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REVIEW

Environmental aspects of tributyltin

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The tributyltin species, the active ingredient in some antifouling paint formulations, is perhaps the most acutely toxic chemical to aquatic organisms ever deliberately introduced to water. It has been demonstrated to have an adverse effect on shellfish in France and England, and as a consequence the use of tributyltin-containing antifouling paints has been restricted in these countries. Other countries have banned the use of tributyltin-containing antifouling paints or are contemplating restrictions. This article reviews such environmental aspects of tributyltin as methods of analysis, toxicity, environmental occurrence, persistence and fate. Tributyltin concentrations in many locations may be high enough to cause chronic toxicity or harmful effects in some aquatic organisms, and in some locations the tributyltin concentrations may be high enough to be acutely toxic to some organisms. Biological degradation of tributyltin in water and sediment appears to be the most important factor limiting the persistence of tributyltin in aquatic environments. To some degree, then, the persistence of tributyltin in aquatic environments depends upon the nature of the ecosystem. Tributyltin exhibits low-to-medium persistence in water and moderate persistence in sediment. A summary is given of the regulatory status of tributyltin in some countries, and recommendations are made for further research.

Keywords: Tributyltin, tri-n-butyltin, organotin, antifouling, persistence, occurrence, toxicity, analysis, review

INTRODUCTION

Tin as a metal and in organic compounds has a wide variety of uses. In the past 30 years organotin compounds have developed into important industrial commodities. Tin is unsurpassed by any other metal in the number of its organic applications, which include uses as poly(vinyl chloride) stabilizers, industrial catalysts, industrial and agricultural biocides, and wood-preserving and antifouling agents, to mention only the major applications.

The annual world consumption of tin in all forms was about 200×10^6 kg in 1976, and of this total about 28×10^6 kg was in the form of organotin compounds.[1] The United States of America consumed about 11×10^6 kg of organotin compounds in that year, and an 11–13% annual growth in consumption was predicted for the period 1978–1988. World consumption of organotins in 1986 was 35×10^6 kg.

The increasing annual use of organotin compounds, some of which are very toxic, attracted the attention of environmental protection agencies in a number of countries in the 1970s. The main organotin compounds which may be released to the environment are those of triphenyltin, tricyclohexyltin, di-n-octyltin, di-n-butyltin, dimethyltin and tri-n-butyltin. Triphenyltin and tricyclohexyltin species are agricultural pesticides. Di-n-octyltin compounds are used as stabilizers in some food wrappings. Di-n-butyltin compounds are used as poly(vinyl chloride) stabilizers (as are dimethyltin species) and as catalysts, in a number of industrial processes. Tri-n-butyltin compounds are used as antifouling agents in some paints for boats, ships and docks, as general lumber preservatives and as slimicides in cooling water.

Several aspects of the chemistry and behaviour of tin and organotin compounds in general have been the subjects of excellent reviews.[1–24] This article reviews mainly aquatic environmental aspects of the tri-n-butyltin species such as methods of analysis, toxicity, environmental occurrence, persistence and fate. It contains some information found in earlier reviews. In addition, it reviews the considerable amount of research

published over the past few years on the tri-n-butyltin species (hereafter referred to as tributyltin or Bu_3SnX). Tributyltin is by far the most toxic to aquatic organisms of all organotin compounds, and may be the most acutely toxic chemical to aquatic organisms ever deliberately introduced to water. For this reason several countries have restricted its use or are contemplating restrictions.

METHODS OF ANALYSIS

It is assumed in this review that all tributyltin compounds dissolved in water yield the same species. Support for this contention comes from (i) observations that the thin layer[25,26] and high-performance liquid[27] chromatographic behaviour of Bu_3SnX compounds (X = F, Cl, Br, OAc and $OSnBu_3$) is independent of the nature of X, probably because of anion exchange on chromatography in acidic solvents, (ii) the observation that the nature of the metabolites of Bu_3SnX (X = Cl, OAc and $OSnBu_3$) produced by rat liver microsomal mono-oxygenase at pH 7.4 is independent of X,[25] and (iii) observations that the variation of X within any particular series of R_3SnX compounds usually has little effect on the biological activity.[14,28] By analogy with the more soluble lower trialkyltin compounds,[4,29] therefore, the dissolution of tributyltin compounds in pure water likely produces the hydrated Bu_3Sn^+ ion, which behaves as a simple monoprotic acid (in 44% ethanol the pK_a is 6.58[30]). For brevity, the tri-n-butyltin, di-n-butyltin and n-butyltin species are referred to in this review as though they existed only in cationic form (e.g. Bu_3Sn^+). It is recognized that for Bu_3Sn^+ dissolved in water, phenomena such as partitioning into organic solvents and volatilization will involve not the solvated cation but, for example, either bis(tri-n-butyltin) oxide or a halide or organic complex of Bu_3Sn^+, depending upon the nature and concentration of other solutes.

The most desirable methods of analysis are those that determine tributyltin directly, and that can differentiate tributyltin from dibutyltin, monobutyltin and inorganic tin. This is important since tributyltin is much more toxic to aquatic organisms than the lesser butylated species.[14,31,32] Most of the commonly used methods of analysis for tributyltin in environmental media are shown in Table 1, in roughly chronological order. Some of these methods were inspired by methods of determination of various methyltin species in water, and are also suitable for the determination of dibutyltin, monobutyltin and inorganic tin. Other methods of analysis for these lesser butylated species and for methyltin species have been reviewed up to 1984 elsewhere,[22,77] and are not shown here. The figures in Table 1 in the column entitled 'Minimum detectable concentration' should be regarded with caution since it is not yet common practice, however desirable, to distinguish 'limit of detection' from 'limit of quantitation'.[78]

The most sensitive methods of analysis are those which involve conversion of tributyltin (and its metabolites) to volatile hydride or alkyl derivatives for subsequent chromatographic separation and determination.

In the analysis of water for tributyltin there are two methods which have become popular because of their high sensitivity, gas chromatography (GC) with a flame photometric detector (FPD), and atomic absorption spectrophotometry (AA) employing a quartz tube furnace with sample introduction from a gas chromatograph or by sweeping from a cold trap.

The application of the GCFPD to the determination of volatile organotin compounds had its origin in the work of Aue and coworkers,[39,79–83] who demonstrated the remarkable sensitivity and selectivity against hydrocarbons that could be obtained in hydrogen-rich flames, both with the FPD and the less sensitive flame ionization detector (FID). Other modifications involved using filters, no filters and metal foil masks. With the use of a quartz wool plug mounted above the flame of a FPD, Aue and Flinn[83] were able to detect as little as 0.02 pg (as Sn) of tetrapropyltin. This early work was done with packed column GCs, and tailing of the organotin peaks was observed, as was detector fouling due to SnO_2 formation.[39,49,84] To a large degree, the development of capillary columns has removed these difficulties.[64,72,75] Mueller's method[75] employing capillary column GCFPD is currently the most sensitive method for tributyltin, with a minimum detectable concentration in water of 0.3 ng Sn dm^{-3}. This detection limit could probably be lowered if the simultaneous hydridization/extraction technique of Matthias *et al.*[73] were used before analysis by capillary column GCFPD. Using a packed column

Table 1 Analytical methods for tributyltin[a]

No.	Medium containing tributyltin	Method	Minimum detectable concentration or amount	Comments	Reference
1	Bu_3SnBr in diethyl ether	Conversion to Bu_3MeSn, then GCTCD			33
2	Standards	Conversion to Bu_3PrSn, then GCTCD			34
3	$(Bu_3Sn)_2O$ in air	Glass fibre filters extracted with methyl isobutyl ketone, then flame AA			35
4	Sea-water	Extraction with carbon tetrachloride, oxidation to Sn(IV), then spectrophotometric determination of phenylfluorone complex	320 $\mu g\ Sn\ dm^{-3}$		36
5	50% Ethanol	DPPD	12 $\mu g\ Sn\ dm^{-3}$		37
6	Acidic aqueous solution	ASV after dealkylation by UV light	10 $\mu g\ Sn\ dm^{-3}$		38
7	Rat liver microsomes	TLC separation from metabolites, UV irradiation and spot identification with 8-hydroxyquinoline			26
8	Bu_3SnH standards	GCFPD	1 pg (as (Sn)		39
9	Soil	Radiolabelled compound extracted with acetic acid, partitioned into hexane, then TLC and scintillation counting			40
10	Water	Extraction of acidified solutions with 0.05% tropolone in benzene or chloroform, conversion to Bu_3MeSn, then GCMS		70–90% recovery at 1 mg Sn dm^{-3}. GCMS requires at least 0.2 ng derivative	41
11	Water	Adsorption to silica gel column, elution, TLC, spot scraped off, elution, then GF AA	100 $\mu g\ Sn\ dm^{-3}$	72% recovery	42
12	Soil	Soxhlet extraction with acetic acid, dilution, centrifugation, neutralization, then method 11	1 mg Sn kg^{-1}	40% recovery	42
13	Air	Method 11	0.1 $\mu g\ Sn\ m^{-3}$	Variable recoveries	42
14	Water	Direct aqueous injection of Bu_3SnCl solutions, into (hydrogen-rich) FID	about 5 ng (as Sn)		43
15	Textiles	Extraction with 0.05% HCl in methanol, partitioning into hexane, alumina clean-up, then GF AA		>95% recovery	44
16	Standards	Bu_3SnH generation with cold trapping and determination by sweeping into AA with quartz tube furnace		Absolute detection limit 0.7 ng (as Sn)	45
17	Water	Extraction with hexane, oxidation to Sn(IV) with H_2SO_4–H_2O_2, then spectrophotometric determination of phenylfluorone complex	0.1 μg (as Sn)	>95% recovery	46
18	Methanol	GF AA	8–22 pg (as Sn)	Graphite tubes pretreated with Zr for greater sensitivity	47

Table 1 Continued

No.	Medium containing tributyltin	Method	Minimum detectable concentration or amount	Comments	Reference
19	Soil	Radiolabelled compound extracted with wet diethyl ether/formic acid (98/2), TLC, then scintillation counting			48
20	Water	Extraction with tropolone in benzene, conversion to Bu_3PeSn, then GCFPD	3 ng Sn dm^{-3} for 8 dm^{-3} sample	96% recovery at 10 mg Sn dm^{-3}; limit of quantitation is 0.01 μg Sn dm^{-3} for 8 dm^{-3}	49
21	Fish	Homogenization, dispersion in HCl, extraction with hexane, complexation with tropolone, washing with alkali to remove any Bu_2Sn^{2+}, then GF AA		Absolute detection limit 40 pg (as Sn)	50
22	Standards or antifouling paint extracts in acetone	Injection of underivatized extract into GC with FID or hydrogen-rich FID		Hydrogen-rich FID as sensitive as FID, but much more selective for organotin compounds over hydrocarbons	51
23	Methanol	Ion exchange HPLC–GF AA	16 ng (as Sn)	Discontinuous introduction of HPLC effluent to GF AA with autosampler	27
24	Methanol	HPLC–DPPD			52
25	Water	Spectrophotometric determination of 3-hydroxyflavone complex		$E^{1\,cm}_{385\,nm} = 1.2 \times 10^4$ dm^3 mol^{-1} cm^{-1}	53
26	Rabbit tissues	Extraction as Bu_3SnCl into ethyl acetate, partitioning into hexane, clean-up, then GC–ECD	0.4 μg Sn kg^{-1} (wet weight)	96% recovery at 5 μg Sn kg^{-1}	54
27	Water	Extraction of HBr-acidified sample with benzene, then method 16	0.02–0.4 μg Sn dm^{-3} for 100 cm^3 sample		55
28	Water	Extraction of HBr-acidified sample with benzene, conversion to Bu_3PeSn, then GC–FID	0.6–1.2 μg Sn dm^{-3} for 1 dm^3 sample		55
29	Fishing nets	Extraction with ethanol, then DPPD		Detection limit 26 μg Sn dm^{-3} in ethanol extract	56
30	Air	Adsorption to glass fibre filters or XAD-2 resin, extraction with 1% acetic acid in acetonitrile, then HPLC–GF AA with Zr-treated L'vov platforms			57
31	Human urine	Extraction with hexane, then fluorimetric determination of 2',3,4',5,7-pentahydroxyflavone complex	60 μg Sn dm^{-3}		58
32	Rat tissues	Homogenization in normal saline solution, addition of HCl and NaCl, extraction into ethyl acetate, transfer into hexane, then method 31		>93% recovery from liver, kidney, spleen, brain and thymus	58
33	Benzene	Oxidation to Sn(IV) with H_2SO_4–NaBr–$NaBrO_3$, then substoichiometric determination of salicylideneamino-2-thiophenol complex			59

34	Sea-water	DPASV	1 μg Sn dm^{-3}		60
35	Sediment	Dry sediment extracted with tropolone in benzene, conversion to Bu_3PeSn, clean-up with silica gel, then GCFPD	3 μg Sn kg^{-1} (dry weight) for 10 g sample	Limit of quantitation is 10 μg Sn kg^{-1} for 10 g sample	61
36	Hexane	HPLC on cyanopropyl-bonded silica with hexane eluent containing 0–5% acetic acid and 0–5% ethyl acetate, and determination by RID			62
37	Water	Conversion to Bu_3SnH, which was purged from solution *and* extracted into diethyl ether. Determination by capillary column GCFID		Purging alone was not sufficient to remove all Bu_3SnH from solution	63
38	Water	Extraction of acidified sample with pentane, conversion to Bu_3MeSn, then capillary column GCFPD or GCMS	< 0.4 ng Sn dm^{-3}	This method will not extract Bu_2Sn^{2+} or $BuSn^{3+}$	64
39	Water	Adsorption to macroreticular resin, elution with acidified diethyl ether, then method 38			64
40	Sediment	Acidification of wet sediment to pH 2 with HCl, extraction with diethyl ether, then method 38	< 0.2 μg Sn kg^{-1}		64
41	Sediment	Bu_3SnH evolution from sediment–water slurries, followed by method 16		High hydrocarbon and sulfide concentrations interfere; Bu_3Sn^+ in water frozen in polycarbonate containers stable for 100 d	65
42	Oysters	Tissue stirred with HCl, extracted with dichloromethane, then (a) transferred to hexane for conversion to Bu_3PeSn and GCFID, or (b) transferred to ethanol, then water for conversion to Bu_3SnH, then cold trapping and flame AA			66
43	Sea-water	Method 16	3 ng Sn dm^{-3}	Fuel oils interfere	67
44	Water	Method 16	200 pg (as Sn)		68
45	Water	Cf. method 43, but with direct coupling of column to quartz furnace	45 pg (as Sn)		69
46	Fish and shellfish	Extraction as Bu_3SnCl with ethyl acetate/hexane (3/2), conversion to Bu_3SnH, silica gel clean-up and GCECD	0.7 μg Sn kg^{-1} (wet weight)	No less of Bu_3SnH in rotary evaporation; recoveries > 85% at 0.03–0.3 mg Sn kg^{-1}	70
47	Sediment	Extraction as Bu_3SnCl with hexane, then method 46	0.4 μg Sn kg^{-1} (wet weight)	Recoveries > 85% at 0.02–0.2 mg Sn kg^{-1}	70
48	Fish	Homogenization, dispersion in HCl, dilute, extraction with tropolone in benzene, conversion to Bu_3PeSn, clean-up with silica gel, then GC AA with quartz tube furnace	3 μg Sn kg^{-1} (wet weight) for 10 g sample	Limit of quantitation is 10 μg Sn kg^{-1} for 10 g sample	71
49	Water	Extraction with tropolone in hexane, conversion to Bu_3HexSn, then capillary column GCFPD or GCMSCI	1 ng Sn dm^{-3}	> 90% recovery in range 5–30 ng Sn dm^{-3}	72

Table 1 Continued

No.	Medium containing tributyltin	Method	Minimum detectable concentration or amount	Comments	Reference
50	Water	Simultaneous extraction and formation of Bu_3SnH, then GCFPD	7 ng Sn dm^{-3} for 100 cm^3 sample	Threefold greater recoveries by this technique compared with carrying out method in separate stages	73
51	Water	Automated time-integrated remotely moored sampling by adsorption on C18 silica, elution, then method 43			74
52	Water	Extraction as Bu_3SnCl with tropolone–C18 silica cartridge, conversion to Bu_3EtSn, then capillary column GCFPD or GCMS	0.3 ng Sn dm^{-3}	Absolute detection limit of 1 pg (as Sn); FPD fouling minimal and easily reversed; GCMSPCI more sensitive than GCMSEI	75
53	Sediment and sewage sludge	Extraction as Bu_3SnCl with tropolone in diethyl ether, conversion to Bu_3EtSn, then method 52	4 μg Sn kg^{-1}	See method 52	75
54	Sea-water	Bu_3SnCl extracted under acidic conditions with C18 silica catridge, eluted with aqueous HCl in ethyl acetate, then capillary column GCECD		Absolute detection limit 2 pg (as Sn); extraction can be done in field, saving time, solvent and shipping costs. Non-specific detector. Some degradation of stationary phases	76

[a]Abbreviations used: AA, atomic absorption spectrophotometry; ASV, anodic stripping voltametry; Bu, n-butyl; DPASV, differential pulse anodic stripping voltametry; DPPD, differential pulse polarographic detector; ECD, electron capture detector; EI, electron impact; Et, ethyl; FID, flame ionization detector; FPD, flame photometric detector, GC, gas chromatography; GF, graphite furnace; Hex, n-hexyl; HPLC, high pressure liquid chromatography; Me, methyl; MS, mass spectrometry; PCI, positive chemical ionization; Pe, n-pentyl; Pr, n-propyl; RID, refractive index detector; TCD thermal conductivity detector; UV, ultraviolet.

GCFPD, Matthias *et al.*[73] demonstrated a three-fold improvement in sensitivity with the simultaneous hydridization/extraction technique, compared with combinations of sequential techniques.

The quartz tube furnace AA technique was apparently first used by Chu *et al.*[85] in the determination of arsine. It was first applied to butyltin species by Hodge *et al.*[45] and has since undergone a number of refinements in the determination of hydride and alkyl derivatives of tributyltin. Valkirs *et al.*[65] currently have the most sensitive quartz tube furnace AA technique, with a minimum detectable concentration of tributyltin in water of $3\,ng\,Sn\,dm^{-3}$. This procedure has been automated, allowing four to eight analyses per hour.[86].

In 1984 the US National Bureau of Standards[87] conducted an interlaboratory analytical methods comparison for tributyltin in water. Twenty-seven laboratories worldwide participated, using such techniques as direct solvent extraction, direct hydridization, extraction with hydridization, extraction with alkylation, complexation with spectrophotometric determination and direct injection–high pressure liquid chromatography. The conclusion was that all the methods employed can give accurate results for total tin in an aqueous sample. In an effort to compare speciation methods, the US NBS plans[88] in 1987/1988 to conduct another interlaboratory comparison with aqueous solutions containing the three species di-, tri-, and tetra-butyltin. A limited comparison along these lines has already been performed.[89] Di- and tri-butyltin compounds present in marine and estuarine waters at less than $1\,\mu g\,Sn\,dm^{-3}$ were determined using (i) simultaneous hydride generation–dichloromethane extraction followed by packed column GCFPD, and (ii) hydride generation followed by sweeping into a quartz tube furnace AA. Generally good agreement was obtained from split samples.

In the analysis of media other than water for tributyltin, GCFPD and AA methods have also been used successfully, as has GC with an electron capture detector (ECD), which is quite sensitive, but perhaps not as selective as the AA or FPD. Currently, the most sensitive methods for tributyltin are (i) for sediment, extraction of acidified slurries with diethyl ether, conversion to Bu_3MeSn, clean-up and determination by capillary column GCFPD[64] ($<0.2\,\mu g\,Sn\,kg^{-1}$), (ii) for fish and shellfish, acidification of the homogenate with HCl, extraction as Bu_3SnCl with ethyl acetate/hexane (3/2), conversion to Bu_3SnH, clean-up and determination by packed column GCECD[70] ($0.4\,\mu g\,Sn\,kg^{-1}$), and (iii) for mammalian tissues, acidification of the homogenate with HCl, extraction as Bu_3SnCl with ethyl acetate, transferring to hexane, clean-up and determination by packed column GCECD[54] ($0.4\,\mu g\,Sn\,kg^{-1}$).

TOXICITY OF TRIBUTYLTIN

The toxicity of tin compounds to humans,[90] terrestrial animals[91] and phytoplankton[31] has been extensively studied. Organotin compounds are more toxic than inorganic tin compounds. Progressive introduction of organic groups to the tin atom in any $R_nSn^{(4-n)+}$ series produces maximal biological activity against all species when $n=3$, i.e., for the triorganotin compounds. However, within the class of trialkyl compounds there are considerable variations in toxicity with the nature of the alkyl group.[14] For insects, trimethyltin compounds are the most toxic; for mammals, the triethyltin compounds; for Gram-negative bacteria, the tri-n-propyltin compounds; for Gram-positive bacteria, fish and fungi, the tri-n-butyltin compounds. Further increase in the n-alkyl chain length produces a sharp drop in biological activity. Triphenyltin compounds are particularly toxic to phytoplankton[31] whilst tricyclohexyltin compounds show high acaricidal activity.[14]

Some of the more important acute and sublethal effects of tributyltin compounds on aquatic biota are shown in Table 2. This table updates the 1985 review of toxicity by Hall and Pinkney.[116]

Tributyltin is very toxic to aquatic organisms. The data presented in Table 2 show that acutely lethal concentrations to some organisms and life stages are less than $1\,\mu g\,Sn\,dm^{-3}$ and that some chronic toxicity concentration values are lower than $0.1\,\mu g\,Sn\,dm^{-3}$. In addition, decreased growth and other harmful effects have been noted at concentrations as low as $0.002\,\mu g\,dm^{-3}$. The work of Polster and Halacka[28] indicates that, for guppies at least, the toxicity of tributyltin compounds is largely independent of the nature of the counter-ion to the tributyltin species.

Many studies on the toxicity of tributyltin to aquatic organisms have been done with no measurement of the actual concentration of

Table 2 Toxicity of tributyltin compounds to aquatic organisms[a]

Organism	Compound	Parameter	Concentration ($\mu g\,Sn\,dm^{-3}$)	Reference
Marine fouling algae and barnacles	Various	Control	4–2050	92
Various fouling organisms	TBT	90 d-LC_{100}	0.2	93
Phytoplankton (fresh-water)	TBTO	50% growth inhibition	5.0	31
Guppy (*L. reticulatus*)	TBTO	7 d-LC_{50}	16.0	28
	TBTAc	7 d-LC_{50}	11.5	28
	TBTOle	7 d-LC_{50}	13.5	28
	TBTBz	7 d-LC_{50}	10.2	28
	TBTCl	7 d-LC_{50}	8.6	28
	TBTLau	7 d-LC_{50}	12.3	28
Rainbow trout yolk sac fry (*S. gairdneri*)	TBTCl	12 d-LC_{100}	1.8	94
		Growth retardation	0.4	94
Rainbow trout (*S. gairdneri*)	TBTO	24 h-LC_{50}	11.2	95
		48 h-LC_{50}	8.4	95
Marine algae (*S. costatum* and *T. pseudonana*)	TBTO	50% growth inhibition	0.06–0.18	96
Marine algae (*P. lutheri, D. tertiolecta* and *S. costatum*)	TBTO	2 d-LC_{100}	1.0	97
Marine alga (*S. costatum*)	TBTO	100% growth inhibition	0.02	97
Cladoceran (*D. magna*)	TBTCl	96 h-LC_{50}	1.3–2.2	98
		Sign reversal of phototaxis	0.2	98
Copepod (*N. spinipes*)	TBTO	96 h-LC_{50}	0.8	99
Copepod (*A. tonsa*)	TBTO	96 h-LC_{50}	0.4	100
Worm (*T. tubifex*)	TBTO	24 h-LC_{50}	2.4	28
Lugworm (*A. cristata*)	TBTO	96 h-LC_{100}	0.8	101
Snail (*B. glabrata*)	TBTO	6 d-LC_{100}	3.0	102
Mussel larvae (*M. edulis*)	TBTO	15 d-LC_{50}	approx. 0.04	103
Mussel (*M. edulis*)	TBT	66 d-LC_{50}	0.4	104
		Decrease in shell length (over 66 d)	0.1–0.3	104
		Decrease in body weight (over 66 d)	0.3–0.8	104
	TBTO	Reduction in length growth rate	0.08	105
		14 d-LC_{100}	1.1	106
Oyster (*C. gigas*)	TBTO	Growth inhibition	0.3	107
		Shell valve thickening	0.03	107
	TBTF	50 d-LC_{100}	0.8 (est.)	108
		110 d-LC_{30}	0.8 (est.)	108
	TBTAc	No effect found	0.007	109
		Slow growth, high mortality after 10 d	0.02	109
		Slow growth, almost total mortality after 12 d	0.03	109
		12 d-LC_{100}	0.07	109
		8 d-LC_{100}	0.16	109
Oyster spat (*C. gigas*)	TBTO	Decreased O_2 consumption and feeding rate	0.01	110
		Decreased growth	0.004	110
		Decreased compensation for hypoxia	0.002	110
Oyster (*C. virginica*)	TBT	30 d-LC_{50}	1	93
		Reduction in general health	0.04	93

Table 2 Continued

Organism	Compound	Parameter	Concentration ($\mu g\ Sn\ dm^{-3}$)	Reference
Bivalves (*C. gigas*, *M. edulis* and *V. decussata*)	TBT	Growth reduction	0.1	106
Brittle star (*O. brevispina*)	TBTO	Inhibition of arm regeneration (30 d exposure)	0.02	111
Mysid shrimp (*A. sculpta*, juvenile)		96 h-LC_{50}	0.3	104
Mysid shrimp (*A. sculpta*, adult)		96 h-LC_{50}	0.7	104
Crab larvae (*R. harrisii*)	TBTO	12 d-LC_{50}	6.4	112
Fiddler crab (*U. pugilator*)	TBTO	Slowing of regenerative limb growth	0.1	113
Lobster larvae (*H. americanus*)	TBTO	24 h-LC_{50}	8.0	114
Sheepshead minnow (*C. variegatus*)	TBTO	7 d-LC_{50}	7.3	56
		14 d-LC_{50}	0.4	50
		21 d-LC_{50}	0.4	50
Bleak (*A. alburnus*)	TBTO	96 h-LC_{50}	6.0	99
Chinook salmon (*O. tshawytscha*, juvenile)	TBTO	6 h-LC_{50}	11	115
		12 h-LC_{50}	4	115
		96 h-LC_{50}	0.3	115

[a]Abbreviations used: Ac, acetate; Bz, benzoate; Lau, laurate; LC, lethal concentration; Ole, oleate; TBT tributyltin (no anion specified); TBTC, tributyltin chloride; TBTF, tributyltin fluoride; TBTO, bis(tributyltin) oxide.

tributyltin in the water, i.e. with nominal concentrations. Because of the possibilities of degradation of tributyltin and adsorption of tributyltin to the walls of the containers used, such studies may have underestimated the toxicity. The best approach for toxicity testing is one employing flow-through conditions and measurement of the tributyltin species throughout the course of the experiment. In addition, it should be borne in mind in making comparisons of toxicity values with concentrations of tributyltin observed in aquatic environments that variables such as temperature, pH, water hardness, size of organism and nature and concentration of suspended solids and dissolved organic material may all exert some influence on toxicity.

A moderate potential for the bioaccumulation of tributyltin by aquatic organisms is indicated by values of its octanol–water partition coefficient in the range 1550–7000.[117,118] Some bioaccumulation factors observed are 1000–6000 for oysters,[119] 2600 for whole sheepshead minnows (and higher in some tissues),[50] 4000 in mud crabs[120] and up to 30000 in an alga.[121] Degradation of tributyltin has also been observed in several aquatic organisms. Short and Thrower[122] have found residues of butyltin species in salmon raised for market in sea pens whose nets had been coated with tributyltin to control fouling. Their method did not distinguish tributyltin from dibutyltin. The concentration range reported for the sum of these two species was 0.03–0.08 $mg\ Sn\ kg^{-1}$. These butyltin species were not effectively destroyed or removed by common cooking practices.

ENVIRONMENTAL OCCURRENCE OF TRIBUTYLTIN

Table 3 summarizes the environmental occurrence of tributyltin, dibutyltin and monobutyltin. The latter two species are included since they are degradation products of tributyltin and are frequently found in environmental samples in association with tributyltin. It is acknowledged that it is possible that the less toxic di- and mono-butyltin found in some areas may be the result of uses of tributyltin other than antifouling (e.g. slimicidal uses in industry), or may be because the compounds themselves are used, e.g. in the stabilization of poly(vinyl chloride). The environmental occurrence of inorganic tin is not shown here. This subject was reviewed to 1984[22] and later work is described in some of the

Table 3 Environmental occurrence of tributyltin, dibutyltin and monobutyltin[a]

Species	Medium	Concentration	Location	Reference
Bu_3Sn^+	Fresh water	nd–1200 ng Sn dm^{-3}	Rivers and lakes in Ontario, Canada	123
		0.4–5.5 ng Sn dm^{-3}	Rivers and lakes in Switzerland	64
		nd–70 ng Sn dm^{-3}	Detroit and St Clair Rivers, Canada and USA	124
		nd–200 ng Sn dm^{-3}	Toronto harbour, Canada	125
		nd–2300 ng Sn dm^{-3}	Across Canada	71
		1.8–5.5 ng Sn dm^{-3}	Lake Zurich and Swiss rivers	75
	Fresh water surface microlayer	nd–24900 ng Sn dm^{-3}	Rivers and lakes in Ontario, Canada	123
		nd–30 ng Sn dm^{-3}	St Clair River, Canada	124
		nd–470 000 ng Sn dm^{-3}	Canadian rivers and lakes	126
	Estuarine water	< 1–66 ng Sn dm^{-3}	Elizabeth River and Sarah Creek, Chesapeake Bay, USA	72
		< 1.8–490 ng Sn dm^{-3}	Chesapeake Bay, USA	127
		nd–40 ng Sn dm^{-3}	Sarah Creek, Chesapeake Bay, USA	128
		nd–170 ng Sn dm^{-3}	Chesapeake Bay, USA	129
		nd–600 ng Sn dm^{-3}	Various locations in England	130
		nd–61 ng Sn dm^{-3}	Chesapeake Bay, USA	131
	Estuarine surface microlayer	nd-125 ng Sn dm^{-3}	Great Bay estuary, NH, USA	68
		nd–1900 ng Sn dm^{-3}	Baltimore harbour and Annapolis marina, Chesapeake Bay, USA	73
		nd–430 ng Sn dm^{-3}	Chesapeake Bay, USA	129
	Sea-water	nd–900 ng Sn dm^{-3}	Burnham-on-Crouch, England	132
		10–60 ng Sn dm^{-3}	San Diego Bay, USA	65
		nd–68 ng Sn dm^{-3}	Baltimore harbour, Annapolis marina, San Diego Bay, USA	73
		nd–300 ng Sn dm^{-3}	San Diego Bay, USA	67
		< 1–2.7 ng Sn dm^{-3}	Esquimalt harbour, BC, Canada	133
		< 20–110 ng Sn dm^{-3}	San Diego Bay, USA (tidal variation)	86
		90–290 ng Sn dm^{-3}	San Diego Bay, USA	134
		nd–130 ng Sn dm^{-3}	Various harbours in USA	135
		0.4–86 ng Sn dm^{-3}	San Diego Bay, USA	136
		< 1.8–31 ng Sn dm^{-3}	Annapolis and San Diego harbours, USA	76
		1.8–135 ng Sn dm^{-3}	San Diego Bay, Baltimore and Annapolis harbours, USA	89
		200–620 ng Sn dm^{-3}	Japan	137
	STP effluent	5.5 ng Sn dm^{-3}	Switzerland	75
	Sediment	nd–200 μg Sn kg^{-1} (dry weight)	Rivers and lakes in Ontario, Canada	61
		400 μg Sn kg^{-1}	Japanese river	138
		0.7–5.8 μg Sn kg^{-1} (dry weight)	Lakes Constance and Zurich, Switzerland	64
		nd–70 μg Sn kg^{-1} (dry weight)	Detroit and St Clair Rivers, Canada and USA	124
		nd–1800 μg Sn kg^{-1} (dry weight)	Toronto harbour, Canada	125
		8–44 μg Sn kg^{-1} (wet weight)	San Diego Bay, USA	65
		nd–11 000 μg Sn kg^{-1} (dry weight)	Across Canada	71
		nd–0.9 μg Sn kg^{-1} (wet weight)	Lake Biwa, Japan	70
		300–7 000 μg Sn kg^{-1} (dry weight)	Esquimalt harbour, BC, Canada (jetties and dry docks)	133

Table 3 Continued

Species	Medium	Concentration	Location	Reference
		nd–100 μg Sn kg^{-1} (dry weight)	San Diego Bay, USA	139
		12–44 μg Sn kg^{-1} (dry weight)	Great Bay estuary, NH, USA	140
		102 μg Sn kg^{-1} (dry weight)	Lake Zurich, Switzerland (dated 1980–1984)	75
		33–52 μg Sn kg^{-1} (dry weight)	Japan	137
	Fish	nd–200 μg Sn kg^{-1} (wet weight)	Great Lakes and Vancouver harbour, Canada	71
		1.3–8.5 μg Sn kg^{-1} (wet weight)	Lake Biwa, Japan	70
	Oysters	nd–4 500 μg Sn kg^{-1} (dry weight)	Burnham-on-Crouch, England	132
		< 40–135 μg Sn kg^{-1} (wet weight)	Dengie Flats, River Roach, River Crouch, England	141
	Shellfish	11 μg Sn kg^{-1} (wet weight)	Lake Biwa, Japan	70
Bu_2Sn^{2+}	Fresh water	4–630 ng Sn dm^{-3}	Lake Michigan, USA	45
		nd–3 700 ng Sn dm^{-3}	Rivers and lakes in Ontario, Canada	123
		nd–100 ng Sn dm^{-3}	Detroit and St Clair Rivers, Canada and USA	124
		nd–100 ng Sn dm^{-3}	Toronto harbour, Canada	125
		nd–1 400 ng Sn dm^{-3}	Across Canada	71
		2.4–16 ng Sn dm^{-3}	Lake Zurich and Swiss rivers	75
	Fresh water surface microlayer	nd–1 330 000 ng Sn dm^{-3}	Rivers and lakes in Ontario, Canada	123
		nd–5 ng Sn dm^{-3}	St. Clair River, Canada	124
		nd–365 000 ng Sn dm^{-3}	Canadian rivers and lakes	126
	Estuarine water	1.6–67 ng Sn dm^{-3}	Elizabeth River and Sarah Creek, Chesapeake Bay, USA	72
		< 2–275 ng Sn dm^{-3}	Chesapeake Bay, USA	127
		nd–110 ng Sn dm^{-3}	Chesapeake Bay, USA	129
		nd–20 ng Sn dm^{-3}	Chesapeake Bay, USA	131
	Estuarine surface microlayer	21–91 ng Sn dm^{-3}	Baltimore harbour and Annapolis marina, Chesapeake Bay, USA	73
		nd–450 ng Sn dm^{-3}	Chesapeake Bay, USA	129
	Sea-water	20–60 ng Sn dm^{-3}	San Diego Bay, USA	65
		4–109 ng Sn dm^{-3}	Baltimore harbour, Annapolis marina, San Diego Bay, USA	73
		nd–200 ng Sn dm^{-3}	San Diego Bay, USA	67
		< 1–0.8 ng Sn dm^{-3}	Esquimalt harbour, BC, Canada	133
		120–270 ng Sn dm^{-3}	San Diego Bay, USA	134
		1.6–58 ng Sn dm^{-3}	San Diego Bay, USA	136
		0.8–106 ng Sn dm^{-3}	San Diego Bay, Baltimore and Annapolis harbours, USA	90
	STP effluent	9.8 ng Sn dm^{-3}	Switzerland	75
	Sediment	nd–200 μg Sn kg^{-1} (dry weight)	Rivers and lakes in Ontario, Canada	61
		200 μg Sn kg^{-1}	Japanese river	138
		nd–30 μg Sn kg^{-1} (dry weight)	Detroit and St Clair Rivers, Canada and USA	124
		nd–300 μg Sn kg^{-1} (dry weight)	Toronto harbour, Canada	125
		3–22 μg Sn kg^{-1} (wet weight)	San Diego Bay, USA	65
		nd–8 500 μg Sn kg^{-1} (dry weight)	Across Canada	71

Table 3 Continued

Species	Medium	Concentration	Location	Reference
		0.5–1.6 μg Sn kg^{-1} (wet weight)	Lake Biwa, Japan	70
		100–1 400 μg Sn kg^{-1} (dry weight)	Esquimalt harbour, BC, Canada (jetties and dry docks)	133
		nd–70 μg Sn kg^{-1} (dry weight)	San Diego Bay, USA	139
		1–15 μg Sn kg^{-1} (dry weight)	Great Bay estuary, NH, USA	140
		55 μg Sn kg^{-1} (dry weight)	Lake Zurich, Switzerland (dated 1980–1984)	75
	Fish	nd–50 μg Sn kg^{-1} (wet weight)	Great Lakes and Vancouver harbour, Canada	71
		nd–2 μg Sn kg^{-1} (wet weight)	Lake Biwa, Japan	70
$BuSn^{3+}$	Fresh water	9.3–515 ng Sn dm^{-3}	Lake Michigan, USA	45
		nd–5 700 ng Sn dm^{-3}	Rivers and lakes in Ontario, Canada	123
		nd–100 ng Sn dm^{-3}	Detroit and St Clair Rivers, Canada and USA	124
		nd–100 ng Sn dm^{-3}	Toronto harbour, Canada	125
		nd–1 900 ng Sn dm^{-3}	Across Canada	71
		5–21 ng Sn dm^{-3}	Lake Zurich and Swiss rivers	75
	Fresh water surface microlayer	nd–67 000 ng Sn dm^{-3}	Canadian rivers and lakes	126
	Estuarine water	50–300 ng Sn dm^{-3}	Baltimore harbour, USA	142
		nd–1.2 ng Sn dm^{-3}	Tejo River estuary, Portugal	143
		nd–125 Sn dm^{-3}	Great Bay estuary, NH, USA	68
		< 1–12.6 ng Sm dm^{-3}	Elizabeth River and Sarah Creek, Chesapeake Bay, USA	72
		< 1–2 ng Sn dm^{-3}	Tamar River, England; Tejo River, Portugal; Delaware Bay, USA	144
		< 8–310 ng Sn dm^{-3}	Chesapeake Bay, USA	127
	Estuarine surface microlayer	28–143 ng Sn dm^{-3}	Great Bay estuary, NH, USA	68
		165 ng Sn dm^{-3}	Baltimore harbour, MD, USA	73
	Sea-water	nd–20 ng Sn dm^{-3}	San Diego Bay, USA	65
		nd–50 ng Sn dm^{-3}	San Diego Bay, USA	67
		< 0.7–0.8 ng Sn dm^{-3}	Esquimalt harbour, BC, Canada	133
		10–30 ng Sn dm^{-3}	San Diego Bay, USA	134
		nd–8 ng Sn dm^{-3}	San Diego Bay, USA	136
	STP effluent	8.4 ng Sn dm^{-3}	Switzerland	75
	Sediment	nd–4.8 μg Sn kg^{-1} (dry weight)	California coast, USA	145
		nd–400 μg Sn kg^{-1} (dry weight)	Rivers and lakes in Ontario, Canada	61
		nd–30 μg Sn kg^{-1} (dry weight)	Detroit and St Clair Rivers, Canada and USA	124
		nd–100 μg Sn kg^{-1} (dry weight)	Toronto harbour, Canada	125
		3–19 μg Sn kg^{-1} (wet weight)	San Diego Bay, USA	65
		nd–3 400 μg Sn kg^{-1} (dry weight)	Across Canada	71
		300–7 000 μg Sn kg^{-1} (dry weight)	Esquimalt harbor, BC, Canada (jetties and dry docks)	133
		nd–60 μg Sn kg^{-1} (dry weight)	San Diego Bay, USA	139

Table 3 Continued

Species	Medium	Concentration	Location	Reference
		3–30 $\mu g\,Sn\,kg^{-1}$ (dry weight)	Great Bay estuary, NH, USA	140
		22 $\mu g\,Sn\,kg^{-1}$ (dry weight)	Lake Zurich, Switzerland (dated 1980–1984)	75
	Fish	nd–60 $\mu g\,Sn\,kg^{-1}$ (wet weight)	Great Lakes and Vancouver harbour, Canada	71
	Marine algae	Present, but not quantitated	Mission and San Diego Bays, CA, USA	146

[a]Abbreviations used: nd, not detected; STP, sewage treatment plant.

references of Table 3 and elsewhere.[147–154] Not included also is work which reports 'organic tin' but which does not differentiate between the different butyltin species.[147,150,151,155,156]

The work summarized in Table 3 is mainly from Canada, the United States and England, and makes a convincing case for the use of tributyltin-containing antifouling paints as the main source of tributyltin in aquatic environments. Many researchers have noted concentrations of tributyltin in the water and sediment of harbours, marinas and shipping chennels which are much higher than those from the more open areas of bays, lakes and the oceans. In addition, Alzieu *et al.*[150,155–157] have provided strong correlations between the use of tributyltin-containing antifouling paints in coastal areas of France and both (i) total tin and organotin concentrations in sea-water and Pacific oysters, and (ii) decreased shell growth and reproduction of Pacific oysters. Moreover, Alzieu[157] has noted a progressive decline of tin contamination, concurrent with more normal oyster spatfall and an improvement in oyster shell quality, in Arcachon Bay, France, since the 1982 ban on tributyltin-containing antifouling paints on vessels smaller than 25 m.

Tributyltin concentrations in subsurface water have been found as high as 2.3 $\mu g\,Sn\,dm^{-3}$ in fresh water in Canada and 0.9 $\mu g\,Sn\,dm^{-3}$ in estuarine water in England. Bearing in mind the provisos stated in the section on toxicity above, such high concentrations would be acutely lethal to some aquatic organisms (cf. Table 2). Tributyltin concentrations in many locations appear to be high enough to cause chronic toxicity or harmful effects in some aquatic organisms, if there were continuous exposure, either through a constant source or if tributyltin were to persist over, for example, a two to three month period. Tributyltin in natural waters appears to be present largely in the operationally-defined dissolved phase, i.e. that which passes a 0.45 μm filter,[65,158,159] a finding which confirms the prediction made on the basis of its solids–water partition coefficient of 3000 $\mu g\,kg^{-1}/\mu g\,dm^{-3}$ at a suspended solids concentration of 10 $mg\,dm^{-3}$ [21]

In attempting to determine the effects of tributyltin at any particular location it is of course important to establish the temporal variability of its concentration in water. Hall *et al.*[129] and Waldock *et al.*,[130] for example, have examined the seasonal variation in tributyltin concentration in water in harbours, marinas and shipping channels and have noted increased concentrations in the summer months after boats are painted in the spring. The most extensive work in this regard has been done by the research group in San Diego, USA, which demonstrated increasing concentrations of tributyltin in part of San Diego Bay over a two-year period,[67] and which has demonstrated a tidal variation in tributyltin concentration.[86]

High concentrations of tributyltin have also been observed in the surface microlayer of natural waters.[68,73,123,124,126,129] The surface microlayer, which contains a lipophilic film of long-chain fatty acids, alcohols, esters and other chemicals, may be important in the aquatic environmental distribution of pollutants. The thickness of the surface microlayer is operationally defined by the type of collector used, and values from 60 μm to 200 μm are common.[160–164] Several articles have demonstrated higher concentrations of contaminants in surface microlayers relative to subsurface waters (e.g. refs 165–167, and references therein). This finding has important

implications (i) for organisms which spend part or all of their lives at the air–water interface, and (ii) for estimates of amounts of toxic substances in aquatic ecosystems. In addition, the possibility exists for enhanced sunlight photolysis of chemicals in surface microlayers since there is little attenuation of sunlight compared with the attenuation experienced in penetration to greater depths in the water column. The highest concentrations of tributyltin in the surface microlayer of natural waters have been found in fresh water in Canada,[126] up to 470 $\mu g\,Sn\,dm^{-3}$ This concentration is 42 times the 24 h LC_{50} value for adult rainbow trout. In addition, the concentration of tributyltin in the surface microlayer was occasionally so much greater than that in subsurface water that the microlayer contained a significant *amount* of tributyltin relative to that in the whole depth of subsurface water.[126] This finding has important implications for the calculation of loadings of tributyltin to aquatic environments. It should be borne in mind, however, that there will likely be large temporal fluctuations of concentrations of tributyltin in microlayers due to turbulence. This aspect deserves further study.

Tributyltin appears to concentrate in sediments of harbours, marinas and shipping channels. The highest concentrations observed have been in marine harbours in Canada (7–11 $mg\,Sn\,kg^{-1}$ dry weight[71,133]). There is, however, always the possibility that paint chips in the sediment which contain tributyltin could give an artificially high value for the concentration of tributyltin in sediment. The biological availability, hence toxicological significance, of residues of tributyltin in sediment is a matter which has received little attention, but which must be addressed. There is some evidence that oligochaete worms can take up tributyltin from sediment, thus making it available to higher organisms.[125] These oligochaete worms also appear to be able to degrade tributyltin.

There are as yet few data in the open literature on concentrations of tributyltin itself in aquatic organisms. The most extensive data are those of Waldock *et al.*[132,141] on residues in oysters in England. In addition, Alzieu *et al.*,[150,155–157] using less specific methods of analysis, have reported on concentrations of total tin and organotin in oysters in France.

In addition to tributyltin, dibutyltin, monobutyltin and inorganic tin, other related organotin species such as Bu_4Sn, Bu_3MeSn, Bu_2Me_2Sn and $BuMe_3Sn$ have been detected occasionally, usually at lower concentrations.[61,71,73]

The presence of tetrabutyltin in environmental samples may simply be due to tetrabutyltin contamination of tributyltin-containing antifouling paint formulations, or it may be an environmental redistribution product of tributyltin and/or dibutyltin. In a study of microbial degradation of tributyltin, Olson and Brinckman[131] observed the formation of tetrabutyltin only in light-incubated samples, and not in sterile samples exposed to light, which suggested the involvement of photosynthetic microorganisms in tetrabutyltin production. Tetrabutyltin was not observed consistently in their experiments, however.

Since mixed tetra-alkyltin compounds do not have dispersive uses with regard to the environment but are mainly used as intermediates in the production of other organotin compounds,[168] it is unlikely that the Bu_3MeSn, Bu_2Me_2Sn and $BuMe_3Sn$ observed in water and sediment[61,71] were of anthropogenic origin. It appears, therefore, that these mixed butylmethyltin compounds resulted from the methylation of tributyltin and its degradation products. They were, however, only found infrequently.

The monomethyltin, dimethyltin and trimethyltin species have also been detected in aquatic environments. Their presence is probably the result of environmental methylation of tin. They are not the subjects of this review, however, and will not be discussed in any detail here (cf. refs 169 and 170, and references therein, for appropriate reviews).

PERSISTENCE OF TRIBUTYLTIN IN AQUATIC ENVIRONMENTS

The hazard posed by tributyltin to an organism in water or sediment may be regarded as a function of its toxicity, its concentration and its persistence in water or sediment. The toxicity and concentration of tributyltin in water and sediment have been described above. The persistence of tributyltin or any 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. (for example cf. refs 171 and 172). Table 4

Table 4 Chemical/physical properties, accumulation, persistence, and degradation of Tributyltin[a]

Medium	Property/transformation	Half-life	Value/Comments	Reference
Neat (TBTO)	Reaction with atmospheric CO_2		Production of $(Bu_3Sn)_2CO_3$ in substantial yield	173
	UV photolysis		Wavelength not stated; after 24 h, products were 1-butene and traces of polymeric Bu_2SnO and aldehydes	174
	Vapour pressure		6.7×10^{-7} mm Hg (est.)	117
Distilled water	Solubility (as TBTO)		Minimum of 0.75 mg Sn dm^{-3} pH 6.0–6.6; increases with increasing or decreasing pH	117
	$\log K_{ow}$		3.2 at pH 6	117
	$\log K_{ow}$		3.84 (3.74 at 32% salinity)	118
	Volatilization		None over 62 d	117
	Stability in dark		No debutylation over 63 d at pH 2.9–10.3	117
	Abiotic degradation	>40 d	Bu_2Sn^{2+} and $BuSn^{3+}$ found, as well as 1- and 2-butene, 1- and 2-butanol, and 2-butanone	175
	UV spectrum in 9/1 H_2O/MeOH		λ, nm (ε, $dm^3\,mol^{-1}\,cm^{-1}$): 360 (0.06); 350 (0.10); 340 (0.16); 330 (0.26); 320 (0.40); 310 (0.64); 300 (0.98); 290 (1.62); 280 (2.72)	117
	Photolysis at 300 nm	1.1 ± 0.2 d	Bu_2Sn^{2+}, $BuSn^{3+}$ and tin products; product yield 50%	117
	Photolysis at 300 nm, sensitized with 15 mg dm^{-3} fulvic acid	0.6 ± 0.2 d		117
	Photolysis at 350 nm	>18 d		117
	Photolysis at 350 nm, sensitized with 15 mg dm^{-3} fulvic acid	6.2 ± 1.8 d		117
	Persistence	19 d	Products not given; reaction is described as 'hydrolysis'	176
Distilled or fresh water	Sunlight photolysis	>89 d (>4×10^4 langleys)	Small amounts of Bu_2Sn^{2+}, $BuSn^{3+}$ and tin found	117
12% HCl	Photolysis	<1 h	Wavelength not stated; dealkylation eventually to tin	38
	Dealkylation		Solution boiled; no product yield or kinetics given	38
Fresh water	Stability	>3 months		38
	Persistence	10.5 d	Products not given; reaction is described as 'hydrolysis'	176
	Volatilization	>11 months		125
	Biological degradation (aerobic)	5 months	Bu_2Sn^{2+}, $BuSn^{3+}$ and tin produced	125
Fresh water and sea-water (pH 5–9)	Stability in dark		Little or no debutylation over 35 d; solubility exceeded in some tests, with possibility of adsorption to glass container	177
	Photolysis with GE F40BL flourescent lights (sunlight spectral distribution)	18.4 d for TBTO; 2 d for TBTF	Half-life varied with source of Bu_3Sn^+ and was shorter in the presence of acetone photosensitizer	177
Fresh water and sand mixture	Persistence	3.8 d	Products not given; reaction is described as 'hydrolysis'	176

Table 4 Continued

Medium	Property/transformation	Half-life	Value/comments	Reference
Fresh water/sediment mixtures (sterile)	Degradation	>11 months		177
Fresh water/sediment mixtures	Aerobic degradation	4 months	Bu_2Sn^{2+}, $BuSn^{3+}$ and tin produced	125
Estuarine water		6–11 d	Degradation faster in light than in dark; Bu_2Sn^{2+} was main product	178
Sea-water	Solubility (as TBTO)		1.6–2 mg Sn dm^{-3}	41
	Reaction with CO_2 to form $(Bu_3Sn)_2CO_3$		No supporting evidence on yield or kinetics	179
	UV photodegradation	11 d (est.)		180
Sea-water (harbour site)	Degradation in light	6 d	Bu_2Sn^{2+} was main product	158
	Degradation in dark	7 d	Bu_2Sn^{2+} was main product	158
Sea-water (clean site)	Degradation in light	9 d	Bu_2Sn^{2+} was main product	158
	Degradation in dark	19 d	Bu_2Sn^{2+} was main product	158
Sediment (from fresh water)	Desorption	>10 months		125
Sediment (marine)	Degradation	162 d	Some Bu_2Sn^{2+} produced, but BuSn was main product	139
Soil	Aerobic degradation	15–20 weeks	$^{14}CO_2$ and Bu_2Sn^{2+} among products; considerable formation of unextractable residues	48
	Leaching		Little leaching after 16 weeks (2.5 cm rain per week)	181
	Leaching	>180 d	Bu_2Sn^{2+} and $BuSn^{3+}$ found; substantial unextractable residue	40
	Aerobic dissipation	60 d	Combination of (at least) debutylation and formation of unextractable residue	40
	Anaerobic degradation	>180 d	Substantial production of Bu_2Sn^{2+}, $BuSn^{3+}$ and unextractable residue	40
	Anaerobic dissipation	>200 d	Combination of (at least) debutylation and formation of unextractable residue	40
Plant surface	Photolysis	4 h	Wavelength not stated; Bu_2Sn^{2+}, $BusSn^{3+}$ and tin produced	38
Wood posts	Mobility from wood posts in terrestrial microcosm		93.6% ^{14}C radiolabel retained in wood after 2.5 months, 4.5% in soil, indicating very little migration; earthworms accumulated 1.6 mg Sn kg^{-1}, but radiolabel not unequivocably Bu_3Sn^+	182
Micro-organisms (fresh water)	Aerobic degradation	16 d (est.)	$BuSn^{2+}$, $BuSn^{3+}$ and tin produced	183
	Anaerobic degradation	8 d	Bu_2Sn^{2+}, and $BuSn^{3+}$ and tin produced	183
Micro-organisms (estuarine)	Biodegradation	1 week	Degradation faster in light than in dark; Bu_2Sn^{2+} and $BuSn^{3+}$ produced	131

Table 4 Continued

Medium	Property/transformation	Half-life	Value/comments	Reference
Bacterial culture	Aerobic degradation by *P. aeruginosa*	5–10 d	$BuSn^{3+}$ found, but not Bu_2Sn^{2+}, which may have been rapidly converted to $BuSn^{3+}$ by reducing sugars in the medium	184
	Uptake by estuarine bacteria		Bu_3Sn^+ accumulated to 3.7–7.7 mg Sn g^{-1} dry weight; no debutylation noted	185
Algal culture	Uptake and degradation by *A. falcatus*	4 weeks	Maximum apparent bioconcentration factor of 3×10^4; 50% conversion over 4 weeks to Bu_2Sn^{2+} and small amounts of $BuSn^{3+}$ and tin	121
Fungal culture	Aerobic degradation by *C. puteana*	3–4 d	Debutylation to Bu_2Sn^{2+} and $BuSn^{3+}$	184
	Degradation		Bu_2Sn^{2+} and $BuSn^{3+}$ produced; no kinetics given	186
Sheepshead minnow (*C. variegatus*)	Uptake and degradation		Maximum observed bioconcentration factor of 2.6×10^3; depuration 'first half-life' 7 d; metabolism by sequential debutylation	50

[a]Abbreviations used: GE, General Electric Ltd; K_{ow}, octanol–water partition coefficient; TBTF, tributyltin fluoride; TBTO, bis(tributyltin) oxide; UV, ultraviolet.

summarizes data relevant to the persistence of tributyltin in aquatic environments.

In considering the aquatic persistence of tributyltin there are a few points to bear in mind:

(1) The persistence of tributyltin should not be defined in terms of the time required for anion exchange. This gives a false impression of degradation kinetics when what is significant is the loss of butyl groups. The toxicity of tributyltin is largely independent of the nature of the counter-ion,[14,28] but the toxicity declines greatly with decreasing number of butyl groups.[14]

(2) The persistence of tributyltin in a model ecosystem should not be defined solely in terms of dissipation from water if it is not known whether the tributyltin is simply adsorbed to the sediment or container walls. Tributyltin adsorbed to sediment could be mobilized through simple desorption, sediment resuspension, or ingestion by benthic biota. This point underscores the importance of a mass balance in degradation or persistence experiments.

(3) Although the use of high-pressure mercury lamps in the laboratory yields much useful information on chemical mechanisms, the use of environmentally more appropriate light sources such as sunlight or filtered light of suitable intensity will yield more reliable information on persistence with regard to sunlight photolysis.

In general, the persistence of tributyltin in aquatic systems 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. These factors will be discussed in turn.

Volatilization of tributyltin from natural water–sediment mixtures is negligible over a period of 11 months,[125] possibly because of adsorption of tributyltin to the sediment. Such adsorption to sediment is fairly strong,[125] and simple desorption appears to be a slow process. However, even in distilled water there is negligible volatilization of tributyltin over a period of at least two months.[117]

Chemical degradation of tributyltin under

environmental conditions is also a fairly slow process, with a half-life of greater than 11 months in a fresh water–sediment mixture.[125] Sunlight photolysis of tributyltin appears to be the fastest physical or chemical route of degradation in, or dissipation from, water, but even then the half-life is greater than three months in fresh water in the laboratory,[117] and because of the attenuation of sunlight with depth in water, photolysis is probably not important at depths greater than 0.5–1 m anyway. The rate of photolysis can be accelerated by dissolved organic material such as fulvic acid,[117] which indicates the potential influence that an ecosystem-specific property can have on persistence. There is some evidence that the photolysis of tributyltin in water proceeds through a sequential debutylation pathway.[38,117]

Tributyltin in water appears to be much more susceptible to biological degradation than chemical or photochemical degradation. There are reports of degradation in fish[50] and by micro-organisms[121, 125, 131, 139, 158, 177, 178, 183, 184, 186] in natural waters and sediments as well as in more concentrated cultures of micro-organisms. Biological degradation of tributyltin has also been demonstrated in soil.[40,48] Although there are some exceptions, in general it appears that aquatic organisms degrade tributyltin through a sequential debutylation pathway in a manner analogous to mammalian metabolism[25,26] and to photolysis. This mechanism probably involves hydroxylated butyltin intermediates which are unstable and which lose butene, yielding, for example, dibutyltin, monobutyltin or tin species. This was demonstrated in mammalian microsomal preparations,[25,26] and recently in microsomal preparations from crab stomach and fish liver.[187]

Since biological degradation in water and sediment appears to be the most important factor limiting the persistence of tributyltin in aquatic ecosystems, it is expected that ecosystem-specific characteristics such as temperature and the kinds and concentrations of tributyltin-degrading micro-organisms will be important determinants of the persistence of tributyltin in any particular location. For example, Seligman *et al.*[158] found that half-lives of biological degradation of tributyltin in water in San Diego Bay were 50–170% greater at clean sites than at harbour sites. In addition, we have observed that degradation by micro-organisms from Toronto Harbour, Canada, is about twice as fast under anaerobic conditions as under aerobic conditions.[159,183] Estimates of the half-life of biological degradation of tributyltin in water range from 6–19 days in sea-water in San Diego Bay[158,178] and the Skidaway estuary, Georgia[178] to four months in fresh water in Toronto Harbour.[125] Half-lives of biological degradation in sediment from Toronto Harbour and San Diego Bay are four to five months.[125,139] Thus, in the locations examined in detail to date, tributyltin exhibits low-to-moderate persistence in water and moderate persistence in sediment.

As noted in the section above on the occurrence of tributyltin, methylated derivatives of tributyltin and its degradation products have occasionally been observed in water and sediment. We have also detected low concentrations of Bu_3MeSn, Bu_2Me_2Sn, $MeSn^+$ and Me_2Sn^{2+} in our work on the biological degradation of tributyltin.[125] It is likely that these methylated species resulted from the methylation of the butyltin species or inorganic tin in water or sediment. These methyltin species were, however, not detected consistently, and they were usually present in much smaller concentrations than tributyltin and its degradation products. On the timescale of these experiments, therefore, it appears that methylation of tributyltin and its degradation products is not a significant pathway of transformation; however, the potential importance of methylation on much longer timescales cannot be dismissed.

REGULATION OF TRIBUTYLTIN

France was the first country to restrict the use of tributyltin in antifouling paints. French authorities had observed a decrease in growth rates of oysters in some Atlantic coastal areas as early as 1975. Abnormal spatfall, decrease in survival rates and shell malformations had also been observed since about 1974. Because these conditions were most prevalent around mooring areas, tributyltin was suspected to be the cause of the problems. In 1982 the French government banned the use of tributyltin-containing antifouling paints on vessels shorter than 25 m.[157] Since that time there has been a progressive decline in tin contamination, concurrent with more normal oyster spatfall and an improvement in oyster shell quality, in Arcachon Bay, the site of 10% of France's oyster production.[157]

In England, similar problems were noticed in oyster fisheries, and it was shown that where boats were present at high density and in

relatively enclosed waters, tributyltin concentrations were high enough to kill many commercial and non-commercial species (particularly larvae and plankton) and to affect growth and reproduction in others.[188-190] More recent work has confirmed that non-commercial species such as the dogwhelk can be affected by tributyltin.[191,192] In 1986, England prohibited the retail sale and supply for retail sale of antifouling paints containing tributyltin compounds if the total concentration of tin in dried copolymer paints exceeded 7.5% tin by weight, or if the total concentration of tin in other non-copolymer paints exceeded 2.5% tin by weight.[189] These regulations were seen as an initial measure, and tighter regulations may be required depending upon the results of monitoring programs and the establishment of 'safe' target concentrations of tributyltin in water. Very recently the UK has banned the retail sale of paint formulations containing tributyltin compounds. From July 1987 all antifouling paints in the UK (whether or not they contain tributyltin) become subject to the UK Food and Environment Protection Act (1985).[130] The use of organotin compounds in fresh-water antifouling paints is prohibited in Germany and Switzerland.[193]

The US Environmental Protection Agency is currently carrying out a special review of tributyltin.[194,195] After the risk/benefit analysis, the US EPA may take action under the Federal Insecticide, Fungicide and Rodenticide Act to cancel, suspend and/or require modification of the terms and conditions of registration.

In Canada, tributyltin is registered under the Pest Control Products Act for use as a slimicide and for general lumber preservation. Its use as a preservative for nets is not allowed. In 1987, the Department of Agriculture served notice that antifouling uses of tributyltin compounds would require registration under the Act.[196] It is proposed that such antifouling uses meet three criteria: (1) a maximum short term (first 14 days) cumulative release rate from paint formulations of 168 μg organotin/cm^2, (2) a long term average daily release of 4 μg/cm^2, and (3) a minimum hull length of 19.5 m for the use of TBT antifouling paints on non-aluminum-hulled vessels.[197]

Available formulations of tributyltin-containing antifouling paints have changed significantly over the past 15 years, in response to both environmental and economic concerns.[198] The earliest paints were the 'free association' or 'contact leaching' paints from which tributyltin simply diffused into the water. In the 'soluble matrix/ablative' paints, the paint film matrix is a mixture of insoluble and soluble material designed to break down over time, thus allowing the tributyltin, which is physically dispersed in the paint film, to be released. In the 'self-polishing copolymer' paints, tributyltin is chemically bound to a polymer, e.g. tributyltin methacrylate/methyl methacrylate copolymer. At the surface of the paint, tributyltin is hydrolysed from the copolymer backbone and released into water. When this happens the residual film dissolves in the water also, thus renewing the surface. The paint film is thus 'self-polishing'. The advantages of this controlled release are antifouling protection for a period up to five years compared with one to two for the other formulations, and significantly reduced amounts of tributyltin leaching into water.

RESEARCH RECOMMENDATIONS

In the past few years there has been a great deal of interest in environmental aspects of tributyltin, as shown by a proliferation of articles in the literature and special symposia on tributyltin such as the one at the *Oceans '86* Conference in Washington DC, in 1986, and the one held during the *Oceans '87* Conference in Halifax, Canada, in September 1987. Research is presently being done in all of the areas discussed above. Some recommendations for research are:

(1) continuation of interlaboratory comparisons of analytical methods for tributyltin and its degradation products in water, sediment, fish and shellfish tissue;

(2) further development of low-cost resin sampling techniques for tributyltin in water, and extension to degradation products;

(3) determination of the biological availability of tributyltin in sediment;

(4) determination of the temporal variability of the concentration of tributyltin in subsurface water and the surface microlayer at any particular location;

(5) determination of the persistence of tributyltin in a variety of different ecosystems in order to develop predictions in other locations.

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