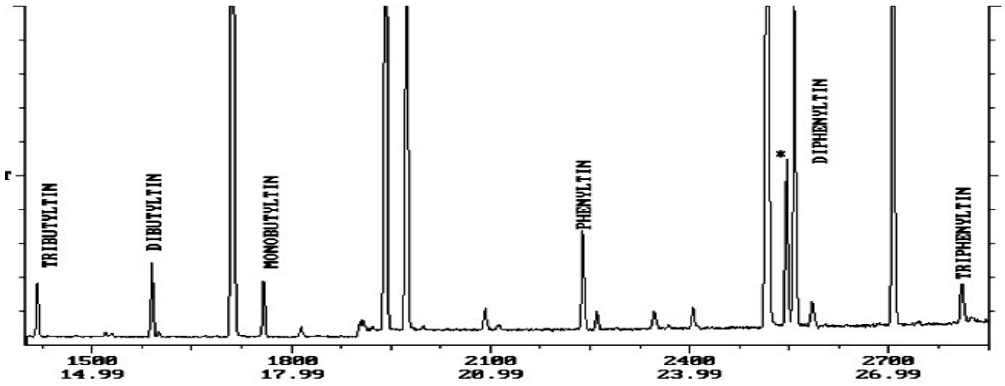

Fig. 2. G.C chromatogram of some organotin compounds.
*Unlabeled peaks show internal standards.

RESULTS AND DISCUSSION

As mentioned, OTC is one of the major pollutants in marine environment. Pollution of aquatic system by TBT and TPT causes various symptoms on organs like thickening of shell and failure of spat in oyster and the reduction of dogwhealk population also cause disturbance in sexual hormones and causes imposex in some marine organs. To overcome these problems, the detection and measurement of these compounds with quick and accurate methods with acceptable detection limit is unavoidable. All measurement should be done in aqueous media thus using Grignard reagent is difficult.

Most of OTC has high boiling point thus needs to derivatise these compou-nds. One of the best chemical methods for derivation is using $NaB(Et)_4$,in this method extraction and derivatisation can be done simultaneo-usly. Derivatisation with $NaB(Et)_4$ make the sample preparation faster and easier because it combines an in-situ derivation into an organic phase. One scientist after comparing chemical analysis with biomarker method concludes, biomarker is better than chemical

methods. The relative Penis Index Size (RPSI) is mostly used to indicate the stage of imposex. Analysis of water, sediment and organs in some seaside such as Osaka, Black Sea, Netherlands, Canada and New Zealand show these places were polluted, therefore we should find some approaches for decreasing of pollution (Harino Fukushima, 1998) .Some approaches are:

I-Replacement of TBT and TPT by other compounds

Many works have been done to replace these compounds. In response to the negative performance and environmental effects of marine antifouling paints that contains TBT, tributyltin methacrylate, a copolymer system was developed which has self-polishing behavior. This new compound can controll leaching and it doesn't leach to water. Extensive research for replacement products for TBT paints is based on binder systems made of copper acrylate and zinc acrylate.Recently a new antifouling agent in the name of sea nine was used (Jacobson *et al*., 2000).

II-Banning or regulation of usage by governments

Damage effects of consumption of TBT caused by application of these compound to be abandoned in France in 1982. United State and England, and European countries banded their application since 1990. World legislation is being considered for trialkyl tin.In 1982 France was the first country to band the use of OTC based antifouling paints on ships less than 25meters long.

Similar regulation have also been imposed in North Africa,Australia,New Zealand , South Africa Hong Kong and most European countries. European countries environmental quality targets of 10ng/l of water sample and 1-2 ng/gm sediments are now implemented for di and mono OTC that will be formed through degradation and metabolization of triorganotin .No legal standard have been established. In spite of the banning of OTC in 1992 in Japan analyses of these compounds in water, sediment, plankton and mussels shows OTC in aquatic environment of port of Osaka is at level that may be cause adverse effect for aquatic organism. Canadian government regulated TBT under Pest Control Product Act.Inspite of banning or regulation using of TBT in some countries the concentration of this compound is high enough and addition to banning need to other approaches (Champ, 2000).

Pollution of OTC in marine:

One of the main environmental pollution in marine is TBT. In Peninsular Malaysia, the concentrations of TBT in seawater ranged from <3.4 - 20 ng/L in unexposed areas (i.e., away from boat and shipping activity), and from 30 - 281.8 ng/L in coastal areas with high boat and ship activities .Concentrations of TBT in sediments were reported to be <0.7 ng/g in an unexposed area and 27.6 - 216.5 ng/g in exposed areas .It was reported that TBT concentrations in the tissue of cockles (Anadara granosa) and clams (Paphia sp.) collected from Peninsular Malaysia waters ranged from <0.5 - 5.6 ng/g wet weight, while concentrations in green mussels (Perna sp.) collected from the market and from farms contained 23.5 ng/g wet weight and 14.2 ng/g wet weight, respectively. Also reported that market-purchased clamscontained as much as 670 ng/g TBT and that farm culture of oysters had to be extended from four years to six years due in part to TBT contamination. Pollutions of sediments is most important because the half life of TBT in sediments was estimated as 1.3-4.4 years. Concent-ration of TBT in sediments in Thailand 36-4500 in Hong Kong 1000-1700 in Auckland (New Zealand) 2-1360 ng/g. The highest reported concentration of TBT in sediment was 38000 ng/g in Fiji.

III- Degradation of OTC

Degradation of OTC may be defined as the sequential removal of the alkyl or aryl groups attached to the Sn atom.

This process should be shown as below.

$R_3SnX \rightarrow R_2SnX_2 \rightarrow RSnX_3 \rightarrow SnX_4$

The breaking of Sn-C bond may occur through:

1-Biotic reaction

2-Photochemical reaction

3-Chemical reaction

Micro algae and bacteria play an important role in the TBT biodegr-adation in aquatic systems, but only a limited number of these microorganisms have been identified via Pseudonomas aeruginosa, Pseudomonas pudiac and Alcaligenes facalis are known to

degradate OTC.

Micro algae species such as Skeletonem costatum and Chlorella vulgrais and chlorella sp. can degredates and metabolize TBT to less toxic species DBT via dealkylation process. TPT is converted to DPT and inorganic tin by the presence of these bacteria.

Photo degradation of OTC has the same sequence as biotic degradation .Average bond energy for Sn-C is about 200 KJ/mol. UV radiation with a wavelength of 200 nm provides energy about 300 KJ/mol. Therefore, UVradiation of the proper wavelength can cleave the Sn-C band. Under natural condition, photodegradation is less important than biological action.The Sn-C bond can be attacked by both nucleophilic and electrophilic reagents (Skinner, 1964).
For example mineral acid,carboxylic acid and alkali metal are agents which are able to hetrolytically cleave of Sn-C bonds.

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