screening procedures for pesticide mixtures in a wide variety of substrates.

Registry No. GLYPH, 1071-83-6; AMPA, 1066-51-9; TFE, 75-89-8; PFP, 28302-70-7; TFAA, 407-25-0; HFBA, 336-59-4; $CF_3CH_2OC(O)CH_2N[C(O)CF_3]CH_2P(O)(OCH_2CF_3)_2$, 97280-52-9; H_2O, 7732-18-5.

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Degradation of the Tri-*n*-butyltin Species in Water and Sediment from Toronto Harbor

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Contamination of water and sediment in Toronto Harbor by the highly toxic tri-*n*-butyltin species (Bu_3Sn^+) and its less toxic degradation products, the di-*n*-butyltin species (Bu_2Sn^{2+}), *n*-butyltin species ($BuSn^{3+}$), and inorganic tin, is demonstrated. At some locations the concentration of Bu_3Sn^+ in water is high enough to warrant concern with regard to chronic toxicity to sensitive organisms. The Bu_3Sn^+ species (i) is bound fairly strongly to sterile Toronto Harbor sediment and the half-life of desorption is at least 10 months at 20 °C, (ii) can be taken up from sediment and degraded by oligochaetes, and (iii) is degraded by a sequential debutylation pathway at 20 °C in Toronto Harbor water and water–sediment mixtures with half-lives of 5 and 4 months, respectively. On the basis of this and earlier work it is concluded that the main factors limiting the persistence of the tri-*n*-butyltin species in aquatic ecosystems are photolysis in water and biological degradation in water and sediment, and with the temperatures and sunlight intensities prevalent in Canada, the half-life is likely to be at least a few to several months.

Organotin compounds are used in three main ways, viz., as stabilizers for poly(vinyl chloride), as catalysts, and as pesticides (Zuckerman et al., 1978). Organotin compounds are a class of compounds about which more information is sought under Canada's Environmental Contaminants Act (Canada Department of Environment and Department of National Health and Welfare, 1979) regarding toxicology and environmental fate. We have been attempting to determine the aquatic environmental occurrence, persistence, and fate of the highly toxic tri-*n*-butyltin species (Bu_3Sn^+), which is used as an antifouling agent in some paints for boats, ships, and docks, as a general lumber preservative, and as a slimicide in industrial cooling water (Davies and Smith, 1980). Recently we reported the occurrence of Bu_3Sn^+ and its less toxic degradation products Bu_2Sn^{2+}, $BuSn^{3+}$, and inorganic tin in water (Maguire et al., 1982) and sediment (Maguire, 1984) at 30 locations in Ontario. Although inorganic tin was practically ubiquitous, the three butyltin species were usually found in the water and sediment of harbors, marinas, and other areas of heavy boating and shipping traffic, which reflects the antifouling use of Bu_3Sn^+ noted above.

Our earlier work suggested that Bu_3Sn^+ might be moderately persistent in water. For example, it neither volatilized nor lost butyl groups over a period of at least two months in the dark at 20 °C. Bu_3Sn^+ did undergo slow ($t_{1/2} > 89$ d) sunlight photolytic degradation, at least partially by stepwise debutylation to inorganic tin (Maguire et al., 1983). In addition, it underwent 50% conversion to Bu_2Sn^{2+} by a green alga, *Ankistrodesmus falcatus*, over a 4-week period at 20 °C, but at algal cell concentrations up to one hundred times higher than what might be expected in Lake Ontario or Toronto Harbor (Maguire et al., 1984). The sequential debutylation observed in the above experiments appears to be a general phenomenon, observed in mammals (Kimmel et al., 1977), bacteria and fungi (Barug, 1981), and soil (Sheldon, 1978; Barug and Vonk, 1980).

This article discusses the adsorption of Bu_3Sn^+ to sediment and the degradation of Bu_3Sn^+ in water and sediment from nearby Toronto Harbor, which, as will be shown below, is contaminated with butyltin species and inorganic tin.

For brevity, each of the *n*-butyltin species is referred to in this article as though it existed only in cationic form (e.g., Bu_3Sn^+). This formalism is not meant to imply exact

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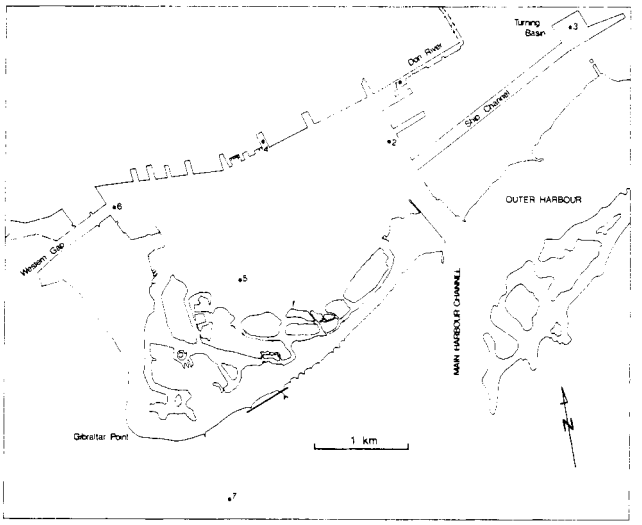

Figure 1. Sampling locations in Toronto Harbor. Site 8, not shown, is at the mouth of the Humber River, 5 km west of the Western Gap.

identities for these species in water, sediment, or biota. We were more interested in debutylation reactions than in the nature of the cation since in general the toxicity of butyltin compounds decreases with decreasing number of butyl groups and is independent of the nature of the counter ion (Davies and Smith, 1980).

EXPERIMENTAL SECTION

Materials. Bis(tri-*n*-butyltin) oxide (97%), di-*n*-butyltin dichloride (96.5%), *n*-butyltin trichloride (95%), tin (99.99%), and methylmagnesium bromide in diethyl ether were from Ventron (Danvers, MA). *n*-Pentylmagnesium bromide was prepared from readily available chemicals. 2-Hydroxy-2,4,6-cycloheptatrien-1-one (tropolone) was from Aldrich (Milwaukee, WI). All organic solvents were pesticide grade from Caledon (Georgetown, Ont.). Sulfuric and hydrochloric acids were reagent grade, but the HCl was washed with a solution of tropolone in benzene to remove traces of inorganic tin. Water was distilled and passed through a "Milli-Q" system (Millipore, Mississauga, Ont.).

Butylpentyltin ($Bu_nPe_{4-n}Sn$, where $n \leq 4$) and butylmethyltin ($Bu_nMe_{4-n}Sn$, where $1 \leq n \leq 3$) standards were prepared and purified according to the method of Maguire and Huneault (1981), which does not result in redistribution of alkyl groups. Since butylmethyltin compounds were occasionally detected in water and sediment, particular attention was paid to the possibility of contamination of the *n*-pentylmagnesium bromide by methylmagnesium bromide, but no such contamination was evident.

Sample Collection. Most of the water and sediment samples were collected in June, 1983 at six locations in Toronto Harbor (cf. Figure 1), one location close to a drinking water inlet pipe outside the harbor, and one location at the mouth of the Humber River, about 5 km west of the harbor. The boat used in sample collection had not been painted with antifouling paint.

To assess the degree of contamination of the harbor, 8 L of samples of subsurface water were collected in amber glass bottles from a depth of 0.5 m, and the contents were acidified to pH 1 and stored at 4 °C until extraction. These preservation conditions were effective over a period of at least three months (Maguire, 1982). Sediment samples were 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 a 850-μm screen. At four sites (2, 3, 4, and 5), 7 cm diameter sediment cores were taken with a lightweight benthos corer and kept at 4 °C overnight. 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.

Samples of water which were to be used to determine the biological degradation of Bu_3Sn^+ were collected from 0.5 m above the sediment–water interface at site 2 and stored at 4 °C for a few days before experiments began. Samples of sediment (top 2 cm only) to be used in the same experiments were collected at the same site with an Ekman dredge and stored in a similar fashion. Oligochaetes (primarily *T. tubifex* and *L. hoffmeisteri*; Barton, 1984) were picked from sediment collected at sites 1 and 2 in May, 1984 for experiments on uptake and metabolism of sediment-associated Bu_3Sn^+.

Sample Analyses. The methods of analysis for water (Maguire et al., 1982) and sediment (Maguire, 1984) are documented elsewhere. In essence, they involve extraction of the three butyltin species Bu_3Sn^+, Bu_2Sn^{2+}, and $BuSn^{3+}$ and inorganic tin, 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, $Bu_nPe_{4-n}Sn$, purification by silica gel column chromatography, concentration of the purified solution, and gas chromatographic determination of the derivatives (vide infra).

The analysis of the oligochaetes required a simple modification. One gram of oligochaetes (about 100 of them) was dispersed in 1–2 mL of HCl for 2 h at room temperature. The resulting mixture was diluted 5-fold with water, then extracted, and treated in the same way as the water samples described above.

Determination of the $Bu_nPe_{4-n}Sn$ derivatives from extracts of water, sediment, and oligochaetes was done by packed-column gas chromatography with a quartz tube furnace atomic absorption spectrophotometric detector (Maguire and Tkacz, 1983), which has been found to be more reliable than the flame photometric detector used previously. Considering that a fairly specific detector was used in the analyses, identities of the $Bu_nPe_{4-n}Sn$ species were deemed to be confirmed by cochromatography with authentic standards on two column packing materials of very different polarity. The same criterion of identification was employed for the mixed butylmethyltin compounds which were occasionally observed in the water and sediment samples.

In the quantitation of the analytes, use was made of appropriate reagent blanks. The results reported in this article are above the limit of quantitation (LOQ), which is defined (Keith et al., 1983) as the reagent blank value plus ten times its standard deviation.

The recoveries of Bu_3Sn^+, Bu_2Sn^{2+}, and $BuSn^{3+}$ from spiked water samples at 1–10 mg/L varied from 96 ± 4 to 103 ± 8% (Maguire and Huneault, 1981). Recoveries of the three butyltin species from spiked sediment at 0.01, 0.2, 1, and 10 mg of Sn/kg dry weight ranged from 55 ± 26 to 180 ± 100% (Maguire, 1984); in general, however, recoveries of the three butyltin species from spiked sediment were quantitative within a fairly wide range of experimental error. Recoveries of Sn(IV) were poor (35 ± 23%) from water at pH 5–8 probably because of the formation of unextractable SnO_2 at neutral pH (Maguire et al., 1983). Reoveries of the three butyltin species and Sn(IV) from spiked oligochaetes ranged from 65 ± 19 to

Table I. Experimental Conditions in Determination of Degradation of Bu_3Sn^+ in Toronto Harbor Water and Sediment[a]

expt	distilled water	Toronto Harbor water	sediment	Bu_3Sn^+	KCN
A	x				
B	x			x	
C	x			x	x
D		x			
E		x			x
F		x		x	
G		x		x	x
H		x	x		
I		x	x		x

[a] All experiments were done in triplicate. All water volumes were 50 mL and all sediment wet weights were 50 g. The Bu_3Sn^+ spike in water was at 1 mg of Sn/L and 1 g of KCN was used to suppress biological activity in the controls. "A" is the reagent blank.

77 ± 11% at the 0.1 mg of Sn/kg level. No concentrations reported in this article are corrected for recovery.

Although Sn(IV) was the only inorganic tin species for which recoveries were determined, the tin present in our water, sediment, and oligochaete samples is reported as inorganic tin, since any Sn(II) which might have been present would likely have been oxidized to Sn(IV) during extraction or pentylation.

Sediment–Water Partitioning of Bu_3Sn^+. All experiments reported in this section were done in triplicate at 20 °C in the dark by using sediment from the harbor and water collected 0.5 m above the sediment–water interface. The water was not filtered, and the sediment was not dried, since drying might have changed its adsorption characteristics. All results were corrected for reagent contamination and for butyltin species and inorganic tin present in the water and sediment before the Bu_3Sn^+ spike was introduced.

To estimate the extent of binding of Bu_3Sn^+ to sediment, 100 mg of wet sediment was shaken with 10 mL of a solution of 0.1 μg of Sn/L of Bu_3Sn^+ for periods of 4–16 d. The aqueous phase also contained 0.5 g of KCN to suppress biological degradation. At the end of the shaking period, both phases were analyzed for Bu_3Sn^+.

The kinetics of desorption of the butyltin species and inorganic tin from sediment were also examined. In this case it was not necessary to spike the sediment since it already contained all four species. The Bu_3Sn^+ species was of most concern, and with the knowledge of the sediment–water partition coefficient determined above, conditions were adjusted so that any desorbed Bu_3Sn^+ could be detected. Each flask contained 10 g of sediment in 2 L of water which also contained 10 g of KCN to suppress biological degradation. The desorption of Bu_3Sn^+ from sediment was determined as a function of time and degree of agitation.

Degradation of Bu_3Sn^+ in Water and Sediment. A kinetic experiment was designed to account for (i) differences between abiotic and biological degradation in water alone or in water–sediment mixtures, (ii) butyltin species and inorganic tin present in the water and sediment before the Bu_3Sn^+ spike was introduced, and (iii) reagent blanks.

Experiments in water alone were conducted at two different initial concentrations of Bu_3Sn^+, viz., 1 mg of Sn/L and that concentration which was already present in the water upon collection. Although the latter concentration was more appropriate, it was felt that the use of 1 mg of Sn/L of Bu_3Sn^+ would aid in determining the mechanism of degradation since concentrations of degradation products could be more easily determined.

Experiments with the water–sediment mixtures were conducted with no Bu_3Sn^+ spike since the sediment already contained about 1 mg of Sn/kg of dry weight of Bu_3Sn^+.

The experimental design is shown in Table I. All flasks were shaken once and then allowed to stand in the dark at 20 °C for periods up to 11 months. At each sampling date the contents of the 27 flasks of designations A–I were analyzed for the butyltin species and inorganic tin. Care was taken to rinse the insides of the flasks with solutions of tropolone in benzene to remove any adsorbed butyltin species or inorganic tin.

Uptake of Bu_3Sn^+ from Sediment by Oligochaetes. An experiment was done to determine if sediment-associated Bu_3Sn^+ could be accumulated by a benthic organism, hence made available to bottom-feeding fish. Fifteen kilograms of Toronto Harbor sediment was added to a 30 × 60 cm glass aquarium to a depth of 8 cm. Fifty mL of a methanolic solution of bis(tri-*n*-butyltin) oxide was added to the sediment, which was then mixed manually and electrically for 2 h to give a nominal concentration of Bu_3Sn^+ (including that already present in the sediment) of 1.5 mg of Sn/kg wet weight. Then 32 L of Toronto Harbor water was added and aeration was provided with compressed air. Two weeks after the water was added, 13 g of oligochaetes, picked from unspiked sediment, were added to the aquarium and the mixture was kept in the dark at 20 °C, with continuous aeration of the water, for 5 months, during which time 1 g of oligochaete samples were periodically collected and analyzed for Bu_3Sn^+ and its degradation products. This experiment was not done in triplicate.

Table II. Concentration of Butyltin Species and Inorganic Tin in Unfiltered Subsurface Water and in the Top 2 cm of Sediment[a]

			subsurface water (μg of Sn/L)				sediment (mg of Sn/kg dry weight)			
site	description	depth, m	Bu_3Sn^+	Bu_2Sn^{2+}	$BuSn^{3+}$	inorganic tin	Bu_3Sn^+	Bu_2Sn^{2+}	$BuSn^{3+}$	inorganic tin
1	Keating Channel (mouth of Don River)	4	0.02	0.01	0.01	0.14	0.13	0.10	0.04	
2	off Polson St.	8	0.02	0.01	det	0.20	1.28	0.01		0.62
3	turning basin	8	0.01	det		0.75	0.21	0.02	0.02	0.42
4	Yonge St. slip	6	0.11	0.04	0.05	0.06	0.38	0.26	0.08	0.38
5	Center Island ferry lane	7	0.20	0.10	0.09	0.20	0.08	0.04	det	0.16
6	Western Gap	8	0.04	0.02	0.02	0.08	0.25			
7	Toronto Islands filtration plant inlet pipe 2	18				0.88				
8	Humber River mouth	1	0.01	det	det	0.03				0.06

[a] "Blanks" mean below limit of detection (LOD; Keith et al., 1983) and "det" means that a species was detected but its concentration was below the limit of quantitation (LOQ). For sample sizes of 8 L for subsurface water and 10 g of dry weight for sediment, the LOQ values for each species were about 0.01 μg of Sn/L and 0.01 mg of Sn/kg of dry weight, respectively. LOD values were generally about one third of LOQ values.

Table III. Concentrations of Butyltin Species and Inorganic Tin in Sediment Cores (mg of Sn/kg dry weight) and Unfiltered Overlying Water (μg of Sn/L)[a]

depth in	site 2				site 3				site 4				site 5			
core, cm	Bu_3Sn^+	Bu_2Sn^{2+}	$BuSn^{3+}$	tin	Bu_3Sn^+	Bu_2Sn^{2+}	$BuSn^{3+}$	tin	Bu_3Sn^+	Bu_2Sn^{2+}	$BuSn^{3+}$	tin	Bu_3Sn^+	Bu_2Sn^{2+}	$BuSn^{3+}$	tin
b					det	det	0.29			det			18.10	0.72		0.11
0–1	0.04	0.04	0.06	0.62	det				1.84	0.02		0.12	det			
1–2	0.02			0.06					0.86	0.01		0.13	1.67	0.03		0.06
2–3	0.01	det	det	0.08					1.22	0.02	0.02	0.16	0.08	det		det
3–4	0.08	det	0.02	det					0.77	0.01	0.02	0.10	3.52	0.22	0.03	10.22
4–5	0.03								2.56	0.01	0.02	0.67	2.51	0.05	0.02	10.51
5–6									2.60	0.30		0.27	2.36	0.13	0.03	8.76
6–7									1.03	0.07		0.08	nd	nd	nd	nd
7–8	0.09								1.30	0.15		0.19	1.99	0.10	0.02	7.49
8–9	0.24								2.59	0.45		0.34	3.35	0.09	0.06	
9–10	0.34												2.57	0.16	det	8.11
10–15													2.36	0.32	0.05	6.87
15–20					0.01				0.32	0.02			3.17	0.15	0.06	13.80
20–25					0.22								2.30	0.42	0.02	6.74
25–30													1.49	0.53		1.17
30–35																
35–40																
40–45																

[a] "Blanks" mean below limit of detection (LOD; Keith et al., 1983), "det" means that a species was detected but its concentration was below the limit of quantitation (LOQ), and "nd" means not done. In the core tubing there was generally 20 cm of water above the sediment, and it was this water that was analyzed. For sample sizes of 500 mL for overlying water and 10 g of dry weight for sediment, the LOQ values for each species were about 0.08 μg of Sn/L and 0.01 mg of Sn/kg of dry weight, respectively. LOD values were generally about one third of LOQ values. [b] Overlying water.

RESULTS

Occurrence of Butyltin Species and Inorganic Tin. Table II shows that contamination of water and sediment in Toronto Harbor by Bu_3Sn^+ and the other species is widespread. The Bu_3Sn^+ concentrations are the most important since the toxicity decreases significantly with decreasing number of butyl groups (Davies and Smith, 1980). There was little contamination at the two locations (7 and 8) outside the harbor, which supports earlier conclusions that such contamination is mainly due to the use of tri-*n*-butyltin compounds as antifouling agents in paint for boats, ships, and docks. The subsurface water at sites 4 and 5 was the most heavily contaminated by Bu_3Sn^+, with concentrations 6–10% of the LC_{100}^{12d} (i.e., that concentration which killed 100% of the test organisms in 12 days) value of 1.8 μg of Sn/L for rainbow trout yolk sac fry (Seinen et al., 1981). The concentrations of all butyltin species and inorganic tin are in general similar to what has been observed before in Toronto Harbor water and sediment (Maguire et al., 1982; Maguire, 1984). Tributylmethyltin and dibutyldimethyltin were only rarely detected in these water and sediment samples, and at low concentrations relative to the butyltin species, and thus their concentrations are not shown.

Table III shows concentrations of butyltin species and inorganic tin in sediment cores and overlying water at four sites in Toronto Harbor. These data, combined with those from Table II, reveal sites 5, 4, and 2 to be the most heavily contaminated by Bu_3Sn^+ of all locations sampled. Particularly noteworthy from the point of view of chronic and acute toxicity is the concentration of Bu_3Sn^+ of 18.1 μg of Sn/L in water just above the sediment at site 5, a value ten times higher than the LC_{100}^{12d} value for rainbow trout fry (Sinen et al., 1981) and almost twice the LC_{50}^{24h} value of 11.2 μg of Sn/L for adult rainbow trout (Alabaster, 1969).

Smoothly decreasing concentrations of butyltin species and inorganic tin were not observed in any sediment core. One reason for this at sites 2 and 3 is that large ships frequently stir up the sediment (Fricbergs, 1984). Such mechanical mixing is possible but less likely at sites 4 and 5, since ferries and pleasure craft constitute most of the traffic in these latter locations. Oligochaetes might be expected to mix the sediment to a depth of only 2–10 cm (Brinkhurst and Jamieson, 1981). There has been no dredging or disposal of dredged material at sites 2–5 since 1972 (Fricbergs, 1984).

Table IV. Desorption of Butyltin Species and Inorganic Tin from Unshaken Toronto Harbor Sediment[a]

time,	% of total bound species released			
months	Bu_3Sn^+	Bu_2Sn^{2+}	$BuSn^{3+}$	inorganic tin
0	0	0	0	0
3.9	0	0	4	0
5.9	0	0	3	1
10.6	6	1	2	1

[a] Percentages are based on what could be extracted from dried sediment with tropolone in benzene under reflux.

A comparison of the concentrations of the butyltin species and inorganic tin in the top 2 cm of the sediment grab samples at sites 2–5 (shown in Table II) with corresponding concentrations in the top 2 cm of sediment cores taken only a few meters away (shown in Table III) illustrates the significant variability inherent in the environmental distribution of toxic substances.

Sediment–Water Partitioning of Bu_3Sn^+. The partition coefficient, calculated as the ratio of the weight of Bu_3Sn^+ in sediment to its weight in water, multiplied by the ratio of the weight of water to weight of sediment used in the experiment, was determined to be $(2.18 \pm 0.35) \times 10^3$ at 20 °C after 4 days of shaking (equilibrium Bu_3Sn^+ concentration 5 ng of Sn/L, ionic strength 0.77 M, sediment organic carbon content 2.4%). This is presumed to be an equilibrium value since a value determined after 16 days of shaking was practically identical. In addition, the mass balance at the end of the experiment indicated that there was no degradation of Bu_3Sn^+ over a period of 4 or 16 days. This finding of relatively strong binding to sediment agrees with earlier work on the binding of Bu_3Sn^+ to soils of various types (Schatzberg and Harris, 1978).

The rate of desorption of Bu_3Sn^+ from sediment was a function of agitation. For example, shaking of the test mixtures with a wrist-action shaker for 3 days released 80% of the Bu_3Sn^+ which could be extracted by tropolone in benzene, whereas none was released from unshaken sediment. A much longer experiment was carried out with unshaken sediment on the assumption that such a condition was more relevant to environmental situations.

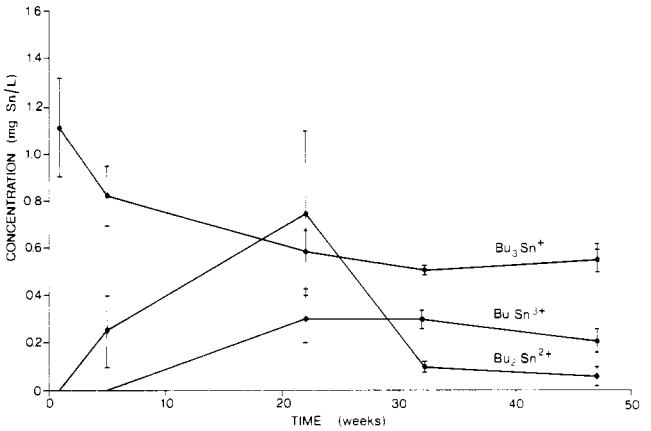

Figure 2. Biological degradation of Bu_3Sn^+ in Toronto Harbor water in the dark at 20 °C (experiment F in Table I).

Table IV shows that very little butyltin species or inorganic tin were released from unshaken sediment, even after 10 months.

Degradation of Bu_3Sn^+ in Water and Sediment. In those experiments in which biological degradation was suppressed by KCN there was, within experimental error, no strictly chemical degradation of Bu_3Sn^+ in distilled water, Toronto Harbor water, or Toronto Harbor water–sediment mixtures over approximately 11 months in the dark at 20 °C (i.e., experiments B, C, E, G, and I of Table I).

Bu_3Sn^+ present in unspiked Toronto Harbor water alone was degraded, presumably biologically, in those flasks which did not contain KCN (experiment D of Table I). The half-life, calculated by least-squares analysis, was 20 ± 5 weeks at 20 °C in the dark. Bu_2Sn^{2+}, $BuSn^{3+}$, and inorganic tin were detected as products, but the large experimental error in their concentrations precluded a determination of the mechanism of degradation. The degradation pattern was clearer in experiments conducted at initial concentrations of Bu_3Sn^+ of 1 mg of Sn/L, as shown in Figure 2, and is suggestive of a series of first-order reactions in which, as the concentration of Bu_3Sn^+ declines, that of Bu_2Sn^{2+} increases and then decreases as the concentration of $BuSn^{3+}$ increases. At the end of the experiment, the concentrations of Bu_3Sn^+, Bu_2Sn^{2+}, and $BuSn^{3+}$ accounted for about 80% of the initial concentration of Bu_3Sn^+, and no inorganic tin was detected. At 1 mg of Sn/L of Bu_3Sn^+ the half-life was 35 ± 8 weeks at 20 °C in the dark. One reason that this half-life is so much longer than that of 20 ± 5 weeks determined at microgram per litre concentrations of Bu_3Sn^+ may be that high concentrations inhibit or kill degradative microorganisms (Seligman, 1984).

Bu_3Sn^+ present in unspiked Toronto Harbor water–sediment mixtures was also degraded, presumably biologically, in those flasks which did not contain KCN (experiment H of Table I). Individual contributions from water and sediment were not separated in this case, since the procedure was simply to freeze-dry the mixtures and analyze the dry sediment. The results are shown in Figure 3. The half-life of Bu_3Sn^+, shorter than in water alone, was 16 ± 2 weeks at 20 °C in the dark. The degradation pattern was similar to that in water alone (cf. Figure 2), with the exception that inorganic tin was detected, and it was the major species at the end of the experiment. Within experimental error the concentrations of the three butyltin species and inorganic tin at the end of the experiment accounted for all of the original concentraion of Bu_3Sn^+. This demonstration of a sequential debutylation pathway (of which at least one step is biologically mediated) for

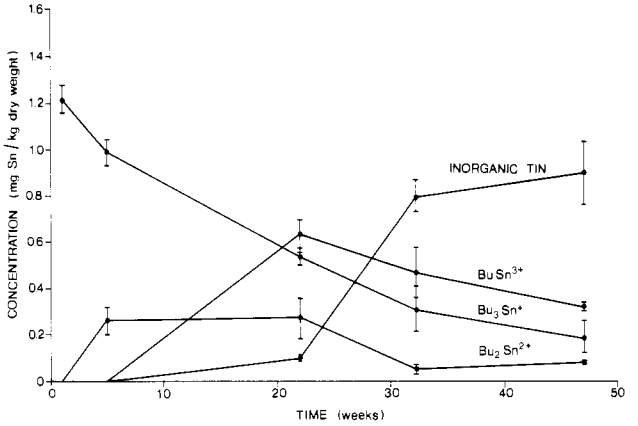

Figure 3. Biological degradation of Bu_3Sn^+ in a Toronto Harbor water–sediment mixture in the dark at 20 °C (experiment H in Table I). Results are given in terms of concentrations in sediment for the freeze-dried mixture and are corrected for Bu_2Sn^{2+}, $BuSn^{3+}$, and inorganic tin initially present in the sediment.

Table V. Concentrations of Butyltin Species and Inorganic Tin in Oligochaetes (mg of Sn/kg) in Experiment on Uptake from Sediment[a]

incubation time, weeks	Bu_3Sn^+	Bu_2Sn^{2+}	$BuSn^{3+}$	inorganic tin
0	det	det	det	0.38
4	0.25	0.06	0.08	1.08
12	0.26	0.17	det	1.93
22	0.11	det		4.41

[a] After spiking, the sediment contained 0.98 mg of Sn/kg of dry weight of Bu_3Sn^+. "Blanks" mean below limit of detection (LOD; Keith et al., 1983) and "det" means that a species was detected but its concentration was below the limit of quantitation (LOQ). For a sample size of 1 g of oligochaetes, the LOQ values for each species were about 0.05 mg of Sn/kg. LOD values were generally about one third of LOQ values.

Bu_3Sn^+ in unspiked water–sediment mixtures is more convincing than the evidence obtained for water alone spiked with 1 mg of Sn/L of Bu_3Sn^+, since the latter case it is always possible that the mechanism might be different at higher concentrations than at lower concentations such as are observed in aquatic environments.

Some methylated tin species were occasionally detected in these degradation experiments in water alone and in the water–sediment mixtures, but not in the sterile controls. The compounds identified were the $MeSn^{3+}$ and Me_2Sn^{2+} species and the compounds Bu_3MeSn and Bu_2Me_2Sn. These four methylated species were not, however, detected consistently in the degradation experiments—there was no clear pattern for their appearance or disappearance. One reason for this is that at least two (i.e., Bu_2Me_2Sn and Me_2Sn^{2+} as Me_2Pe_2Sn) and possibly three (including $MeSn^{3+}$ as $MePe_3Sn$) of these species suffer some evaporative loss in the determination of the $Bu_nPe_{4-n}Sn$ species. Nevertheless, a mass balance on the butyltin species and inorganic tin at the end of the experiment depicted in Figure 3 indicates that they account, within experimental error, for virtually all of the original Bu_3Sn^+ spike, so methylation of Bu_3Sn^+ and its degradation products does not appear to be significant on the time scale of these experiments.

Uptake of Bu_3Sn^+ from Sediment by Oligochaetes. The initial concentration of Bu_3Sn^+ in the spiked sediment was 0.98 mg of Sn/kg dry weight. Table V shows that at the beginning of the incubation period the oligochaetes contained 0.38 mg of Sn/kg and only traces of the three butyltin species. Over the next 22 weeks the concentrations of Bu_3Sn^+, Bu_2Sn^{2+}, and $BuSn^{3+}$ increased and then

Table VI. Toxicity of Tri-*n*-butyltin Compounds to Some Aquatic Organisms

organism	compound	parameter	concn, μg of Sn/L	ref
marine fouling algae and barnacles	various	control	4–2050	Evans and Smith, 1975
worms (*T. tubifex*)	bis(tri-*n*-butyltin) oxide	LC_{50}^{24h}	2.4	Polster and Halacka, 1971
copepod (*Nitocra spinipes*)	bis(tri-*n*-butyltin) oxide	LC_{50}^{96h}	0.8	Linden et al., 1979
copepod (*Acartia tonsa*)	bis(tri-*n*-butyltin) oxide	LC_{50}^{96h}	0.4	U'ren, 1983
snail (*Biomphalaria glabrata*)	bis(tri-*n*-butyltin) oxide	LC_{100}^{6d}	3.0	Deschiens et al., 1966
mussel larvae (*Mytilus edulis*)	bis(tri-*n*-butyltin) oxide	LC_{50}^{15d}	approx 0.04	Beaumont and Budd, 1984
crab larvae (*Rhithropanopeus harrisii*)	bis(tri-*n*-butyltin) oxide	LC_{50}^{12d}	6.4	Laughlin et al., 1984
lobster larvae (*Homarus americanus*)	bis(tri-*n*-butyltin) oxide	LC_{50}^{24h}	8.0	Laughlin and French, 1980
sheepshead minnow (*Cyprinodon variegatus*)	bis(tri-*n*-butyltin) oxide	LC_{50}^{7d}	7.3	Ward et al., 1981
	bis(tri-*n*-butyltin) oxide	LC_{50}^{14d}	0.4	Ward et al., 1981
	bis(tri-*n*-butyltin) oxide	LC_{50}^{21d}	0.4	Ward et al., 1981
bleak (*Alburnus alburnus*)	bis(tri-*n*-butyltin) oxide	LC_{50}^{96h}	6.0	Linden et al., 1979
guppy (*Lebistes reticulatus*)	bis(tri-*n*-butyltin) oxide	LC_{50}^{7d}	16.0	Polster and Halacka, 1971
guppy (*Lebistes reticulatus*)	tri-*n*-butyltin acetate	LC_{50}^{7d}	11.5	Polster and Halacka, 1971
guppy (*Lebistes reticulatus*)	tri-*n*-butyltin oleate	LC_{50}^{7d}	13.5	Polster and Halacka, 1971
guppy (*Lebistes reticulatus*)	tri-*n*-butyltin benzoate	LC_{50}^{7d}	10.2	Polster and Halacka, 1971
guppy (*Lebistes reticulatus*)	tri-*n*-butyltin chloride	LC_{50}^{7d}	8.6	Polster and Halacka, 1971
guppy (*Lebistes reticulatus*)	tri-*n*-butyltin laurate	LC_{50}^{7d}	12.3	Polster and Halacka, 1971
rainbow trout yolk sac fry (*Salmo gairdneri*)	tri-*n*-butyltin chloride	LC_{100}^{12d}	1.8	Seinen et al., 1981
rainbow trout (*S. gairdneri*)	bis(tri-*n*-butyltin) oxide	LC_{50}^{24h}	11.2	Alabaster, 1969
rainbow trout (*S. gairdneri*)	bis(tri-*n*-butyltin) oxide	LC_{50}^{48h}	8.4	Alabaster, 1969

decreased while the concentration of inorganic tin increased throughout the period. Although Table IV contains few data and no replication, the results are at least in qualitative agreement with the sequential debutylation depicted in Figure 3. It appears that oligochaetes (i) can accumulate sediment-associated Bu_3Sn^+, thus making it potentially available to bottom-feeding fish, and (ii) can degrade Bu_3Sn^+.

DISCUSSION

The hazard posed by Bu_3Sn^+ to an organism in water or sediment may be viewed as a function of its toxicity and its concentration and its persistence in water on sediment. These factors will be discussed in turn.

Table VI demonstrates the high toxicity of Bu_3Sn^+ to some aquatic organisms. Although many of the data are for marine organisms, it is reasonable to assume that the toxicity would be comparable for comparable fresh water species. Table VI also shows that, for guppies at least, the toxicity of tri-*n*-butyltin compounds is largely independent of the nature of the counter ion to the Bu_3Sn^+ species.

Concentrations of Bu_3Sn^+ observed in unfiltered subsurface water from about 120 locations in Ontario (Maguire et al., 1982; Maguire, 1985) are generally less than those concentrations lethal to rainbow trout shown in Table VI. However, long-term exposures of trout to concentrations of Bu_3Sn^+ as low as 0.07 μg of Sn/L can cause diminished glycogen storage, growth retardation, and a decrease in body weight (Seinen et al., 1981). Since higher concentrations than this have been observed in Toronto Harbor and elsewhere in Ontario, there may be cause for concern with regard to chronic effects in sensitive organisms in these locations.

In general, the persistence of a chemical in aquatic ecosystems is a function of physical (e.g., volatilization and adsorption to suspended solids and sediment), chemical (e.g., chemical and photochemical degradation), and biological (e.g., uptake and biological degradation) removal mechanisms, in addition to simple water flow.

Volatilization of Bu_3Sn^+ from water is negligible over a period of at least 2 months (Maguire et al., 1983). Adsorption to sterile sediment is fairly strong, and the half-life of desorption appears to be at least 10 months (this work). The rate of adsorption to sediment would be a function of currents and the rate of sedimentation of suspended solids.

In natural waters Bu_3Sn^+ is chemically stable, but does degrade photochemically with a half-life of at least 3 months (Maguire et al., 1983). The rate of photolysis would increase in the presence of photosensitizers and would decrease with depth in the water column. Zepp and Schlotzhauer (1983) found that algae could enhance the rate of photolysis of some chemicals, but this possibility was not considered in this study.

We have shown (i) that Bu_3Sn^+ can be taken up from sediment and degraded by oligochaetes (this work), (ii) the presence of Bu_3Sn^+ in perch, sucker, and carp taken from some harbors in Ontario (Maguire, 1985), and (iii) that Bu_3Sn^+ can be degraded by a common alga, but at algal cell concentrations far in excess of natural populations (Maguire et al., 1984). We believe, however, that more appropriate estimates of persistence vis-a-vis biological degradation are provided by this study at environmental concentrations of Bu_3Sn^+. The half-lives at 20 °C are 5 months in water alone and 4 months in a water–sediment mixture. With a more realistic temperature of, e.g., 10 °C for Canadian waters, one might expect a doubling of these half-lives.

In conclusion it appears that the main factors limiting the persistence of Bu_3Sn^+ in aquatic ecosystems are photolysis in water and biological degradation in water and sediment, and with the temperatures and sunlight intensities prevalent in Canada, the half-life of Bu_3Sn^+ is likely to be at least a few to several months.

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UV-Ozonation of Paraquat

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The use of ultraviolet (UV) irradiation in the presence of O_2 or O_3 was investigated as a method for degrading paraquat (1,1′-dimethyl-4,4′-bipyridinium ion) prior to soil disposal. A solution of 1500 ppm of formulated paraquat was slowly degraded after 7 h in a unit containing 66 low-pressure mercury vapor lamps with a maximum energy output at 254 nm. Addition of acetone as a photosensitizer accelerated the rate of oxidative cleavage of paraquat in laboratory-scale studies. Loss of ^{14}C from [*methyl*-^{14}C]-paraquat was observed in paraquat solutions at 150 ppm but not 1500 ppm. Reaction products identified from paraquat were 4-carboxy-1-methylpyridinium ion at 1500 ppm by high-pressure liquid chromatography; 4-picolinic acid, hydroxy-4-picolinic acid, succinic acid, *N*-formylglycine, malic acid, and oxalic acid as their Me_3Si derivatives; and 4,4′-bipyridyl in dilute solutions by gas chromatography–mass spectrometry.

Paraquat (1,1′-dimethyl-4,4′-bipyridinium ion) is a broad spectrum contact herbicide effective against grasses and most broad-leaved plant species. Reactions responsible for decomposing or inactivating paraquat have been reviewed extensively (Calderbank, 1968; Calderbank and Slade, 1976; Summers, 1980). In solution, paraquat is subject to photodecomposition and microbial metabolism. Dilute aqueous solutions of paraquat are rapidly photochemically degraded to methylamine and 4-carboxy-1-methylpyridinium ion (Slade, 1965). *Aerobacter aerogenes*, *Agrobacterium tumefaciens*, *Pseudomonas fluorescens*, and *Bacillus cereus* in culture solution used paraquat as a sole source of nitrogen (Tu and Bollen, 1968). In soils paraquat is rapidly inactivated by adsorption to clay minerals (Calderbank and Slade, 1976). In the bound state it is believed that paraquat is not available to living organisms (Riley et al., 1976) and is stable to most soil chemical processes (Hance, 1967). Early long-term soil persistence studies (Fryer et al., 1975) indicated essentially no loss of paraquat residues based on almost quantitative recovery from previous applications. When this study was continued for a longer period (Hance et al., 1980), a 10% per year loss rate was reported based on paraquat residues in soils, regardless of when it was applied. The half-life was calculated to be about 6.6 years.

Field trials with a 66-lamp ultraviolet (UV) unit to pretreat pesticide waste water prior to land disposal showed that paraquat was more slowly degraded than atrazine and 2,4-D (Kearney et al., 1984). The objective of the present study was to investigate (1) the effect of a photosensitizer on the rate of decomposition of formulated paraquat solutions and (2) the products resulting from UV-ozonation of dilute and concentrated paraquat solutions.

METHODS AND MATERIALS

Rate Studies. Formulated paraquat (ortho paraquat +, 29.1% ai, 70.9% inerts) was purchased from the Ortho Agricultural Chemicals Division, Chevron Chemical Co.,

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