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# CHAPTER 23

### TRIBUTYLTIN IN CANADIAN WATERS

bу

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## MANAGEMENT PERSPECTIVE

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A summary is given of the occurrence of tributyltin in water, sediment and fish in Canada. Recently announced regulations against tributyltin by the Department of Agriculture are also explained.

### PERSPECTIVE GESTION

Ce sommaire traite du tributylétain dans l'eau, les sédiments et les poissons au Canada. L'auteur donne également des précisions au sujet de la réglementation récemment adoptée par le ministère de l'Agriculture limitant l'utilisation de cette substance chimique.

#### I. Introduction

In the mid to late 1970s concern was raised in Canada about the increasing annual use of organotin compounds, some of which were known to be toxic to aquatic organisms. Organotin compounds as a class were placed on Canada's Environmental Contaminants Act Category III list, which essentially meant that further information was required on their occurrence, persistence and toxicity in order to make environmental and human health risk assessments (1).

The main organotin compounds which are likely to be released to the environment in Canada are those of triphenyltin ( $Ph_{9}Sn^{+}$ ), tricyclohexyltin ( $Cy_{9}Sn^{+}$ ), di-n-octyltin ( $Oct_{8}Sn^{8+}$ ), di-n-butyltin ( $Bu_{8}Sn^{2+}$ ), dimethyltin ( $Me_{8}Sn^{2+}$ ) and tri-n-butyltin ( $Bu_{9}Sn^{+}$ ) (2). Triphenyltin and tricyclohexyltin are agricultural pesticides. Di-n-octyltin is used as a stabilizer in some food wrappings. Di-n-butyltin is used as a poly(vinyl chloride) stabilizer, as is dimethyltin, and as a catalyst in a number of industrial processes. Tri-n-butyltin was used as an antifouling agent in some paints for boats, ships and docks prior to 1989. It is also used as a general lumber preservative and as a slimicide in cooling towers. It is by far the most toxic to aquatic organisms of all organotin compounds used in Canada (2).

Persistence studies on prominent organotin pesticides have indicated that abiotic degradation generally occurs, as does biological degradation, through mechanisms of sequential dealkylation (3) or dearylation (4). Therefore the series  $Ph_nSn^{(4-n)+}$ ,  $Cy_nSn^{(4-n)+}$  and  $Bu_nSn^{(4-n)+}$  (where in each

case n < 4), Dct\_Sn<sup>(4-n)+</sup> (where n < or = 2) and Me<sub>n</sub>Sn<sup>(4-n)+</sup> (where n < or = 4) may be present in the Canadian environment. The last series includes triand tetramethyltin, which are not released <u>per se</u> to the environment, since methylation of tin and methyltin species has been demonstrated in natural water-sediment mixtures (5,6).

We have been interested in tributyltin because its antifouling use results in direct contact with aquatic environments, and because of its high toxicity to aquatic organisms. Lethal concentrations are in the range 0.04+16 ug Sn/L for short term exposures of copepods (7,8), mussel larvae (9), crab larvae (10), lobster larvae (11), sheepshead minnow (12), bleak (7), guppy (13) and rainbow trout (14,15). Over the past ten years we have developed methods of analysis for butyltin species in water, sediment and biota (16-20), reported their occurrence in Canadian waters (17,19-23), determined the persistence of tributyltin in fresh water and sediment (3,21,24,25), and determined the toxicity of tributyltin to rainbow trout (and its accumulation in various tissues) (26). This chapter summarizes our findings on the occurrence of tributyltin in Canada. The occurrence of the other butyltin species and inorganic tin is also described. These other species are far less toxic than tributyltin (27).

In addition to subsurface water, sediment and fish samples, some samples of the surface microlayer of natural waters have also been analyzed for tributyltin and its degradation products. We have been interested in the role of the surface microlayer in the aquatic environmental dynamics of contaminants since it is often enriched in metals, lipophilic contaminants,

nutrients, dissolved and particulate organic matter, and microorganisms (<u>e.g.</u>, 28). Enrichment of contaminants at the air-water interface will have a negative impact on organisms which spend part or all of their lives at the interface. Surface microlayer enrichment is also an important phenomenon in the cycling of contaminants between air and water. An enormous quantity of material can be transferred from water to the atmosphere as jet and film drops ejected from air bubbles bursting at the surface of water (29-32). In addition, there is evidence that volatilization of lipophilic pesticides from the surface microlayer of natural water after aerial spraying is the main route of dissipation (33,34).

For brevity the tributyltin, dibutyltin and monobutyltin species are referred to in this chapter as though they existed only in cationic form  $(\underline{e}.\underline{q}., \underline{Bu}_{9}Sn^{+})$ . All tributyltin compounds dissolved in water appear to yield a species which has a readily exchangeable counter ion depending upon the nature and concentration of other solutes. Support for this contention comes from chromatographic evidence (35-37) and from mammalian (27,35) and fish (13) toxicity studies which have indicated that the toxicity of tributyltin compounds is independent of the nature of the counter ion.

II. Experimental Section

The water analyses were done on unfiltered samples. Eight L samples of subsurface water were collected from a depth of 0.5 m in glass bottles, and the contents were acidified to pH 1 and stored in the dark at 4 °C until analysis (17). Care was taken to open the bottles below the surface to avoid

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contamination by the surface microlayer. These preservation conditions were effective over a period of at least three months.

The thickness of the surface microlayer is operationally defined by the type of collector used (38-44), and estimates up to 300 um are common. Our samples of surface microlayer were either collected with a glass plate sampling technique for 100 mL samples (40) or a rotating drum sampler for 4 L samples (39), and were preserved in the same way as the subsurface water samples.

Sediment samples were usually collected with an Ekman dredge. The top 2 cm was scraped off into glass jars and frozen as soon as possible, then freeze-dried, ground and sieved to pass an 850 um screen (19,20). In a more detailed study of four sites in Toronto Harbor, 7 cm diameter sediment cores were taken with a lightweight benthos corer and kept at 4 °C overnight (21). The cores were then extruded in 1-cm slices, and these sediment slices were treated in the same way as the sediment grab samples described above. The water above the sediment in these cores was also preserved for analysis.

Only 18 fish were analyzed, and these were provided by other agencies.

The tributyltin species and its degradation products dibutyltin, monobutyltin and inorganic tin were determined by extraction from acidified water samples, or dry sediments, with the complexing agent tropolone dissolved in benzene, pentylation of the extract to produce the volatile mixed butylpentyltin derivatives, Bu Pe, Sn, cleanup by silica gel column chromatography, concentration and analysis by packed column gas chromatography initially with a modified flame photometric detector (3,16,17,19,24), and subsequently with a quartz tube furnace atomic absorption spectrophotometric detector (18,20-23) which was found to be more reliable. Considering that a fairly specific detector for tin was used in the analyses, identities of the butylpentyltin species were deemed to be confirmed by co-chromatography with authentic standards on two column packing materials of very different polarity.

The analyses of the fish required a few modifications. Whole fish (5-200 g) were homogenized in a blender, and the homogenate was dispersed in concentrated HCl, with 10 mL HCl per g of homogenate (20). Practically complete solution was usually effected in less than 2 hr with magnetic stirring. Higher temperatures and longer stirring times should be avoided. The resulting mixture was diluted five-fold with water, then extracted in the same way as the water samples described above. Emulsions were broken with large quantities of Na<sub>2</sub>SO<sub>4</sub>, and lipids were removed by using 3% water-deactivated silica gel in the final clean-up, rather than the activated silica gel used in the water and sediment analyses.

Recoveries of tributyltin, dibutyltin and monobutyltin from spiked water samples at 1-10 mg/L varied from 96 +/- 4 to 103 +/- 8% (16). Recoveries of Sn(IV) from water at pH 5-8 were poor (35 +/- 23%), probably because of the formation of unextractable  $SnO_{e}$  (3). Recoveries of the three butyltin species and inorganic tin from spiked sediment at 0.01, 0.2, 1 and

100 mg Sn/kg dry weight ranged from 55 +/- 26 to 180 +/+ 100% (19). Concentrations were not corrected for recovery. Although Sn(IV) was the only inorganic tin species for which recoveries were determined, the tin present in the above samples was reported as total inorganic tin, since any Sn(II) which might have been present would likely have been oxidized to Sn(IV) during extraction and derivatization.

In the quantitation of the analytes, use was made of appropriate reagent blanks. All results reported were above the limit of quantitation, which is defined as the reagent blank value plus ten times its standard deviation (45). In practice this was equivalent to stating that a chromatographic peak was not accepted as real unless it was at least 2-3 times as large as any corresponding peak in the reagent blank.

Three major surveys were made for tributyltin, in Ontario generally in 1980-81 (30 locations) (17), the Detroit River - St. Clair River area in 1983 (29 locations) (22) and across Canada in 1982 - 1985 (265 locations) (20). Toronto Harbor was also sampled in 1983 at 8 locations in a study of the persistence of tributyltin in water and sediment (21).

III. Results and Discussion

Subsurface Water

Table 1 summarizes the occurrence of tributyltin, dibutyltin, monobutyltin and inorganic tin in subsurface water in Canada. Tributyltin was

mainly found in harbors, marinas and shipping channels, which is consistent. with its use as an antifouling agent. In unfiltered subsurface water, tributyltin was determined in about one quarter of all survey samples. The highest concentration found, 18.1 ug Sn/L, may be suspect since it was not taken at a depth of 0.5 m like all the other samples, but was the water overlying a sediment core taken from Toronto Harbor (21), and it may have been contaminated with sediment which contained tributyltin. This value is almost twice the 24 hr LC-50 value of 11.2 up Sn/L determined for adult rainbow trout Even discounting this one water sample, in 28 of the remaining 66 (14).locations at which tributyltin was determined reliably, its concentration exceeded 0.07 ug Sn/L, a concentration above which there may be cause for concern with regard to chronic toxicity or growth retardation in a sensitive species, rainbow trout yolk sac fry (15). These 28 locations represent about 10% of all locations at which water samples were taken.

The biological availability of the tributyltin found in unfiltered water samples is a matter of critical importance. A solids-to-water partition coefficient of 3000 ug/kg/ug/L has been determined at a suspended solids concentration of 10 mg/L (46), in substantial agreement with our own work and with estimates made on the basis of the octanol-water partition coefficient of tributyltin (log  $K_{ow}$  = 3.2, ref. 3). Such a value for the partition coefficient indicates that most (97%) of the tributyltin is associated with the aqueous phase of the water column (<u>i.e.</u>, that which passes a 0.45 um filter), and very little is adsorbed to suspended solids. This has been confirmed in samples taken from Toronto Harbor. The tributyltin present in the operationally defined dissolved fraction could still, of course, be

adsorbed to colloidal material which passes the filter. We assume that all the tributyltin which we have found in water is biologically available and potentially toxic to aquatic life.

Dibutyltin was found in about 10% of all survey samples. It could be introduced to water itself since dibutyltin compounds are used as poly(vinyl chloride) stabilizers, or it could be a degradation product of tributyltin, which is more likely since tributyltin was found in the majority of locations at which dibutyltin was found. Monobutyltin was also found in about 10% of the survey samples. Monobutyltin is apparently not used in Canada, so the monobutyltin found in water is probably a degradation product of dibutyltin. The inorganic tin found in water may be present naturally, may be introduced in inorganic form, and/or may be a degradation product of organotin compounds.

## Surface Microlaver

Tributyltin was first found in the surface microlayer of natural waters in our 1980 - 1981 Ontario survey (17), at concentrations up to 10<sup>4</sup> times those of subsurface water. Table 2 describes the microlayer results for all surveys. Only the results of the most extensive survey (23) will be discussed here. Tributyltin was determined in 24 of 74 samples. Concentrations ranged non-detectable to 473 ug Sn/L. When tributyltin was found in the microlayer, in general its concentration was much higher than concentrations which have been observed in subsurface water. At all 24 locations mentioned above, the concentration of tributyltin exceeded the 12-

day LC-100 value of 1.8 ug Sn/L for rainbow trout yolk sac fry (15). In 6 of these 24 locations the concentration exceeded the 24-hr LC-50 value of 11.3 ug Sn/L for adult rainbow trout (14). The highest concentration, observed in the Moira River at Belleville, Ontario, was 473 ug Sn/L, which is 42 times higher than the 24-hr LC-50 value for adult rainbow trout. It should be borne in mind, however, that the concentration of any toxic substance in the surface microlayer may vary significantly with time because of turbulence.

Extremely high concentrations of tributyltin and its less toxic degradation products in surface microlayers relative to subsurface water have led us to estimate the amounts of these chemicals in the microlayer relative to the amounts in the whole depth of subsurface water. With a few spectacular exceptions, the ratios of amounts in the microlayer to amounts in subsurface water are generally negligible, a conclusion reinforced by recent observations with chlorinated hydrocarbons in the Niagara River (28).

## Sediment

Table 3 summarizes the results of the sediment surveys for the butyltin species and inorganic tin. In general the pattern of occurrence of tributyltin in sediment is similar to its pattern of occurrence in water. The ten highest concentrations of tributyltin, up to 10.8 mg Sn/kg dry weight, were all found in Vanvouver Harbor, Canada's busiest harbor. It is possible that the sediment was contaminated by paint chips smaller than 850 um in size. The toxicological significance of sediment-associated tributyltin is at present difficult to assess since relatively little work has been done in this

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 $i_{i}$ 

area. Tributyltin appears to be adsorbed moderately strongly to sediment. Very little was desorbed in laboratory experiments over 10 months (21). It has been shown that oligochaete worms can (i) accumulate sediment-associated tributyltin, thus making it potentially available to bottom-feeding fish, and (ii) can degrade tributyltin (21).

#### Fish.

Table 4 shows concentrations of tributyltin and its degradation products in those few fish which were analyzed. Only 18 fish were analyzed, so it is impossible to generalize on the results. Inorganic tin was found frequently in the fish. The only fish which contained tributyltin were from harbors, which is at least consistent with the findings in water and sediment.

# Other Species Found

The trimethyltin, dimethyltin and monomethyltin species were also observed in water, sediment and fish, but much less frequently than the butyltin species (17,20). The presence of these species may be due to the use of dimethyltin compounds as poly(vinyl chloride) stabilizers, or they may result from the methylation of inorganic tin in aquatic environments. The methyltin species are far less toxic to aquatic organisms than is tributyltin (10,27).

Our early finding of tributylmethyltin and dibutyldimethyltin in the sediments of four harbors in Ontario at relatively high concentrations with

respect to tributyltin and dibutyltin raised the possibility that methylation of butyltin species in aquatic environments was a significant pathway of transformation (19). The cross-Canada survey has shown, however, that butylmethyltin compounds were only found infrequently in water and sediment (20). For example, the compound BusMeSh was found in only 7 water samples and 1 sediment sample, compared with 43 water samples and 78 sediment samples for BugSn<sup>+</sup>. Therefore, although it is likely that the butylmethyltin compounds resulted from the methylation of butyltin species in water or sediment (19), the national survey demonstrated that such methylation is not in general a significant pathway of transformation of butyltin species. Support for such a conclusion is provided by our work on the biological degradation of tributyltin in water and sediment from Toronto Harbor in which it was demonstrated that butylmethyltin compounds occurred infrequently and in very low concentrations (21). Tetrabutyltin was only found rarely in water and sediment in the national survey (20). Its presence may have been due to the disproportionation of other butyltin species or, and perhaps more likely, to contamination of tributyltin antifouling paint formulations by the tetrabutyltin.

### Canadian Regulation of Antifouling Uses of Tributyltin

In Canada, pesticides are regulated by the Department of Agriculture under the authority of the Pest Control Products Act. On February 28, 1989, the Department of Agriculture announced its regulation of antifouling uses of tributyltin (47). Tributyltin-containing antifouling paint is prohibited on vessels of less than 25 m in length with the exception of those with aluminum

hulls. On larger wessels there is a maximum daily release rate for tributyltin of 4 ug/cm<sup>2</sup>

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Location	(Bu <sub>a</sub> Sn <sup>+</sup> )	[BugSn <sup>e+</sup> ]	[BuSn3+]	[Inorganic tin]	Ref.
Ontario lakes, rivers and harbors	nd-1.19	nd-3.73	nd-5.73	nd-50.1	17
Detroit and St. Clair Rivers	nd-0.07	nd-0.10	nd-0.11	nd-2.95	25
Toronto Harbor	nd-0.20	nd-0.10	nd-0.09	nd-0.88	<b>2</b> 1
bottom water	nd-18.10	nd-0.72	nd-0.29	nd-0.11	21
Canadian lakes, řivers, bays and harbors	nd-2.34	nd-1.36	nd-1.89	nd÷37.20	20

Table 1. Concentrations (ug Sn/L) of tributyltin; dibutyltin; monobutyltin and inorganic tin in subsurface water in Canada.\*

"nd - below limit of quantitation

Table 2.	Concentrations (ug	Sn/L)	of tributyltin, dibut	yltin) 🖄	monobutyltin
	and inorganic tin	in the	surface microlayer in	Canada.	<b>*</b>

Location	(Bu <sub>3</sub> Sn <sup>+</sup> )	[Bu <sub>e</sub> Sn <sup>e+</sup> ]	[BuSn <sup>3+</sup> ]	[Inorganic tin]	Ref.
			·		
Ontario lakes, rivers and harbors	nd-24.91	nd-1328	nd	nd-633	17
St. Clair River	nd-0.03	nd-0.01	nd	0.06-2.27	55
Ontario, Quebec and New York lakes, rivers and harbors	nd-473	nd-365	nd-66.8	nd-14000	23

"nd - below limit of quantitation

Location	[Bu <sub>3</sub> Sn <sup>+</sup> ]	[Bu <sub>2</sub> Sn <sup>2+</sup> ]	[BuSn <sup>9+</sup> ]	[Inorganic tin]	Ref.
Ontario lakes, rivers and harbors	nd-0.54	nd-0.35	nd-0.58	0.08-5.13	. 19
Detroit and St. Clair Rivers	nd-0.07	nd-0.04	nd-0.01	nd-0.39	55
Toronto Harbor	nd-1.28	nd-0.26	nd-0.08	nd-0.62	21
sediment core	nd-3.52	nd-0.53	nd-0.06	nd-13.80	21
Canadian lakes, rivers, bays and harbors	nd-10.78	nd-8.51	nd-4.73	nd-15.50	20

Table 3. Concentrations (mg Sn/kg. dry weight) of tributyltin, dibutyltin, monobutyltin and inorganic tin in sediment in Canada.\*

"nd - below limit of quantitation

Table 4. Concentrations (mg Sn/kg wet weight) of tributyltin, dibutyl monobutyltin and inorganic tin in fish in Canada."						
Location	[Bu <sub>3</sub> Sn <sup>+</sup> ]	[Bu <sub>e</sub> Sn <sup>e+</sup> ]	[BuSn <sup>3+</sup> ]	[Inorganic tin]	Ref.	
Ontario harbors	nd-0.02	nd	nd	-0.62	50	
Lakes Ontario, Erie and Huron	'nď	nd	nd	nd-0.90	20	
Vancouver Harbor	0.24	0.05	0.06	0.04	50	

"nd - below limit of quantitation