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**REVIEW OF THE OCCURRENCE, PERSISTENCE
AND DEGRADATION OF TRIBUTYL TIN
IN FRESH WATER ECOSYSTEMS IN CANADA**

R.J. Maguire

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Environmental Contaminants Division
National Water Research Institute
Canada Centre for Inland Waters
Burlington, Ontario, Canada L7R 4A6

• Environment Canada

EXECUTIVE SUMMARY

Review of the Occurrence, Persistence and Degradation of Tributyltin in Fresh Water Ecosystems in Canada

A survey of 300 locations in Canada found the highly toxic pesticide tributyltin mainly in harbours, marinas and shipping channels, which is consistent with its use as an antifouling agent in some paints for boats, ships and docks. In water its concentration in some locations is high enough to cause concern with regard to chronic toxicity or effects in sensitive organisms. Biological degradation in water and sediment appears to be the rate-limiting factor which determines the persistence of tributyltin in aquatic environments, and based upon laboratory experiments the half-life in fresh water at 20 degrees is estimated to be of the order of 6 weeks to a few months.

Management Perspective

These results form the basis of discussions between DOE and Agriculture Canada on the status of tributyltin under the Pest Control Products Act. They are also being used by the US EPA and US Navy in their debates on tributyltin under similar legislation.

RÉSUMÉ EXÉCUTIF

Étude de la présence, la persistance et la dégradation du tributyl-étain dans les écosystèmes d'eau douce au Canada

Une étude réalisée à 300 endroits au Canada a permis de découvrir que le tributyl-étain, un pesticide extrêmement toxique, se trouvait surtout dans les ports, les marinas et les chenaux, ce qui est logique étant donné qu'il est utilisé comme agent de résistance à la pourriture dans certaines peintures de bateaux, de navires et de quais. À certains endroits, sa concentration dans l'eau est suffisamment élevée pour susciter l'inquiétude au sujet de sa toxicité ou de ses effets chroniques sur les organismes sensibles. La dégradation biologique qui se produit dans l'eau et les sédiments semble être le facteur limitatif qui détermine la persistance du tributyl-étain dans les environnements aquatiques; selon les résultats d'expériences en laboratoire, la demi-vie du tributyl-étain à 20° dans l'eau douce est d'environ 6 semaines à quelques mois.

Perspective-gestion

Les résultats de ces expériences constituent la base de discussions entre Environnement Canada et Agriculture Canada au sujet du statut du tributyl-étain dans la Loi sur les produits antiparasitaires. L'Environmental Protection Agency et la Marine des États-Unis utilisent également ces résultats pour discuter du cas du tributyl-étain dans le cadre de lois similaires.

ABSTRACT

In Canada tributyltin has been found mainly in harbours, marinas and shipping channels, which is consistent with its use as an antifouling agent. In water its concentration in some locations is high enough to cause concern with regard to chronic toxicity or effects in sensitive organisms. It has also been found in mg/kg concentrations in harbor sediments, but the toxicological significance of sediment-associated tributyltin is unknown. Biological degradation in water and sediment appears to be the rate-limiting factor which determines the persistence of tributyltin in aquatic environments, and based upon laboratory experiments the half-life in fresh water at 20 degrees is estimated to be of the order of 6 weeks to a few months. Methylation of tributyltin and its degradation products in aquatic environments has been demonstrated, but it does not appear to be a significant pathway of transformation in fresh water.

RÉSUMÉ

Au Canada, on retrouve le tributyl-étain surtout dans les ports, les marinas et les chenaux, ce qui est logique étant donné qu'on s'en sert comme agent de résistance à la pourriture. À certains endroits, sa concentration dans l'eau est suffisamment élevée pour susciter l'inquiétude au sujet de sa toxicité ou ses effets chroniques sur des organismes sensibles. On a également découvert des concentrations du produit en mg/kg dans des sédiments de ports, mais on ne connaît pas encore les effets toxiques des sédiments contenant du tributyl-étain. Il semble que la dégradation biologique qui se produit dans l'eau et les sédiments soit le facteur limitatif qui détermine la persistance du tributyl-étain dans les environnements aquatiques; selon les résultats d'expériences en laboratoires, la demi-vie du tributyl-étain dans l'eau douce à 20° est d'environ 6 semaines à quelques mois. On a déjà réussi à démontrer qu'il y avait méthylation du tributyl-étain et de ses produits de dégradation dans les milieux aquatiques, mais il ne semble pas que ce processus soit une réaction de transformation importante du tributyl-étain dans l'eau douce.

In Canada the tri-n-butyltin species is used in various compounds and formulations mainly as an antifouling agent in some paints for boats, ships and docks, as a general lumber preservative and as a slimicide in cooling water (1). By virtue of its high aquatic toxicity it is perhaps the most prominent of the organotin compounds for which environmental and human health hazard assessments were called under Canada's Environmental Contaminants Act in 1979 (2). This article reviews our contribution to a hazard assessment of tributyltin in fresh water.

For brevity, the tributyltin, dibutyltin and monobutyltin species are referred to in this article as though they existed only in cationic form (e.g., Bu_3Sn^+). We believe that all tributyltin compounds dissolved in water 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 (3-5) and from mammalian (3,6) and fish (7) toxicity studies which have indicated that the toxicity of tributyltin compounds is independent of the nature of the counter ion.

The hazard posed by tributyltin to an organism in any particular "compartment" (e.g., water, suspended solids, sediment, etc.) of an aquatic ecosystem is in general a function of (i) its toxicity to the organism, and (ii) its bioavailable concentration and persistence in that compartment. Our work has mainly dealt with determinations of concentration and persistence in fresh water.

Tributyltin is very toxic to aquatic organisms. Lethal concentrations are in the range 0.04-16 $\mu\text{g Sn/L}$ for short term exposures of copepods (8,9), mussel larvae (10), crab larvae (11), lobster larvae (12), sheepshead minnow (13), bleak (8), guppy (7) and rainbow trout (14,15).

Over the past five years we have analyzed water and sediment from about 300 locations in Canada for tributyltin. Most of these locations have been in fresh water. The results are summarized in Table 1. 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 reliably in 23% of all samples. The highest concentration, 18.1 $\mu\text{g Sn/L}$, may be suspect since it was not taken at 0.5 m depth like all the other samples, but was the water overlying the sediment in a core taken from Toronto Harbor (22), and may have been contaminated with sediment which contained Bu_3Sn^+ . This value is almost twice the 24 hr LC-50 value of 11.2 $\mu\text{g Sn/L}$ determined for adult rainbow trout (14). Even discounting this

one water sample, in 28 of the remaining 66 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 the 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 (26), in agreement with our own work and estimates made on the basis of the octanol-water partition coefficient of tributyltin ($\log K_{ow} = 3.2$, ref. 20). Such a value for the partition coefficient indicates that most (97%) of the tributyltin is associated with the aqueous phase of the water column (i.e., that which passes a 0.45 μ m filter), and very little is adsorbed onto suspended solids. This has been confirmed in a very few 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, therefore, that all the tributyltin found in water is biologically available and potentially toxic to aquatic life.

Tributyltin has also been found in some surface microlayer samples. The surface microlayer of natural waters contains a thin film of natural and anthropogenic surface-active material. The nature and chemical and biological significance of surface microlayers are matters which have received increasing attention over the last fifteen years (cf. ref. 27 and references therein). The thickness of the surface microlayer is operationally defined by the type of collector used (28-32), and values less than 2×10^{-4} m are common. Many workers have demonstrated that surface microlayers can concentrate contaminants relative to subsurface waters (33-36, and references therein). In our work, in 19 of the 22 samples in which tributyltin was determined reliably in the surface microlayer, its concentration exceeded that value of 0.07 ug Sn/L which could cause chronic toxicity or growth retardation in rainbow trout yolk sac fry (15). Unfortunately, there appear to be few other data in the literature on the toxicity of tributyltin to fresh water organisms, let alone those which spend at least part of their lives at the air-water interface. Tributyltin concentrations in the surface microlayer were generally higher than concentrations in subsurface water: concentration factors ranged up to about 6×10^3 . In addition, tributyltin was occasionally found in some surface microlayer samples, but not in subsurface water samples, indicating that the surface microlayer serves as an imperfect indicator of ecosystem contamination. Because the surface microlayer is profoundly affected by turbulence and the presence of both natural and anthropogenic surface-active material, however, in the past we have been inclined to view concentrations of toxic substances in the microlayer as being extremely variable with time. Therefore the toxicological significance of high concentrations of

tributyltin in surface microlayers, and the carrying capacity of the surface microlayer relative to the subsurface water and sediment, remain uncertain. We are presently investigating the temporal variation of contaminant concentrations in surface microlayers relative to subsurface waters.

In sediment, tributyltin was determined reliably in 103 of 294 samples. Little is known of the biological availability, hence toxicological significance, of tributyltin in sediment. The ten highest concentrations of tributyltin in sediment, all over 1 mg Sn/kg dry weight, were all found in Vancouver Harbor, Canada's busiest harbor.

Tributyltin concentrations determined in subsurface water, surface microlayer and sediment in this survey are generally similar to concentrations determined in several other countries (37-42).

Only 18 fish were analyzed, so it is impossible to generalize on the results. The only fish which contained tributyltin were from harbors, which is at least consistent with the findings in water and sediment.

The persistence of a chemical in an aquatic ecosystem is a function of its own physical and chemical properties, and ecosystem-specific properties such as the concentration of suspended organic material, nature and concentration of microbial populations, etc. (e.g., cf. ref. 43,44).

The finding of tributyltin in fish and sediments suggests that it at least persists long enough in aquatic environments to be adsorbed to sediments and taken up by biota. However, we have also found the degradation products dibutyltin and monobutyltin (and inorganic tin) in water, sediment and fish (18,19,21-23), which indicates that tributyltin can in principle be degraded in aquatic environments. We have also shown (i) that tributyltin can be degraded by a common alga, *Ankistrodesmus falcatus*, but at algal cell concentrations far in excess of natural populations (24), and (ii) that tributyltin can be taken up from sediment by oligochaete worms, and can be degraded (22). In addition to these studies, we have investigated a variety of other chemical and biological pathways of dissipation and degradation which are commonly operative in aquatic environments, and the half-lives which we have estimated for such processes are shown in Table 2. From these data we conclude that, of the physical and chemical processes examined, the rate-limiting process would likely be sunlight degradation in water. However, photolysis is probably not important at depths greater than 0.5 - 1 m. Biological degradation in water and sediment appears to be most important factor limiting the persistence of tributyltin in fresh water aquatic ecosystems and we estimate the half-life at 20 degrees to of the order of 6 weeks to a few months.

In the course of our survey work we detected tributylmethyltin, dibutyldimethyltin and butyltrimethyltin

infrequently in water and sediment (19,23). We also detected low concentrations of tributylmethyltin, dibutyldimethyltin, dimethyltin and dimethyltin in our work on the biological degradation of tributyltin (22). Interpretation of these results is complicated by the fact that some of these species (i.e., $\text{Bu}_2\text{Me}_2\text{Sn}$, BuMe_3Sn and perhaps $\text{Me}_2\text{Sn}^{2+}$ as the $\text{Me}_2\text{Pe}_2\text{Sn}$ derivative) will suffer some evaporative loss in our analysis of tributyltin and its degradation products as butylpentyltin derivatives (16). Nevertheless, although it is likely that the methylated species resulted from the methylation of the butyltin species or inorganic tin in water or sediment, our results suggest, from the point of view of mass balance, that methylation is not a significant pathway of transformation of butyltin species or inorganic tin in fresh water.

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Table 1. Summary of Tributyltin Occurrence in Canada*.

	Number of Samples	Samples with Bu_3Sn^+	Concentration Range, ug Sn/L or mg Sn/kg
Subsurface water (unfiltered)	292	67	0.01 - 18.1
Surface microlayer (unfiltered)	34	22	0.01 - 24.9
Sediment (top 2 cm, dry weight)	294	103	0.01 - 10.8
Fish (whole, wet weight)	18	3	0.01 - 0.24

* Results refer to samples in which Bu_3Sn^+ was determined with confidence (cf. ref. 16-25 for analytical methods and details of sampling locations).

Table 2. Summary of the Kinetics of Degradation or Dissipation of Tributyltin in Fresh Water Ecosystems at 20° C *.

	estimated $t_{1/2}$, months
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volatilization from water	> 11
desorption from sediment	> 10
chemical degradation	> 11
photochemical degradation	> 3
microbial degradation in water, aerobic	5
microbial degradation in water-sediment mixtures, aerobic	4
microbial degradation in water, anaerobic	1.5

* Experiments are described in ref. 20, 22 and 25.