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Occurrence of Butyltin Compounds in Mussels in Canada

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The presence of the highly toxic antifouling agent tributyltin (TBT) and its degradation products was determined in four species of mussels collected from 34 locations in fresh water in Ontario and in sea water on Canada's west and east coasts. The purpose of the study was to establish baseline information in order to assess TBT trends in mussels after the 1989 Canadian regulation of antifouling uses of TBT. In fresh water, concentrations of TBT were much higher in zebra mussels (*Dreissena polymorpha*) than in *Elliptio complanata* or *Lampsilis radiata radiata*. High concentrations of TBT were also found in *Mytilus edulus* in sea water. Residues of TBT in all species were similar to those that have been determined in other parts of the world before and after the regulation of antifouling uses of TBT in various countries. Analyses for degradation products indicated that zebra mussels metabolize TBT at about the same rate as *L. radiata radiata* and *M. edulis*, but more slowly than *E. complanata*. © 1997 John Wiley & Sons, Ltd.

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INTRODUCTION

Antifouling uses of tributyltin (TBT) have caused great environmental concern because of its extremely high toxicity to some aquatic organisms. A summary of international regulations of antifouling uses of TBT, and their effect on TBT concentrations in water, sediment and biota has been given elsewhere.[1] In general it may be stated that although the regulations have been effective in reducing TBT concentrations in water, consistent global declines in residues in sediment and benthic organisms have not yet been observed. This has been attributed by many researchers to the long persistence of TBT in sediment.

A survey of TBT residues in water and sediment from across Canada in 1993–1994, five years after the Canadian antifouling regulation was introduced, showed that the 1989 regulation had only been partially effective.[1] It had some effect in the reduction of TBT concentrations in fresh water, but not in sea water. It had less effect in the reduction of TBT concentrations in sediment, probably because of the longer persistence of TBT in sediment than in water. In many locations the TBT concentration was high enough to cause acute and chronic toxicity to aquatic and benthic organisms. In some areas there may be potential for recycling TBT from contaminated sediments back into the water columnn. In addition, it appears that large harbours that handle large ships legally painted with TBT-containing antifouling paints continued to experience ecotoxicologically significant TBT contamination.

It is important also to determine trends in TBT contamination in aquatic biota, in order to assess the effectiveness of the antifouling regulation in Canada. No baseline data are available before the 1989 regulation. This article reports the results of

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a 1995 survey for TBT in mussels in Canada. In addition to TBT, the occurrence of 13 other organotin species was also determined. These species include degradation products of TBT, other organotin pesticides, organotin compounds used industrially as stabilizers for poly(vinyl chloride) (PVC), and species that can be produced through natural methylation processes. These 13 additional species are monomethyltin (MMT), dimethyltin (DMT), trimethytin (TMT), tripropyltin (TPrT), monobutyltin (MBT), dibutyltin (DBT), mono-octyltin (MOT), dioctyltin (DOT), monophenyltin (MPT), diphenyltin (DPT), triphenyltin (TPT), dicyclohexyltin (D-c-HT), and tricyclohexyltin (T-c-HT). All these compounds in aqueous media are present as cations or in complex forms, depending upon the nature and concentration of other solutes. For brevity, they are referred to in this paper as though they exist only in cationic form.

EXPERIMENTAL

Reagents

The carrier gas for the gas chromatograph–atomic emission spectrometry (GC–AED) system used for the organotin analyses was high-purity helium (99.999%), and the reagent gases were oxygen (99.999%) and hydrogen (99.999%), all from Canox Ltd (Mississauga, Ontario, Canada). Monobutyltin trichloride, dibutyltin dichloride, tributyltin chloride, tripropyltin chloride, tripentyltin (TPeT) chloride (used as internal standard) and dicyclohexyltin dichloride were obtained from Alfa Products (Ward Hill, MA, USA). Mono-octyltin trichloride, dioctyltin chloride, monomethyltin trichloride, dimethyltin dichloride, trimethyltin chloride, triphenyltin chloride, tropolone (2-hydroxy-2-4,6-cycloheptatrien-1-one) and ethylmagnesium bromide (1.0 M in tetrahydrofuran) were obtained from Aldrich Ltd (Milwaukee, WI, USA). Diphenyltin dichloride and monophenyltin trichloride were obtained from Gelest, Inc. (Tullytown, PA, USA). All solvents, acids and common laboratory reagents were of analytical grade. Distilled water, further purified by passage through a Milli-Q system (Millipore, Mississauga, Ontario, Canada), was used throughout. Stock solutions of organotin compounds (1000 μg ml^{-1} as Sn) were prepared in methanol or in toluene. The purity of organotin compounds was assessed, after oxidation, by inductively coupled plasma emission spectrometry, and compared with a standard made from high-purity tin metal (99.9%) dissolved in hydrochloric acid. All glassware was solvent-rinsed before use. The sodium sulphate was heated at 450 °C for 24 h before use, and aluminium foil used to line the tops of the sediment jars was also heated at 450 °C for 24 h before use.

Sample collection, extraction, derivatization and clean-up

Mussels were collected from 34 locations on the west and east coasts of Canada, the lower Great Lakes and the upper St Lawrence River. Marine mussels collected on the west and east coasts of Canada were *Mystilus edulis*. Freshwater mussels from the lower Great Lakes included *Elliptio complanata*, *Lampsilis radiata radiata* and the zebra mussel, *Dreissena polymorpha*. Most marinas and harbours in Ontario were seriously infested by zebra mussels, a reltive newcomer to the Great Lakes which has contributed to local extirpations of other mussel species, at least in the upper St Lawrence River.[2] In addition to the mussels, sediment was also collected at some locations and analysed for organotin species.

Mussels were collected by grab sampling techniques and transported to the laboratory in coolers. The mussels were shucked and the whole mussel was freeze-dried, ground and mixed in a blender. Mussel samples (0.2 g dry weight) were digested in a 50-ml Erlenmeyer flask in 5 ml of 25% (w/v) tetramethylammonium hydroxide (TMAH) in water at 60 °C for 1 h.[3] After the digestion period, 10 ml of water, 5 ml of glacial acetic acid, 6 g of NaCl and 4 ml of 0.2% (w/v) tropolone in toluene were added, and the mixture was magnetically stirred for 1 h. Then 2 ml of the toluene layer was removed and reduced in volume to near-dryness in a gentle stream of nitrogen, then reconstituted to about 1 ml with hexane. Volatile ethyl derivatives of the organotin species sought, as well as the internal standard TPeT, were prepared by Grignard reaction.[3] Ethylmagnesium bromide solution (0.5 ml, 1.0 M) was added and the mixture was allowed to stand at room temperature for at least 5 min. The excess ethylmagnesium bromide was destroyed by shaking for 1 min with 2 ml of 0.5 M sulphuric acid. The organic phase was transferred to a glass

centrifuge tube. The acid phase was back-extracted twice with 1 ml of hexane each time. The organic extracts were combined and concentrated under a gentle stream of ntirogen to 1 ml for clean-up. Clean-up of all samples was done using Pasteur pipette mini-columns containing a 1-cm layer of sodium sulphate and a 5-cm layer of activated silica gel on top of a glass wool plug, and pre-rinsed with hexane. The sample was eluted into a glass test-tube with 5 ml of hexane. The extract was then reduced to a final volume of 1.0 ml under a gentle stream of nitrogen. Previous spike recovery experiments showed that the recoveries of the butyltin species from mussel tissues spiked at 500 ng Sn/g dry weight were 85 ± 4% for TBT, 88 ± 5% for DBT, 92 ± 2% for MBT and 93 ± 7% for the internal standard TPeT.

Concentrations of the butyltin species in mussels reported in this paper were not corrected for recovery. Recoveries from mussels were not determined for the other organotin species mentioned above. Determinations were done in triplicate, and the data are presented with standard deviation of the mean (SD).

Sediment samples were collected with an Ekman grab sampler. The top 2 cm of sediment was scraped off into amber glass jars and frozen, then freeze-dried, ground and sieved to pass an 850-μm screen before extraction. The dried samples can be stored frozen for several months without loss of analyte (unpublished observation). Dried sediment samples (2 g) were magnetically stirred for 1 h after the addition of 100 μl of a solution of TPeT chloride (1 μg Sn ml^{-1}) as internal standard, 20 mL of glacial acetic acid, 20 ml of water, 8 g of NaCl and 15 ml of a 0.5% (w/v) solution of tropolone in toluene. An aliquot (7.5 ml) of the extract was removed and evaporated almost to dryness using a stream of nitrogen; 1 ml of hexane was added, and the solution was again evaporated almost to dryness. The volume of the extract was reconstituted to about 1 ml with hexane, and the derivatization with ethylmagnesium bromide, and clean-up, were done as described above.

The overall recoveries of the 14 organotin compounds spiked into sediment at 1 μg Sn/g dry weight were satisfactory (77–134%) except for the three methyltin species (11–57%) and TPrT (42%).[4] Sediment samples were analysed in triplicate, and the data are presented with standard deviation of the mean (SD).

Concentrations of organotin species in sediment reported in this paper are not corrected for recovery.

Analysis

Sample extracts after derivatization and clean-up were analysed for organotin species with a GC–AED system from Hewlett–Packard (Avondale, PA, USA), consisting of a gas chromatograph (HP 5890, Series II) equipped with a split/splitless injection port, a microwave plasma atomic emission detector (HP 5921A) and an autosampler (HP 7673A). The system was factory-interfaced. The operation was computer-controlled using the HP 35920A ChemStation software. Operating parameters for the GC–AED are given elsewhere.[1] Standard mixtures of the ethyl derivatives of all 15 organotin species (including the tripentyltin internal standard) in the expected concentration ranges were prepared and used to calibrate detector responses. Quantitation was by peak area response *vs.* external standards. All concentrations of organotin species in this article are expressed as Sn. Chromatographic 'windows' were typically 0.04 min, at most at 15 min, retention time. The presence of an organotin species was taken to be tentatively confirmed if (1) it occurred within the appropriate chromatographic window, and (2) the concentrations were above the limit of quantitation (LOQ) for the particular sample, defined here as the lower limit of the calibration curve. The limit of detection (LOD), defined as signal three times the noise level, and LOQ values for each organotin species in mussel tissue were 5 and 20 ng Sn/g dry weight, respectively for a 0.2-g dry weight sample. The LOD and LOQ values for each organotin species in sediment were 0.5 and 2 ng Sn/g dry weight, respectively, for a 2-g dry weight sample.

RESULTS AND DISCUSSION

The only organotin species found in mussels in this work were TBT, DBT and MBT, and their concentrations in mussels from the 34 locations sampled are shown in Table 1. Table 1 also shows values for butyltin concentrations in sediment in some locations, primarily where zebra mussels were collected.

In fresh water, at least, the highest concentra-

Table 1. Concentrations (ng Sn/g dry weight) of butyltin species in mussels and sediment from various locations in Canada in 1995[a]

(a) Fresh water

Location	Species	Mussels TBT	DBT	MBT	Sediment TBT	DBT	MBT
Midland Bay at Wye Heritage Marina, Ontario	*E. complanata*	137±6	171±8	298±25	n.d. (sand)	n.d. (sand)	n.d. (sand)
Penetang Harbour, Ontario	*E. complanata*	213±10	100±9	186±39	n.d. (sand)	n.d. (sand)	n.d. (sand)
St Clair River, Bridgeview Marina, Sarnia, Ontario	*D. polymorpha*	587±36	78±5	118±11	n.d. (sand)	n.d. (sand)	n.d. (sand)
Lake St Clair, Mitchell Bay, Ontario	*D. polymorpha*	53±5	d	33±6	n.d.	n.d.	n.d.
Detroit River, Lakeview Marina, Windsor, Ontario	*D. polymorpha*	1890±38	239±23	326±84	38±3	50±4	31±2
Port Stanley, Kettle Creek Marina, Ontario	*D. polymorpha*	2891±12	306±7	201±14	13±5	10±3	9±2
Port Dover, Ontario	*D. polymorpha*	164±14	33±4	41±2	9±1	7±1	8±1
Port Colbourne, Ontario	*D. polymorpha*	73±6	d	32±3	13±4	6±0.3	7±1
Welland Canal at Port Weller	*D. polymorpha*	299±6	35±5	54±3	n.d.	n.d.	n.d.
Moira River at Belleville, Ontario	*D. polymorpha*	288±6	40±4	43±2	155±38	179±23	141±24
Port Hope, Ontario	*D. polymorpha*	109±6	32±6	42±9	26±5	14±1	6±0.2
Whitby Harbour, Ontario	*D. polymorpha*	243±6	41±1	41±5	45±2	32±3	25±6
Port Credit, Ontario	*D. polymorpha*	27±0.3	d	26±6	5	d	d
Toronto Harbour, Ontario	*D. polymorpha*	88±5	22±4	34±5	d	d	d
Kingston Harbour (dry-dock area), Ontario	*D. polymorpha*	8799±303	1330±70	1221±107	698±85	347±59	132±24
St Lawrence River							
Blue Church Bay, Maitland, Ontario	*E. complanata*	54±6	52±11	54±1	n.d.	n.d.	n.d.
	L. radiata radiata	33	d	d	n.d.	n.d.	n.d.
Cornwall, Ontario	*E. complanata*	d	n.d.	n.d.	n.s.	n.s.	n.s.
Montréal, Québec	*E. complanata*	89±14	37±11	34±7	n.s.	n.s.	n.s.
	L. radiata radiata	70±3	29±4	20±3	n.s.	n.s.	n.s.
Sorel, Québec	*E. complanata*	117±15	47±9	41±14	d	d	d
	L. radiata radiata	108±10	272	32±6	d	d	d

(b) Sea water

Victoria Harbour, British Columbia	1	*M. edulis*	286±8	174±11	143±8	n.s.	n.s.	n.s.
	2	*M. edulis*	423±17	168±4	84±7	n.s.	n.s.	n.s.
	3	*M. edulis*	271±14	189±25	122±25	n.s.	n.s.	n.s.
Esquimalt Harbour, British Columbia	1	*M. edulis*	717±20	565±47	600±79	n.s.	n.s.	n.s.
	2	*M. edulis*	787±45	273±15	224±22	n.s.	n.s.	n.s.
St John Harbour, New Brunswick	1	*M. edulis*	25±3	n.d.	n.d.	n.s.	n.s.	n.s.
	2	*M. edulis*	20±3	n.d.	n.d.	n.s.	n.s.	n.s.
	3	*M. edulis*	34±2	n.d.	n.d.	n.s.	n.s.	n.s.
	5	*M. edulis*	76±17	d	d	n.s.	n.s.	n.s.

Table 1. Continued.

Halifax Harbour, Nova Scotia	1	*M. edulis*	249 ± 14	162 ± 14	149 ± 12	n.s.	n.s.	n.s.
	2	*M. edulis*	405 ± 10	131 ± 3	157 ± 5	n.s.	n.s.	n.s.
	3	*M. edulis*	1198 ± 34	1062 ± 70	708 ± 43	n.s.	n.s.	n.s.
	4	*M. edulis*	405 ± 10	185 ± 10	191 ± 12	n.s.	n.s.	n.s.
	5	*M. edulis*	143 ± 2	151 ± 5	113 ± 2	n.s.	n.s.	n.s.
	6	*M. edulis*	175 ± 1	81 ± 4	76 ± 11	n.s.	n.s.	n.s.

TBT, tributyltin; DBT, dibutyltin; MBT, monobutyltin; $n = 3$; d, detected but not quantified; n.d., not detected (for each butyltin species the LOQ was 20 ng Sn/g dry weight for a 0.2-g dry mussel sample, and 2 ng Sn/g dry weight for a 2-g dry sediment sample); n.s., no sample. A detailed description of the sampling locations is available (Ref. 18).

tions of the butyltin species were usually found in areas of high sediment contamination. There was, however, no direct relationship between TBT concentration in mussels and TBT concentration in sediment. Very high concentrations of butyltin compounds were found in zebra mussels collected from a dry-dock area in Kingston Harbour, Ontario (TBT, DBT and MBT concentrations of 8799, 1330, and 1221 ng Sn/g dry weight, respectively). Other areas in which high concentrations of butyltin species were found in zebra mussels were marinas in Port Stanley (Lake Erie) and the Detroit River.

In contrast to zebra mussels, other fresh-water mussels such as *E. complanata* and *L. radiata radiata* contained generally lower concentrations of the butyltin species in those few locations at which they were found (not the same locations as the zebra mussels). Zebra mussels are much smaller in size than *Elliptio* or *Lampsilis* (they are typically 1–1.5 cm long compared with >5 cm for the other adult mussels), but they have higher lipid contents (12–18% dry weight, compared with 2.5–5.5% dry weight for *Elliptio*[6]), and this may be the reason for higher concentrations of butyltin species in zebra mussels than in other mussels taken from marinas and harbours with similar boating and shipping traffic densities. The difference in butyltin concentrations in different mussel species observed in this study is in agreement with the finding that the mussel *Anodonta cygnaea* accumulated much lower concentrations of butyltin species than did zebra mussels.[5]

Table 2 compares concentrations of the three butyltin species in fresh-water mussels determined in this study with concentrations found in fresh-water mussels in Europe. Concentrations of the butyltin species determined in zebra mussels in this study were in the range observed in Europe before and up to four years after introduction of European regulation of antifouling uses of tribyltin that is simlar to Canadian legislation.[5, 7–9] (For purposes of comparison between results reported on a wet weight basis with results reported on a dry weight basis, dry weights of mussels such as *D. polymorpha*, *E. complanata* and *L. radiata radiata* are typically 10% of wet weights[6]). No data were found in the literature on butyltin concentrations in *E. complanata* and *L. radiata radiata*.

In sea water the highest concentrations of butyltin compounds in *M. edulis* were found in the largest harbour sampled, Halifax Harbour (see Table 1). The contamination of *M. edulis* samples by butyltin compounds in this survey was generally higher than in either *E. complanata* or *L. radiata radiata* in fresh water, but it was not as high as in some highly contaminated zebra mussel samples. In general, butyltin concentrations determined in *M. edulis* in this study were similar to those that have been determined in *M. edulis* elsewhere (see Table 2).

The toxicological implications of TBT residues in the mussel species in this survey are impossible to assess because of the lack of data correlating acute and chronic effects of TBT with tissue burdens. This is a major research need. It should be noted that there was no observable sign of physiological damage or deformation in mussels collected in this survey. No data are available on the acute or chronic toxicity of TBT in sediment to the fresh-water or marine mussels studied in this survey. However, a recent survey of TBT in sediment in Canada[1] has shown that concentrations in six of 42 locations exceeded a value of 300 ng Sn/g dry weight, which has been shown to have chronic toxic effects in the marine

Table 2. Comparison of butyltin concentrations in mussels in this study with those in mussels from other studies
(a) Fresh water

	Concentration (ng Sn g^{-1})					
Organism	TBT	DBT	MBT	Location, Date	Comments	Reference
Zebra mussel (*D. polymorpha*)	27–8799 (d.w.)	n.d.–1330 (d.w.)	32–1221 (d.w.)	Ontario, Canada 1995	13 locations	This work
	976–3831 (w.w.)	91–2125 (w.w.)	Not done	Lake Geneva, Switzerland and France, June–September 1988	Five sites, composite samples	5
	n.d.–542 (d.w.)	Not done	Not done	Four lakes in Switzerland, 1990–1993 (reference sites only)		7
	1380–20220 (d.w.)	n.d.–2171 (d.w.)	Not done	Four lakes in Switzerland, 1990–1993 (one marina per lake)		7
	6–11500 (d.w.)	<4–1740 (d.w.)	<6–860 (d.w.)	The Netherlands, 1992	56 locations, homogenates of 20–400 individuals	19
	9760 (d.w.)	960 (d.w.)	1440 (d.w.)	Lake Zurich, Switzerland	$n=3$	9
	180–2500 (d.w.)	<20–160 (d.w.)	21–120 (d.w.)	Lake Westeinder, The Netherlands, 1992–1993	Four locations	8
Mussel (E. complanata)	n.d.–213 (d.w.)	n.d.–171 (d.w.)	n.d.–298 (d.w.)	Ontario and Québec, Canada, 1995	Six locations	This work
Mussel (*L. radiata radiata*)	33–108 (d.w.)	n.d.–272 (d.w.)	n.d.–32 (d.w.)	Ontario, and Québec, Canada, 1995	Three locations	This work
Mussel (*A. cygnaea*)	114–689 (w.w.)	30–107 (w.w.)	Not done	Lake Geneva, Switzerland and France June–September 1988	Five sites, composite samples	5
(b) Sea water						
Mussel (*M. edulis*)	20–1198 (d.w.)	n.d.–1062 (d.w.)	n.d.–708 (d.w.)	Coastal harbours, Canada, 1995	15 locations	This work
	21–144 (w.w.) (mean summer concentrations)	Not done	Not done	UK estuaries, harbours and marinas, 1989	13 locations, composite samples; marked decline in [TBT] from 1986 to 1989	15
	28–438 (w.w.)	44–275 (w.w.)	n.d.–174 (w.w.)	San Diego Bay, CA, USA	Three sites, 15 mussels per site	20
	2.5–124 (d.w.)	Not done	Not done	San Diego Bay, CA USA, July 1990	14 sites, three composite samples per site; general decline in [TBT] since February 1988	21

Table 2. Continued

Organism	Concentration (ng Sn g^{-1})			Location, Date	Comments	Reference
	TBT	DBT	MBT			
Mussel (*M. edulis*)	8–99 (w.w.)	20–276 (w.w.)	14–81 (w.w.)	At wharves in Tokyo Bay, Japan, 1989	26 locations, composites of about 100 mussels at each location	22
	53–944 (d.w.)	3–174 (d.w.)	6–277 (d.w.)	Eastern Scheldt and Grevelingen, The Netherlands, 1988	Four locations	23
	<0.2–135 (w.w.)	Not done	Not done	Coastal waters, Perth, Australia, 1991	35 locations, homogenates of about 20 mussels per site	24
	n.d.–964 (d.w.)	n.d.–173(d.w.)	Not done	Portland and Boothbay Harbors, Maine, USA, 1989	Composites of 25–100 individuals; data also for specific tissues	25
	16–1687 (d.w.)	16–1297 (d.w.)	Not done	Coastal Maine, USA, 1987–1989	Composites of 15–25 individuals from six locations	26
	<4–330 (w.w.)	Not done	Not done	Pacific coast of USA	Five locations, homogenates of composite samples	27
	n.d.–784 (d.w.)			Hudson–Raritan estuary and Long Island Sound, NY, USA, 1989	Composites from 20 sites	28
	369 (d.w.)	192 (d.w.)	Not done	Lynher River, UK, Sept 1993	Composite of ten animals; general decrease in [TBT] between 1987 and 1993	29
	16–492 (d.w.)	5–194 (d.w.)	<14–95 (d.w.)	46 sites on east coast of USA, 1989–1990	Triplicate composite samples (>20 individuals)	16
	4–566 (d.w.)	5–378 (d.w.)	<14–203 (d.w.)	32 sites on west coast of USA, 1989–1990	Triplicate composite samples (>20 individuals)	16
	175 (d.w.)	75 (d.w.)	55 (d.w.)	Huelva, Spain	One homogenate of 40 mussels	30
	2–27 (w.w.)	0.5–2.8 (w.w.)	Not done	South-western Iceland, 1993–1994	Seasonal changes monitored	31

Table 2. Continued

Organism	Concentration (ng Sn g^{-1}) TBT	DBT	MBT	Location, Date	Comments	Reference
Mussel (*M. galloprovincialis*)	193 (w.w.)	25 (w.w.)	73 (w.w.)	Bought in Toulon, France		32
	40–172 (d.w.)	20–61 (d.w.)	Not done	Alexandria Harbour, Egypt	Two locations, composites of 20 individuals each	33
	2–7 (w.w.)	Not done	Not done	Taranto Harbor area, Italy	Composite samples from four sites	34
Mussel (*M. californianus*)	4–193 (d.w.)	5–51 (d.w.)	n.d.–14 (d.w.)	26 sites on west coast of USA, 1989–1990	Triplicate composite samples (<20 individuals)	16
Mussel (*P. viridis*)	9.6 (w.w.)			Malaysia	$n=1$	35
Mussel[b]	5.2±0.6	3.0±0.4	2.0±0.3	Zeeland, The Netherlands	One homogenized composite, four replicate determinations	36
	95±4.9 (d.w.)	48±3.2 (d.w.)	44±7.6 (d.w.)	Boston Harbor, MA, USA	Single homogenized composite, six replicate analyses	37
	180 (w.w.)	79 (w.w.)	40 (w.w.)	Toulon Bay, France		38
	53 (w.w.)	26 (w.w.)	34 (w.w.)	Japan		39
	1050 (d.w.)	820 (d.w.)	630 (d.w.)	La Spezia, Italy		40
	134 (d.w.)	27 (d.w.)	26 (d.w.)	Oristano, Sardinia		40
	406±36 (w.w.)	Not done	Not done	California, USA	One sample, five replicate determinations	41
Bivalves (various mussel and oyster species)	<5–1560 (d.w.)	<5–1280 (d.w.)	<5–1240 (d.w.)	US coastal estuaries	Composites of 15–21 individuals from each of 36 sites	42
	20–1340 (d.w.)	1–872 (d.w.)	<1–212 (d.w.)	US coastal waters	Composites from 23 locations in 1987–1988	43

[a] TBT, tributyltin; DBT, dibutyltin; MBT, monobutyltin; d.w., dry weight; w.w., wet weight; n.d., not detected. In some studies information such as species, year of collection, or concentration by wet or dry weight was not specified. Species names are given when cited in the original article.
[b] Unidentified species.

clam *Scrobicularia plana*.[10, 11] There may be potential for toxic effects in the species studied here in such highly contaminated sediments. Another factor that should not be overlooked in discussions of contamination of zebra mussels in the Great Lakes is that they have only inhabited the Great Lakes ecosystem for about the past ten years and consequently trophic food webs are in a state of flux. It is possible that high concentrations of TBT (and other lipophilic chemicals) may be passed more easily to higher organisms *via* primary consumers of zebra mussels such as diving ducks and the recently introduced round goby than what might have been the case in the absence of zebra mussels.

The ratio of concentrations of TBT to those of its degradation products is often used as an indication of degradability in different media, or by different organsims. An average [TBT]/[DBT] ratio of 22 (±17) has been determined for zebra mussels in Swiss lakes in the period 1990–1993.[7] This value is much higher than the value of 6.6 (±2.0) determined for zebra mussels in this study. Because we also determined MBT in this study, we determined the concentration ratio [TBT]/[TBT]+[DBT]+[MBT] for the four species of mussels in this study. The few data available indicated that zebra mussels (ratio 0.71±0.10) metabolize TBT at about the same rate as *L. radiata radiata* (ratio 0.62±0.37) and *M. edulis* (ratio 0.63±0.25), but more slowly than *E. complanata* (ratio 0.43±0.15).

Becker-van Slooten and Tarradellas determined accumulation factors for TBT between zebra mussels and sediment in the range 21–254 for four Swiss marinas.[7] Accumulation factors for TBT between zebra mussels and sediment in this study were similar, in the range 2–222 for the nine locations at which TBT was confidently determined in both mussels and sediment. It should be noted, however, that there is evidence that sediment-bound TBT is not an important source of zebra mussel contamination.[7, 12] Possibly TBT is available to zebra mussels via water (dissolved or associated with dissolved organic matter) after desorption from sediment, which appears to be a slow process.[7, 13] In support of this possibility, Table 1 shows that in several cases fine sandy sediment contained barely detectable amounts of butyltin species, yet mussels at these sites still contained significant concentrations of butyltin species. The source of the butyltin compounds in these locations must be the overlying water. On the other hand, with species such as *E. complanata* uptake from sediment does appear to be significant.[14]

TBT concentrations in bivalves in some locations have declined after the introduction of TBT regulations in the UK,[15] the USA[16] and Australia,[17] but in other locations TBT concentrations had not declined at the time of sampling, for example in the USA[16] and in Switzerland.[7] This survey will be repeated and expanded at several-year intervals over the next ten years in order to determine trends in TBT contamination in Canada.

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REFERENCES

1. Y. K. Chau, R. J. Maguire, M. Brown, F. Yang and S. P. Batchelor, *Water. Qual. Res. J. Can.* **32**, 453 (1997).
2. A. Ricciardi, F. G. Whoriskey and J. B. Rasmussen, *Can. J. Fish. Aquat. Sci.* **53**, 1434 (1996).
3. Y. K. Chau, F. Yang and M. Brown, *Anal. Chim. Acta* **338**, 51 (1997).
4. Y. K. Chau, F. Yang and R. J. Maguire, *Speciation of Organotin Compounds in Water, Sediment and Sewage Samples by Gas Chromatography/Atomic Emission Detection*, National Water Research Institute Contribution No. 94–70. Department of the Environment, Burlington, Ontario L7R 4A6, Canada, 1994.
5. K. Becker, L. Merlini, N. de Bertrand, L. F. de Alencastro and J. Tarradellas, *Bull. Environ. Contam. Toxicol.* **48**, 37 (1992).
6. M. E. Comba, J. L. Metcalfe-Smith and K. L. E. Kaiser, *Water. Qual. Res. J. Can.* **31**, 411 (1996).
7. K. Becker-van Slooten and J. Tarradellas, *Arch. Environ. Contam. Toxicol.* **29**, 384 (1995).
8. J. A. Stäb, T. P. Traas, G. Stroomberg, J. van Kesteren, P. Leonards, B. van Hattum, and U. A. T. Brinkman, *Arch. Environ. Contam. Toxicol.* **31**, 319 (1996).
9. C. Carlier-Pinasseau, A. Astruc, G. Lespes and M. Astruc, *J. Chromatogr.* **A750**, 317 (1996).
10. W. J. Langston and G. R. Burt, *Mar. Environ. Res.* **32**, 61 (1991).
11. J. M. Ruiz, G. W. Bryan and P. E. Gibbs, *Mar. Ecol. Prog. Ser.* **113**, 119 (1994).
12. K. Becker-van Slooten and J. Tarradellas, *Environ. Toxicol. Chem.* **13**, 755 (1994).
13. R. J. Maguire and R. J. Tkacz, *J. Agric. Food Chem.* **33**, 947 (1985).
14. Y. K. Chau, P. T. S. Wong, G. A. Bengert and J. Yaromich, *Chem. Speciation Biol. Avail.* **1**, 151 (1989).

15. M. E. Waite, M. J. Waldock, J. E. Thain, D. J. Smith and S. M. Milton, *Mar. Environ. Res.* **32**, 89 (1991).
16. A. D. Uhler, G. S. Durell, W. G. Steinhauer and A. M. Spellacy, *Environ. Toxicol. Chem.* **12**, 139 (1993).
17. G. E. Batley, M. S. Scammell and C. I. Brockbank, *Sci. Tot. Environ.* **122**, 301 (1992).
18. M. Brown, Y. K. Chau, R. J. Maguire, F. Yang and S. P. Batchelor, *Description of Sampling Locations for 1995 National Water Research Institute Survey for Organotin Compounds in Mussels in Canada*, Aquatic Ecosystem Protection Branch Technical Note 97–001, National Water Research Institute, Department of the Environment, Canada Centre for Inland Waters, Burlington, Ontario L7R 4A6, Canada, 1997.
19. J. A. Stäb, M. Frenay, I. L. Freriks, U. A. T. Brinkman and W. P. Cofino, *Environ. Toxicol. Chem.* **14**, 2023 (1995).
20. M. O. Stallard, S. Y. Cola and C. A. Dooley, *Appl. Organomet. Chem.* **3**, 105 (1989).
21. A. O. Valkirs, B. Davidson, L. L. Kear, R. L. Fransham, J. G. Grovhoug and P. F. Seligman, *Mar. Environ. Res.* **32**, 151 (1991).
22. T. Higashiyama, H. Shiraishi, A. Otsuki and S. Hashimoto, *Mar. Pollut. Bull.* **22**, 585 (1991).
23. R. Ritsema, R. W. P. M. Laane and O. F. X. Donard, *Mar. Environ. Res.* **32**, 243 (1991).
24. J. S. Burt and G. F. Ebell, *Mar. Pollot. Bull.* **30**, 723 (1995).
25. D. S. Page, T. Dassanayake and E., S. Gilfillan, *Mar. Environ. Res.* **40**, 409 (1995).
26. D. S. Page, T. M. Dassanayake and E. S. Gilfillan, *Bull. Environ. Contam. Toxicol.* **56**, 500 (1996).
27. J. W. Short and J. L. Sharp, *Environ. Sci. Technol.* **23**, 740 (1989).
28. C. S. Peven, A. D. Uhler, R. E. Hillman and W. G. Steinhauer, *Sci. Tot. Environ.* **179**, 135 (1996).
29. D. S. Page, *Mar. Pollut. Bull.* **30**, 746 (1995).
30. J. L. Gomez-Ariza, E. Morales, R. Beltrán, I. Giraldez and M. Ruiz-Benitez, *Analyst (London)* **120**, 1171 (1995).
31. H. Skarphédinsdóttir, K. Ólafsdóttir, J. Savarasson and T. Jóhannesson, *Mar. Pollut. Bull.* **32**, 358 (1996).
32. F. Pannier, A. Astruc and M. Astruc, *Anal. Chim. Acta.* **287**, 17 (1994).
33. A.M.A. Abd-Allah, *Chemosphere* **30**, 707 (1995).
34. N. Cardellicchio, S. Geraci, C. Marra and P. Paterno, *Appl. Organomet. Chem.* **6**, 241 (1992).
35. F. Y. Pang, Y. L. Ng, S. M. Phang and S. L. Tong, *Int. J. Environ. Anal. Chem.* **53**, 53 (1993).
36. M. Ceulemans, C. Witte, R. Lobinski and F. C. Adams, *Appl. Organomet. Chem.* **8**, 451 (1994).
37. G. B. Jiang, P. S. Maxwell, K. W. M. Siu, V. T. Luong and S. S. Berman, *Anal. Chem.* **63**, 1506 (1991).
38. F. Pannier, A. Astruc and M. Astruc, *Anal. Chim. Acta* **327**, 287 (1996).
39. H. Harino, M. Fukushima and M. Tanaka, *Anal. Chim. Acta.* **264**, 91 (1992).
40. F. Pannier, A. Astruc, M. Astruc and R. Morabito, *Appl. Organomet. Chem.* **10**, 471 (1996).
41. M. D. Stephenson and D. R. Smith, *Anal. Chem.* **60**, 696 (1988).
42. T. L. Wade, B. Garcia-Romero and J. M. Brooks, *Environ. Sci. Technol.* **22**, 1488 (1988).
43. A. D. Uhler, T. H. Coogan, K. S. Davis, G. S. Durell, W. G. Steinhauer, S. Y. Freitas and P. D. Boehm, *Environ. Toxicol. Chem.* **8**, 971 (1989).

