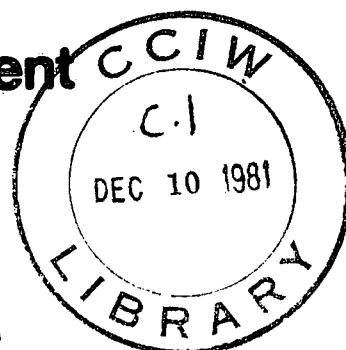


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**BUTYLINS IN THE GREAT LAKES BASIN**

**R.J. Maguire\* and E.J. Hale**

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ABSTRACT

A new series of contaminants, butyltins, is reported in Canadian waters in the Great Lakes basin. Concentrations of tri-n-butyltin ( $\text{Bu}_3\text{Sn}^+$ ) in Collingwood Harbour, a marina in Lake St. Clair, Toronto Harbour and Ramsey Lake are 15-60% of the  $\text{LC}_{100}^{12\text{d}}$  value for a sensitive aquatic species, rainbow trout yolk sac fry.

## INTRODUCTION

Organotin compounds are used in three major ways, viz., as stabilizers for polyvinylchloride, as catalysts and as biocides (1). The increasing annual use of organotins raises the possibility of environmental pollution. Organotins are a class of compounds about which more information is sought under Canada's Environmental Contaminants Act (2) regarding toxicology and environmental fate.

In general, the hazard posed by organotins to aquatic organisms is a function of toxicity, amount (or concentration) and persistence. The appendix to this report addresses these three factors in some detail, but the toxicity of organotins is briefly described below since it provided the impetus for our studies on butyltins.

Progressive introduction of organic groups (R) at the tin atom in any  $R_nSnX_{4-n}$  series (where X is typically oxygen or halogen) produces maximal biological activity against all species when  $n = 3$ , i.e., for the triorganotin compounds (3). If the chain length of the n-alkyl group is increased within the trialkyl series, the highest mammalian toxicity is attained for the triethyl compounds. For insects, however, the trimethyltins are usually most toxic; for gram-negative bacteria the tri-n-propyltins are most toxic; and for gram-positive bacteria and fungi the tri-n-butyltins show the highest activity. Further increase in the n-alkyl chain length produces a sharp drop in the biological activity, and the tri-n-octyltins are essentially not toxic to any species tested. Triphenyltins show high fungicidal activity while tricyclohexyltins

are efficient acaricides. Variation of the inorganic substituent, X, within any particular  $R_3SnX$  series has, in general, very little effect on biocidal activity in mammals (3), but there are not enough data to confirm whether or not this is true for fish.

We chose to examine the aquatic environmental fate of tributyltins, and, by extension, dibutyltins; the particular compound under scrutiny is bis (tri-n-butyltin) oxide (TBTO). Table 1 shows the toxicity of tributyltins to a variety of species (dibutyltins are expected to be less toxic - cf. rat oral  $LD_{50} = 50-800 \text{ mg kg}^{-1}$ -ref. 3). Although tributyltins ( $Bu_3Sn^+$ ) are not particularly toxic to mammals, their toxicity to aquatic species is much greater - cf. the  $LC_{50}^{24h}$  value for rainbow trout of  $28 \text{ } \mu\text{g L}^{-1}$ .

An integral part of our studies on butyltins is to determine the extent of organotin contamination of Canadian fresh waters, and we present here the first results of our investigations on butyltins and  $Sn^{4+}$  in water on the Canadian side of the Great Lakes basin.

#### Experimental Section

At various locations in the Great Lakes basin 8-L samples of subsurface (0.5 m) water were collected in glass bottles, and the contents were acidified to pH 1 and stored at  $4^\circ\text{C}$  until analysis. In addition, surface microlayer samples of volume 100 mL were collected with a glass plate sampler (10).

Analyses of the unfiltered water samples for butyltins ( $\text{Bu}_3\text{Sn}^+$ ,  $\text{Bu}_2\text{Sn}^{2+}$  and  $\text{BuSn}^{3+}$ ) and  $\text{Sn}^{4+}$  were performed according to a method (11) which involved extraction from acidified aqueous solution into benzene/tropolone, adjusting the pH of the water to 7, saturating with NaCl and re-extraction with benzene/tropolone (Y.K. Chau and G.A. Bengert, personal communication), derivatization of the combined benzene/tropolone extracts with pentylmagnesium bromide, clean-up and analysis of the species  $\text{Bu}_n\text{Pe}_{4-n}\text{Sn}$  by gas chromatography with a modified flame photometric detector. Appropriate reagent blanks were prepared. The detection limit for each of the  $\text{Bu}_n\text{Pe}_{4-n}\text{Sn}$  species is about  $0.01 \mu\text{g L}^{-1}$ , and identities were confirmed by co-chromatography with authentic standards on two different columns, and when possible, by gas chromatography-mass spectrometry (11).

## Results and Discussion

Table 2 indicates the common occurrence of butyltins (30 of 90 determinations) and  $\text{Sn}^{4+}$  (23 of 30 determinations) in subsurface water; to our knowledge these data are the first to be reported on organotins in Canadian waters. The presence of butyltins in  $\mu\text{g L}^{-1}$  concentrations has been reported in Lake Michigan (12).

Table 2 shows concentrations of  $\text{Bu}_3\text{Sn}^+$  in Collingwood Harbour, a marina in Lake St. Clair, Toronto Harbour and Ramsey Lake which are 15-60% of the  $\text{LC}_{100}^{12d}$  value for rainbow trout yolk sac fry (6). A possible source

of  $\text{Bu}_3\text{Sn}^+$  in the first three of these locations is boat or ship paint (cf. Appendix for uses of organotins).

The compound  $\text{Bu}_2\text{Sn}^{2+}$  occurs in 20 of the 30 subsurface water samples; it may be derived from  $\text{Bu}_3\text{Sn}^+$  or from polyvinyl chloride stabilizers such as dibutyltin diisooctylmercaptoacetate. The presence of  $\text{Bu}_2\text{Sn}^{2+}$  in water in remote areas such as the Turkey Lakes area (50 km north of Sault Ste. Marie) is suggestive of atmospheric introduction.

The compound  $\text{BuSn}^{3+}$  occurs rarely in subsurface waters, but  $\text{Sn}^{4+}$  is widespread, and especially concentrated in Collingwood Harbour and Ramsey Lake.

Table 3 shows the concentrations of  $\text{Bu}_3\text{Sn}^+$ ,  $\text{Bu}_2\text{Sn}^{2+}$  and  $\text{Sn}^{4+}$  in the surface microlayer, i.e., the top 60  $\mu\text{m}$  as sampled with a glass plate. The compound  $\text{BuSn}^{3+}$  was not detected in any sample. The implications of the surface microlayer concentration of butyltins relative to subsurface water are discussed elsewhere (10). The point to be made here is that the presence of  $\text{Bu}_3\text{Sn}^+$  in 20 of 28 microlayer samples compared to 8 of 30 subsurface water samples indicates, since the microlayer is a concentrating medium for lipophilic substances, that  $\text{Bu}_3\text{Sn}^+$  contamination of subsurface water may be more widespread than is indicated in Table 2.

Analysis of butyltins and  $\text{Sn}^{4+}$  in sediments from these 30 locations is in progress, and investigations are planned on butyltin contamination of water, sediment, fish and algae from other locations in the Great Lakes.

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Table 1. Acute Toxicity of  $n\text{-Bu}_3\text{Sn}^+$

Species	Measurement	Value	Reference
mouse	oral LD <sub>50</sub>	122-703 mg kg <sup>-1</sup>	3
rat	oral LD <sub>50</sub>	148-234 mg kg <sup>-1</sup>	3
		50-100 mg kg <sup>-1</sup>	4
		380 mg kg <sup>-1</sup>	5
	dermal LD <sub>50</sub>	605 mg kg <sup>-1</sup>	3
	percutaneous LD <sub>50</sub>	11,700 mg kg <sup>-1</sup>	3
	intraperitoneal LD <sub>50</sub>	10 mg kg <sup>-1</sup>	4
rabbit	dermal LD <sub>50</sub>	12,000 mg kg <sup>-1</sup>	3
rainbow trout (salmo gairdneri Richardson)	LC <sub>100</sub> <sup>12d</sup>	0.005 mg L <sup>-1</sup>	6
	LC <sub>50</sub> <sup>24h</sup>	0.028 mg L <sup>-1</sup>	7
	LC <sub>50</sub> <sup>48h</sup>	0.021 mg L <sup>-1</sup>	7
guppy (Lebistes reticulatus)	LC <sub>100</sub> <sup>24h</sup>	0.075 mg L <sup>-1</sup>	7
	LC <sub>50</sub> <sup>7d</sup>	0.040 mg L <sup>-1</sup>	8
	LC <sub>50</sub> <sup>30d</sup>	0.007 mg L <sup>-1</sup>	7
	LC <sub>50</sub> <sup>90d</sup>	0.004 mg L <sup>-1</sup>	7
goldfish (Carassius auratus)	LC <sub>100</sub> <sup>24h</sup>	0.075 mg L <sup>-1</sup>	7
jewel fish (Tilapia nilotica)	LC <sub>50</sub> <sup>24h</sup>	0.030 mg L <sup>-1</sup>	7
African mouthbreeder (Tilapia mossambica)	LC <sub>50</sub> <sup>24h</sup>	0.028 mg L <sup>-1</sup>	7
frog (Rana temporaria)	LC <sub>100</sub> <sup>24h</sup>	0.075 mg L <sup>-1</sup>	7
gastropod (Bulimus contortus)	LC <sub>100</sub> <sup>24h</sup>	0.075 mg L <sup>-1</sup>	7

Table 1 (continued)

Species	Measurement	Value	Reference
gastropod (Australorbis glabratus)	LC <sup>24h</sup> <sub>100</sub>	0.075 mg L <sup>-1</sup>	7
gastropod (Biomphalaria glabratus)	LC <sup>24h</sup> <sub>50</sub>	0.05-0.1 mg L <sup>-1</sup>	9
	LC <sup>5d</sup> <sub>100</sub>	0.015 mg L <sup>-1</sup>	7
	LC <sup>30d</sup> <sub>99</sub>	0.0004 mg L <sup>-1</sup>	7
	LC <sup>120d</sup> <sub>100</sub>	0.007 mg L <sup>-1</sup>	7

Table 2. Concentrations ( $\mu\text{g L}^{-1}$ ) of Butyltins and  $\text{Sn}^{4+}$  in Unfiltered Subsurface Water\*

Location	[ $\text{Bu}_3\text{Sn}^+$ ]	[ $\text{Bu}_2\text{Sn}^{2+}$ ]	[ $\text{BuSn}^{3+}$ ]	[ $\text{Sn}^{4+}$ ]
Lake Superior (Thunder Bay)	-	-	-	-
Lake Superior (Red Rock)	-	0.01	-	-
Lake Superior (Marathon)	0.02	0.56	-	0.73
Turkey Lake 1	-	-	-	-
Turkey Lake 2	-	-	-	1.06
Turkey Lake 3	-	-	-	-
Turkey Lake 4	-	0.08	-	0.04
Turkey Lake 5	-	0.02	-	-
Sault Ste. Marie Harbour	-	0.03	-	2.43
Ramsey Lake (Sudbury)	0.75	0.02	-	48.7
Nepewassiss Lake (Sudbury)	-	0.08	-	-
Lake Nipissing (North Bay)	-	0.24	-	-
Plastic Lake	-	0.05	-	0.49
Collingwood Harbour	1.0	-	-	50.1
Owen Sound Harbour	-	0.02	-	0.32
St. Clair River 1	-	0.01	-	0.12
St. Clair River 2	-	0.42	-	0.06
St. Clair River 3	-	0.30	-	0.06
Lake St. Clair (Mitchell Bay)	-	0.02	-	1.88
Lake St. Clair (marina)	2.91	7.30	8.48	6.0
Thames River (400 m upstream from mouth)	-	-	-	0.06
Port Dover Harbour	-	-	-	0.01
Grand River (mouth)	-	-	-	0.02
Hamilton Harbour	0.16	0.02	0.02	0.08
Toronto Harbour	0.84	0.27	-	1.04
Whitby Harbour	0.05	0.09	-	2.11
Belleville Harbour	-	0.01	-	0.53
Kingston Harbour	0.01	0.03	-	0.68
St. Lawrence River 1	-	-	-	0.01
St. Lawrence River 2	-	-	-	0.01

\* minimum detectable concentration of each species approx.  $0.01 \mu\text{g L}^{-1}$ ; precise sampling locations available upon request.

Table 3. Concentrations ( $\mu\text{g L}^{-1}$ ) of Butyltins and  $\text{Sn}^{4+}$  in Unfiltered Surface Microlayer\*

Location	[ $\text{Bu}_3\text{Sn}^+$ ]	[ $\text{Bu}_2\text{Sn}^{2+}$ ]	[ $\text{Sn}^{4+}$ ]
Lake Superior (Thunder Bay)	0.45	-	111
Lake Superior (Red Rock)	0.68	0.71	42
Lake Superior (Marathon)	-	-	11.6
Turkey Lake 1	0.29	-	81.4
Turkey Lake 2	0.85	-	424
Turkey Lake 3	0.48	-	27
Turkey Lake 4	0.29	-	42.2
Turkey Lake 5	0.15	-	83
Sault Ste. Marie Harbour	0.29	-	39
Ramsey Lake (Sudbury)	0.25	-	9.1
Nepewassi Lake (Sudbury)	3.81	-	502
Lake Nipissing (North Bay)	0.18	-	180
Collingwood Harbour	-	-	308
Owen Sound Harbour	-	-	208
St. Clair River 1	60.7	94	8.4
St. Clair River 2	11.9	2600	31
St. Clair River 3	-	2200	0.3
Lake St. Clair (Mitchell Bay)	8.7	119	125
Lake St. Clair (marina)	50.9	107	6.6
Thames River (400 m upstream from mouth)	-	-	12
Port Dover Harbour	11.8	50.5	2.5
Grand River (mouth)	-	-	-
Toronto Harbour	-	1460	57.2
Whitby Harbour	1.4	2250	633
Belleville Harbour	54.6	195	80
Kingston Harbour	4.8	39	46
St. Lawrence River 1	9.7	38	1.4
St. Lawrence River 2	-	-	0.8

\*  $\text{BuSn}^{3+}$  not detected in any surface microlayer sample; minimum detectable concentration of each species  $0.01 \mu\text{g L}^{-1}$ ; precise sampling locations available upon request.

APPENDIX

Organotins - Uses, Biological Effects,  
and Environmental Behaviour

Tin as a metal and in its chemical compounds has a wide variety of use. Characteristically, in many of its applications, only small amounts of tin are needed to see its effect. This is generally true for the organotin compounds which, during the past twenty-five years, have developed into extremely important industrial commodities. A further characteristic of tin is that it is unsurpassed by any other metal in the multiplicity of its organic applications. These involve such widely divergent fields as stabilizers for polyvinyl chloride, industrial catalysts, industrial and agricultural biocides, and wood-preserving and anti-fouling agents, to mention only the most important applications. A third characteristic of tin, particularly true for the organotin compounds, is that in most of its present organic applications it has to compete with quite different materials, either old or new. However important the present-day organotin applications may be, it should be realized that so far no single large-size application has been found in which a particular type of organotin compound is absolutely unique as is, for instance, true for the lead tetraalkyls as anti-knock agents. This implies that cost/performance relations are, and will remain, of paramount significance for the continuation of the present, and the development of future, organotin applications.



## I. Production and Uses of Organotins

The annual world consumption of tin in all forms was about 400 million lbs. in 1976, but of this total only about 55 million lbs. was in the form of organotin compounds (1). The U.S. consumption of organotin compounds was about 24 million lbs. in 1976, and an 11-13% annual growth has been predicted for the period 1978-1988 (1).

### a) PVC Heat Stabilizers

Over two-thirds of the total world annual production of organotins is devoted to the thermal stabilization of polyvinyl chloride (PVC) plastics (13). The mechanism of PVC breakdown is not entirely clear at present, but the most commonly accepted view is that the decomposition is related to a dehydrochlorination reaction at an allylic or tertiary chlorine site with the formation of a double bond. As the degradation continues, conjugated unsaturated systems are formed which diminish optical clarity and lend undesirable colour to the plastic. As little as 0.1% decomposition can lead to blackening. The dehydrochlorination process is autocatalytic, and in the processing of unplasticized PVC resin, temperatures well in excess of those required for the initiation of the degradative process are attained ( $>200^{\circ}\text{C}$ ). The mode of action of the effective stabilizers is not completely known, but probably involves exchange of allylic chloride atoms with the anionic portion of the

organotin compound, and the absorption of liberated hydrogen chloride to release compounds which can add across the unsaturated centers (1).

Typical stabilizers are dialkyltin compounds containing thio or ester groups. The original patents were for the application of dibutyl compounds but dioctyltins are now in use as well. The addition of small amounts of monoalkyltins has a synergistic effect. The groups attached to the alkyltin moieties include the laurate and maleate, and several mercapto derivatives of octyl and isooctyl esters of thioglycolic acid. In the last decade there has been a shift of emphasis from flexible to rigid PVC products, the latter requiring much higher processing temperatures. The need for better stabilization has thus become more acute if PVC with the desired colourlessness and transparency for packaging films, piping, bottles and siding is to be produced. Dimethyltins, because of their extremely great thermal stability, allow the use of high working temperatures and high working speeds, and their application may be economically feasible (14). Following is a list of the commercially more important organotin PVC stabilizers, in descending order of importance (1):

- dibutyltindiisooctylmercaptoacetate
- dimethyltindiisooctylmercaptoacetate
- dibutyltin dilaurate
- bis (tributyltin) oxide
- dibutyltin bis (laurylmercaptide)
- dibutyltin bis (2-ethylhexoate)

The structures of all organotins discussed are given at the end of this appendix.

b) Catalysts

In the production of polyurethane foams, organotin catalysts allow the foam to be made directly from hexamethylene diisocyanate and 1,4-butanediol. In urethane foam production, the rate of generation of CO<sub>2</sub> is extremely important for the properties of the final product. On the other hand, the chain extension reaction has to proceed at a sufficient rate so that the gel will have sufficient strength to retain the CO<sub>2</sub> bubbles which produce the foam. The organotins appear to be effective in catalyzing the chain extension reaction so that the optimal rates of both the chain extension and gas formation reactions are achieved. Following is a list of commonly used organotin catalysts (15):

- dibutyltin diacetate
- dibutyltin dilaurate
- dibutyltin dichloride
- dibutyltin dilaurylmercaptide
- dimethyltin dichloride
- stannous octoate

Dibutyltin dioctate and dibutyltin dilaurate are commonly used to catalyze the room temperature curing of silicone rubbers used in making dental impressions and encapsulating electronic parts. The catalytic activity of the organotin compounds has been attributed to low-energy 5d orbitals of the tin atom which can form hexa- and pentacoordinate bonds. In this type of bond, the tin coordinates with either an oxygen or nitrogen. This coordination bond causes polarization of the carbon atom bonded to an

oxygen or nitrogen atom, and makes the carbon atom more susceptible to attack by an electrophilic reagent, such as an alcohol, as in the urethane and esterification reactions.

c) Biocides

Organotin compounds, because they have been found to be effective in the control of many fungi and bacteria, have been used as preservatives for wood, textiles, cordage fibers, paper, leather, electrical and electronic equipment, and glass. Most biologically active organotin compounds are trialkyl or triaryltin compounds. Following is a list of the major organotin biocides (15):

- bis(tributyltin) oxide
- tributyltin linoleate
- dibutyltin dilaurate
- tributyltin dichloride
- triphenyltin acetate
- triphenyltin chloride
- triphenyltin hydroxide

Bis(tributyltin) oxide (TBT0) gives antibacterial, antifungal and mothproofing properties to treated fabrics. In this application, the tin compounds must compete with such compounds as copper 8-quinolinolate, copper and zinc naphthenates, zinc dimethyldithiocarbamate, pentachlorophenol and quaternary ammonium compounds. Their main disadvantage is cost, but their major advantage is their lack of colour and staining.

TBTO is very effective in controlling bacteria in hospitals, such as Staphylococcus aureus. TBTO has also been used to prevent odours in garbage containers, control athlete's foot, control molds in bathrooms, control mildew on leather goods, textiles, plastics, and mothproof stored garments.

Industrial applications of organotin biocides include their use for slime control in paper and pulp mills and cooling towers. Their use in processes involving food-grade papers, however, has been curtailed. In the control of slime in cooling towers, the tin compounds must compete with less costly, highly effective, but hazardous compounds such as trichlorophenol and organomercurials.

TBTO and tributyltin linoleate are active ingredients in marine lumber preservation. Paint formulations containing TBTO have controlled marine fouling for as long as cuprous oxide paints. Concentrations between 10 and 20% by weight TBTO usually give protection for the entire boating season. In this application the organotins compete with organomercurials and organolead antifouling paints.

Dibutyltindilaurate is effective for the control of Raillietina cesticillus in chickens, and the control of other poultry tapeworms. Dialkyltin compounds have also been used in the control of other parasitic diseases of poultry, sheep and swine.

Tributyltin chloride is an effective rodent repellent.

Triphenyltin acetate and triphenyltin chloride are effective molluscicides for the control of snails which serve as vectors for schistosome infections in man.

Tributyl- and tri-isopropyltin compounds are effective fungicides. Triphenyltin acetate and hydroxide control the fungus causing late blight of potatoes, control sigatoka in bananas, and control other fungal diseases of important crops.

As insecticides, organotin compounds have been very effective. Trialkyltin compounds such as triphenyltin acetate and hydroxide, tributyltin chloride, and dibutyltindilaurate generally repel insects when applied to foliage.

#### d) Summary of Use Patterns

In general, dialkyltin derivatives are used as heat stabilizers and catalysts, and the trialkyl- and triaryltin derivatives are used mainly in biocidal applications. In the U.S. in 1976,  $16 \times 10^6$  lbs were used as heat stabilizers,  $5 \times 10^6$  lbs were used as catalysts and  $2.3 \times 10^6$  lbs were used as biocides. In Canada in 1977, total organotin production and import was estimated to be about  $1.2 \times 10^6$  lbs (P.A. Jones, personal communication).

## II. Biological Effects of Exposure

#### a) Metabolism of Organotin Compounds

Tetraethyltin was shown to undergo destannylation in vivo by a rat liver microsomal enzyme system successively to the tri-, di-, and monoethyl derivatives (16-18). Other trialkyltins behave similarly (17).

The total metabolic yield was <10%, however. More recently, it was demonstrated that a cytochrome P-450 monooxygenase enzyme and not a lipid peroxidase system was responsible for metabolism, and that carbon hydroxylation occurred on the butyl groups of  $^{14}\text{C}$ -labeled tributyltin acetate at the  $\alpha$  - to  $\gamma$  - positions (19,20). The products were compared with authentic samples, and similar in vivo reactions were shown to occur in mice (20). The initial hydroxylated metabolic products of tetrabutyltin-1- $^{14}\text{C}$  were rapidly destannylated to the tributyltin derivatives (20). Tin-113 labeled triphenyltin acetate is apparently not hydroxylated in vitro, but rats can metabolize this organotin to give substantial amounts of di- and monophenyl derivatives (20).

b) Exposure to Organotin Compounds

Maximum toxicity to all types of life occurs with the triorgano-tin derivatives, but there are important variations within this class of compounds. Mammalian toxicity reaches a maximum with the ethyl group ( $\text{LD}_{50}$  4 mg/kg for rats) and falls off rapidly with increasing chain length. Insects, on the other hand, are most affected by the trimethyltins, and the tri-n-propyl- and tri-n-butyltins are most effective against fungi and bacteria (1). The tributyl- and triphenyltin compounds, which are not particularly hazardous to mammals ( $\text{LD}_{50}$  100-200 mg/kg) are very effective against guppies, algae, barnacles and shrimp at levels of 0.1 to 1.0  $\text{mg L}^{-1}$  (21). In addition, 1-8  $\text{mg L}^{-1}$   $\text{Bu}_3\text{Sn}^+$  inhibits the growth of bacteria and fungi, and 30  $\mu\text{g L}^{-1}$  inhibits the growth of water plants such as Elodea and Lemna (8).

c) Human Exposure

Organotin compounds can be assimilated by inhalation, ingestion through food or water, or by absorption through the skin. The lipid-soluble material will probably migrate to fatty tissue. No data concerning the rates of metabolism, degradation or excretion in humans or test animals are available. The total daily intake for tin in the diet has been estimated to be in the range 187-8,800 µg/day, which corresponds to 2.7-126 µg/kg/day for an adult (1). Inorganic tin has been shown to be an essential growth factor in the rat (1).

The vapours of triethyltin acetate cause nausea, headache, general weakness, diarrhea and albuminuria. Widespread poisoning occurred in France and Algeria in 1954 as a result of taking Stalinon capsules, each of which was stated to contain 15 mg of diethyltin diiodide, for the treatment of staphylococcal infections of the skin. The incident involved 210 known cases of harmful effects and 100 deaths. It is estimated that the fatal doses of the diethyltin were in the range 380-750 mg, not the nominal 15 mg, and that the preparation may also have contained tetra-, tri- and monoethyltin (22).

Adverse effects produced by occupational exposure to triphenyltin acetate used as an agricultural fungicide include general malaise, headache, loss of consciousness, epigastric pain, vomiting, irritation of the skin, conjunctivae and mucosae, dyspepsia, diarrhea, foggy vision, dizziness, hyperglycemia, glycosuria and damage to the liver shown by increased collagen, some fibrosis and increased serum glutamic-pyruvic

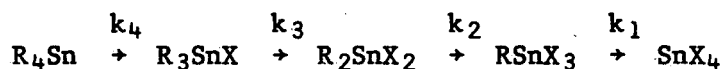


transmutase levels (1). All of these effects were reversible and complete recovery was effected within a few weeks. Organotins have been found to be highly irritating to the skin, and in severe cases of organotin poisoning, involving peralkylated materials, bradycardia, hypotension and abrupt variations in the sinus rhythm of the heart have been noted (23).

### III. Environmental Behaviour of Organotins

The industrially important organotin chemicals are generally liquids and waxy solids, or powders, of low volatility. Solubility data are limited, but the higher trialkyltin compounds are poorly soluble in water (10-50 ppm); solubility in common organic solvents and in lipids is a function of the number of organic groups attached to the tin atom, and is proportional to their size. The methyltin compounds are the most water-soluble of the organotins.

Carbon-tin bonds are thermally stable below 200°C, but are capable of polarization by attacking species in either direction. Organotin compounds are thus susceptible to attack at the carbon-tin bond by both nucleophilic and electrophilic reagents, leading to hydrolysis, solvolysis, acidic and basic reactions (1). The progressive cleavage of organic groups from tin is dependent upon the type of organotin compound, the number of organic substituents, and the solvolytic conditions. The relative ease of removal of aliphatic groups decreases with increasing size of the group, but unsaturated and aromatic groups are cleaved more rapidly. For the series



the reaction rates are  $k_4 \gg k_3 \gg k_2 \sim k_1$ . Laboratory solvolytic reactions have generally been carried out at extreme values of pH (pH  $< 2$  or  $> 14$ ); half-lives range from 1 minute to 115 days (1). Studies of the hydrolysis of organotins at physiologically relevant pH values have not been reported.

The inorganic anionic groups in the organotin compounds react with moisture and air to cleave from tin in an hydrolysis-oxidation reaction to give stannols and oxides. In this way successive reaction of both parts of the molecule leads eventually to completely inorganic hydrated tin oxides.

Microbial degradation of a few organotins has been reported. Barnes *et al.* (24) used  $^{14}C$ -labeled triphenyltin acetate in which the release of  $^{14}CO_2$  from soil samples was monitored in the dark, and a half life of 140 days was determined for concentrations of 5 and 10 ppm. It appears that microbial conversion of organotins to less alkylated and arylated tins proceeds sequentially to produce hydrated inorganic tin oxides, in a manner analogous to chemical hydrolysis.

Preliminary tests on clay-based soils suggest that organotins may be strongly bound to soils and leached only with difficulty (1).

The presence of butyltins (12) and methyltins (25,26) at concentrations of  $ng\ L^{-1}$  to  $\mu g\ L^{-1}$  has been reported in a variety of natural waters in the United States. Butyltins probably occur as a result of anthropogenic activity (1), but methyltins could be the result of

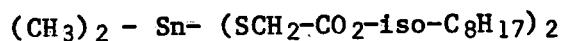
anthropogenic activity or methylation of tin, either biologically or abiotically: (a) increasing concentrations of methyltins with increasing anthropogenic tin influx have been observed in Chesapeake Bay (27), and (b) several reports have now been published on the biomethylation (28-31) and chemical methylation (32,33) of inorganic and organic tin compounds.

Chemical structures of some organotin compounds

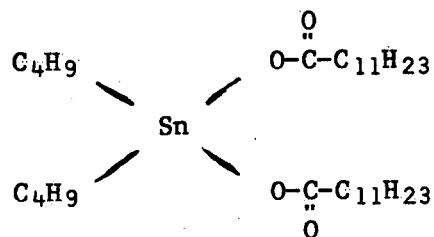
1. dibutyltindiisooctylmercaptoacetate



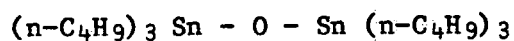
2. dimethyltindiisooctylmercaptoacetate



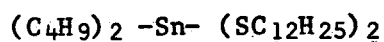
3. dibutyltin dilaurate



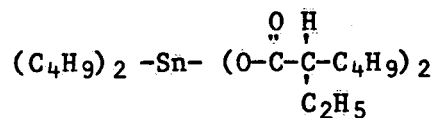
4. bis(tributyltin) oxide



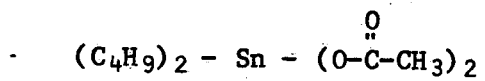
5. dibutyltin bis(laurylmercaptide)



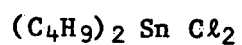
6. dibutyltin bis(2-ethylhexoate)



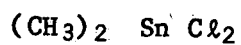
7. dibutyltin diacetate



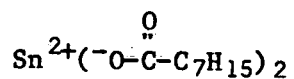
8. dibutyltin dichloride



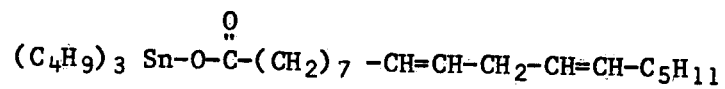
9. dimethyltin dichloride



10. stannous octoate



11. tributyltin linoleate



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