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Recent Studies of Residual Tributyltin in Coastal British Columbia Sediments

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Butyltin concentrations in the sediments of two coastal areas of British Columbia, Canada, are reported. Two recent box cores from the deepest basin in the Strait of Georgia were sectioned and analyzed by GC–atomic emission spectrometry. No butyltin compounds were detected above 0.5 μgSn kg^{-1} (dry weight) in either core. These results are compared to those for a previous (1991) core from the same area. In that study, tributyltin (TBT) concentrations were in the range 1–2 μgSn kg^{-1} down the core and were higher than those of either of the degradation products, dibutyltin (DBT) and monobutyltin (MBT). Radioisotope dating (^{210}Po–^{210}Pb counting methods) was used to establish the rates of sedimentation of 0.25 and 2.6 cm y^{-1} at the two sites. Data suggest that a combination of rapid deposition of new, less-contaminated material and degradation of previously deposited butyltin compounds has resulted in the observed absence. Thirty-three surface sediments from the northern BC coastal harbor at Prince Rupert, collected in 1995, were analyzed for butyltin residues by GC–FPD. Concentrations of TBT, DBT and MBT were in the ranges from below the appropriate limit of detection (LOD) to 1262, to 109 and to 37 μgSn kg^{-1}, respectively. TBT/DBT ratios ranged from 0.2 to 62 with most above unity, indicating that there is continuing fresh input of TBT. The sources are almost exclusively large ocean-going vessels that use the harbor for long-term anchorage. These findings are discussed with reference to the global TBT status. © 1998 John Wiley & Sons, Ltd.

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INTRODUCTION

The impact of the release of organotin biocides into Canadian waters has received much attention since the mid-1980s.[1] Of particular interest was the impact of tributyltin-based marine antifoulants on coastal waters and their resident biota. Research and monitoring programs demonstrated that coastal British Columbia waters, in particular, were some of the most contaminated in North America.[2–4]

In 1994, we reported the presence of low (μg Sn kg^{-1}) concentrations of TBT and its degradation products, dibutyltin (DBT) and monobutyltin (MBT), in deep (400 m) sediments of the Strait of Georgia.[5] Data reported for a core recovered in 1991 indicated that TBT had degraded very little down the sedimentary column and that it was the dominant butyltin component.

More recently, we examined the sediment columns from three major shipping harbors and a marina in southern British Columbia. This exercise was designed to assess the effects of controls imposed on the use of TBT-based hull paints in 1989.[6,7] Data for cores from Vancouver harbor indicated that TBT concentrations remained elevated and showed no signs of decreasing and that there appeared to be continuing input of fresh material. Data for the smaller harbors at Victoria and Esquimalt indicated lower concentrations of TBT and its degradation products. Values for the marina sediments showed a clear maximum that we correlated with the imposition of the 1989 controls. We were also able to estimate a half-life value for

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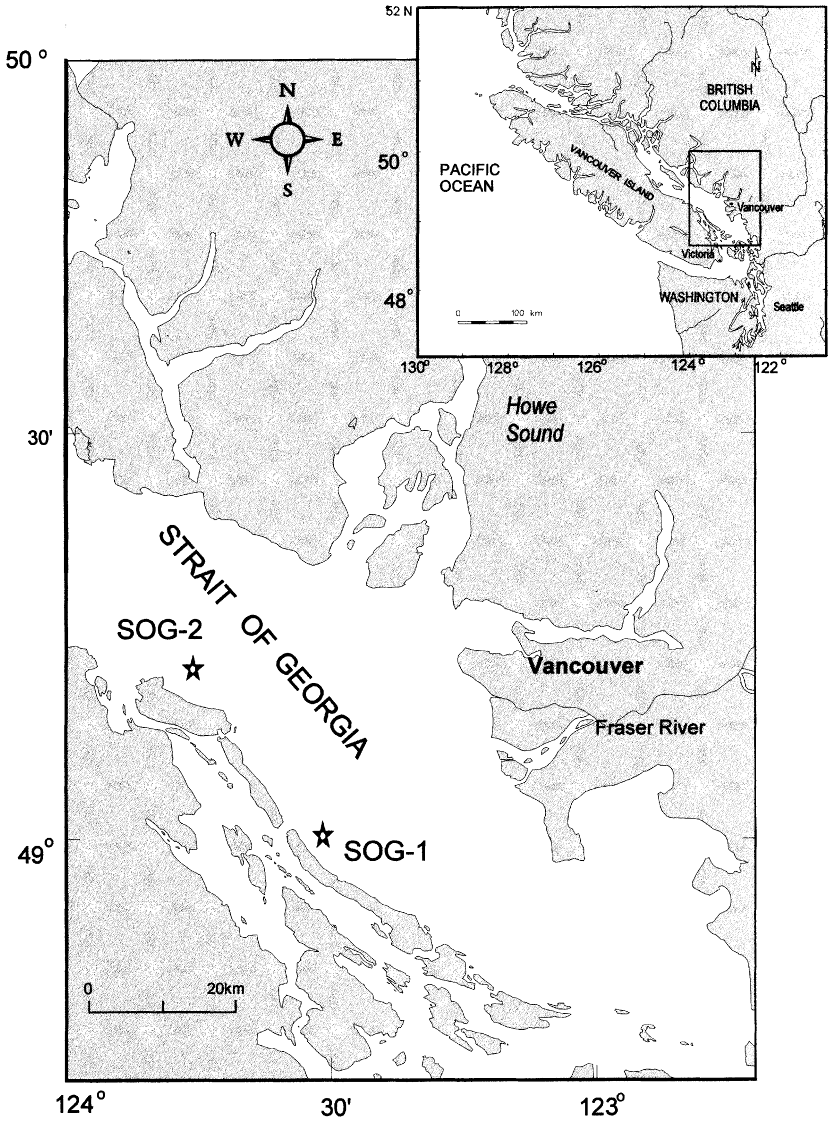

Figure 1 The Strait of Georgia, showing core sites.

TBT in the marina sediments which was longer than any previously reported.[8]

In this report, we present the results of recent studies in two coastal areas of British Columbia. The first is a reassessment of TBT in the deep sediments at two sites in the Strait of Georgia, in which a comparison is made with data from the 1991 core. Secondly, we report results of a sediment study in Prince Rupert harbor, the only major shipping port on the northern BC coast.

MATERIALS AND METHODS

Sampling

Sediment cores were collected at two sites in the Strait of Georgia in September 1995 and May 1996. Coordinates for the two sites, both in deep depositional areas of the strait, are shown in Fig. 1. A modified stainless-steel box corer (Kahlsico, San Diego, USA) was utilized. The depths of the

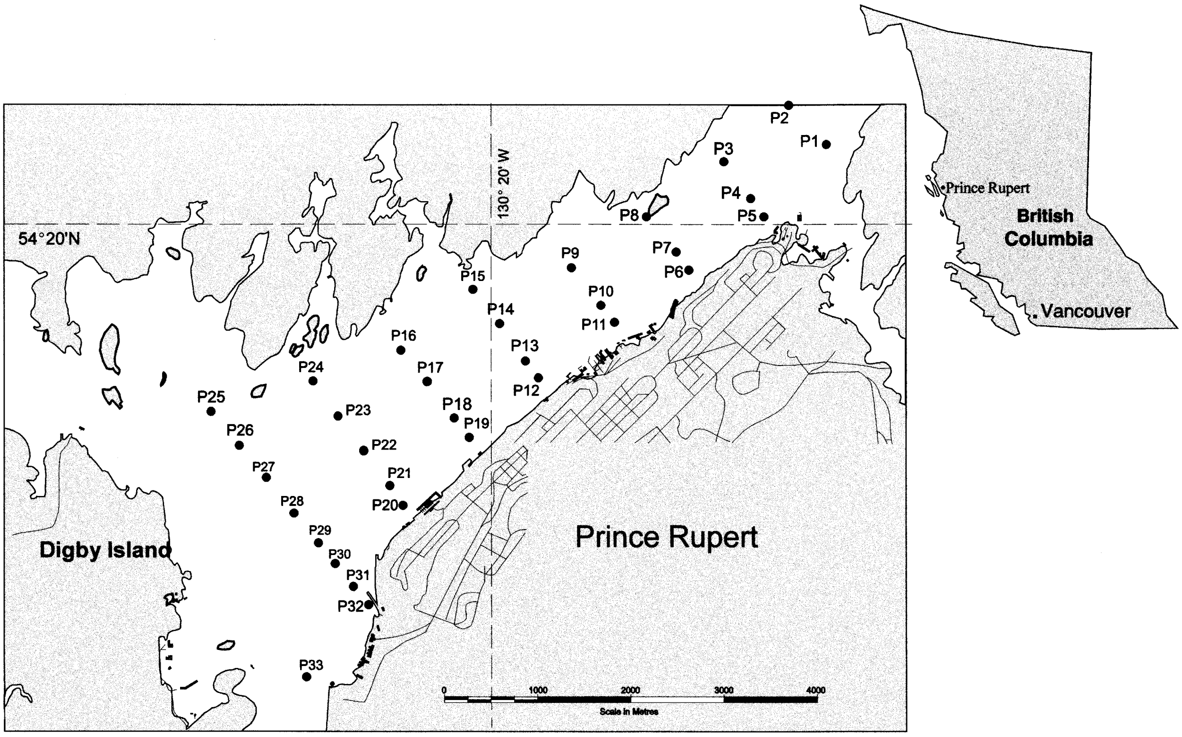

Figure 2 Prince Rupert harbor, with sampling sites. The small map indicates the city location.

two cores, SOG-1 and SOG-2, were 327 m and 405 m, respectively. Cores were frozen immediately after retrieval by complete immersion of the box in an isopropanol–dry ice bath at −78°C. Freezing times were up to 1 h. Frozen cores were wrapped in Teflon film and were returned to the laboratory, where they were sectioned in a cold room (−5°C) using a carbide-tipped rotary saw blade. Previous tests had shown that there was no apparent contamination of samples by this method. No cutting oils were used and the blade was washed with acetone between uses. Samples were taken at 1 cm intervals in the top 10 cm, at 2 cm intervals to 20 cm and at 5 cm intervals to the 40 cm depth. Sections were split for chemical analysis and ^{210}Pb dating. Samples for butyltin determinations were maintained at −20 °C until further work-up.

Thirty-three surficial sediment samples from Prince Rupert Harbor (Fig. 2; general location, 54° 19.2′ N latitude, 130° 20.0′ W longitude) were recovered using a stainless-steel Smith–MacIntyre grab on 25–26 September 1995. A sampling grid of 1 km × 0.3–0.5 km was used. Subsamples representing the top 2–3 cm of the sediment column were removed with a plastic scoop and frozen in polyethylene bags (−20°C).

Samples intended for the determination of butyltin compounds were freeze-dried. Dried samples were homogenized and screened (stainless-steel mesh); the fraction passing 149 µm was retained for analysis. Samples for isotope analysis were sent frozen to Flett Research Ltd, Winnipeg, Canada.

Analysis

Sediment core samples were analyzed at the National Water Research Institute of Environment Canada, Burlington, ON, Canada, according to the method of Chau *et al.*[9] Samples (1g dry wt.) were stirred magnetically for 1 h after the addition of 100 µl of a solution of tripentyltin chloride (1 µg Sn ml^{-1}) as internal standard. Glacial acetic acid (20 ml), water (20 ml), NaCl (8 g) and a 0.5% solution (15 ml) of tropolone in toluene. An aliquot (4.0 ml) of the extract was removed and evaporated almost to dryness with a stream of nitrogen. Hexane (1 ml) was added, and the solution was again

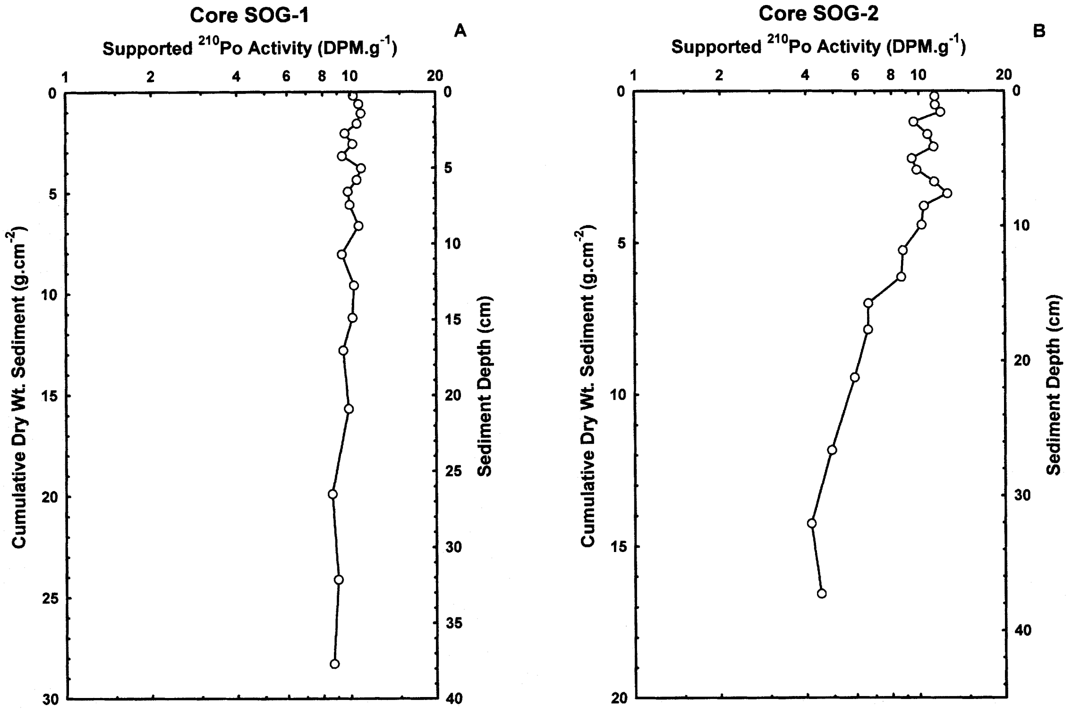

Figure 3 ^{210}Po–^{210}Pb activity versus cumulative dry-weight sediment in Strait of Georgia sediments. It should be noted that ^{210}Po and ^{210}Pb are in secular equilibrium. (A) Core SOG-1; (B) core SOG-2.

evaporated almost to dryness. The volume of the extract was adjusted to 1 ml with hexane and the extract was allowed to react with 0.5 ml of ethylmagnesium bromide (1.0 M) for 10 min. The excess Grignard reagent was destroyed by shaking with 2 ml of 1 M H_2SO_4 (1 min). The colored substances derived from the sediment and the excess tropolone were removed by a silica-gel clean-up using a Pasteur pipette minicolumn (15 cm × 1 cm i.d., containing approx. 4 g of silica gel). The extract was applied to the column and eluted with 5 ml of hexane. The eluate was reduced in volume to 1 ml before analysis. Samples were analyzed in duplicate by gas chromatography–atomic emission detection (Hewlett–Packard).

Limits of quantification and detection (LOQ and LOD) for each organotin species in sediment were 2.5 μgSn kg^{-1} dry weight and 0.5 μgSn kg^{-1} dry weight, respectively, for a 2 g sample.

Grab samples from Prince Rupert harbor were also extracted according to the method of Chau *et al.*[9] Analysis was performed at the Institute of Ocean Sciences, Sidney, BC, Canada, using a Hewlett–Packard model 5990 gas chromatograph fitted with a slit/splitless injector, autosampler and flame photometric detector operating at 610 nm. In this case, 5 g samples were analyzed with diethyltin dichloride as the internal standard. Pentylmagnesium bromide (2 M) was the alkylating agent. Limits of detection ranged from 1 to 5 μgSn kg^{-1}. Recovery efficiencies were measured for the butyltin species using the marine analytical standard, PACS-1 (National Research Council, Canada). Recoveries were 75.4, 66.4 and 147% for TBT, DBT and MBT, respectively. The high recovery for MBT may reflect higher recoveries attributed to the use of toluene (367%), as reported by Chau *et al.*[9]

RESULTS AND DISCUSSION

Strait of Georgia cores

No butyltin compounds were found above the limits of detection (0.5 μgSn kg^{-1}) in any of the core sections obtained from the two sites in the Strait of Georgia.

The two cores in this study were recovered from the deepest areas of the Georgia basin, which has been subjected to input of a wide range of contaminants from metropolitan areas, pulp and paper mills, and mines. It would be expected that such an area should provide valid depositional histories of contaminant distribution.[10,11]

We examined 20 sections from each core. Core SOG-2 (Fig. 1) was removed from a site near one sampled in 1991.[5] Core SOG-1 was obtained at a point several kilometers south, where sedimentation from the Fraser River during spring runoff is more significant. All three butyltin compounds were found in the 1991 core obtained from a site in Ballenas Basin (SOG-2).[5] In that study, gas chromatography/mass spectrometry (GC–MS) was the method of analysis; however, limits of detection were comparable with that used for this work. In the former study, concentrations were in the range of 0.2–2 μgSn kg^{-1}. Although the data are not definitive, it can be inferred from these results that in the four- to five-year period since the previous sampling, degradative and sedimentary processes have acted to reduce the butyltin levels.

Rates of sedimentation were estimated for both of the cores from this current study using $^{210}\mathrm{Pb}$–$^{210}\mathrm{Po}$ counting methods.[12] Accumulated dry-weight sediment and sediment depth are plotted against supported $^{210}\mathrm{Po}$ activity in Fig. 3 for the two cores. Fig. 3(A) shows a nearly vertical plot, indicating conditions of very rapid deposition, or, conversely, a high degree of mixing. Given the depth and the low level of biological mixing observed, the former process would dominate. Data from depths of 4–20 cm were used to model the rate of accumulation. The nearly vertical profile precluded a good linear correlation ($\mathrm{R}^2 = 0.72$) and provided an estimate of 1.4 g cm^{-2} y^{-1} (or approximately 2.6 cm y^{-1}). For core SOG-2, the plot of cumulative sediment dry weight versus $^{210}\mathrm{Po}$ activity (Fig. 3B) was again nearly vertical in the top 8 cm, indicating some mixing at the surface. However, the slope of the regression line below that point (to 30 cm) was lower and permitted a better estimate of the sedimentation rate. Here, a rate of 0.13 g cm^{-2} y^{-1} (0.25 cm y^{-1}) was estimated ($R^2 = 0.97$). Various studies[13,14] have estimated sedimentation rates in the Strait of Georgia to be in the range 0.6–2.7 g y^{-1}. Particulate deposition from all riverine sources, primarily the Fraser River, is in the range $(12–30) \times 10^6$ t y^{-1}.[15]

The half-life of TBT in sediments has been estimated to be between a few days and decades,[7,16] depending on the biogeochemical properties of the substrate. Degradation rates of TBT are highly dependent on the availability of light, heat, oxygen, organic carbon and bacterial activity. In deep sediments of the type reported here, there is no light; temperatures are generally less than 10°C,[10] and anoxia can exist at or near the surface. In shallow, anoxic, marina sediments, a half-life of approximately 9y for TBT was estimated.[7]

As noted above, the core taken in 1991 provided TBT values of about 2 μgSn kg^{-1} and the profile down the core was essentially featureless.[5] In addition, concentrations of DBT and MBT were less than those of TBT. These data suggested that degradation of TBT was extremely slow and, possibly, that the input of TBT from overlying waters had been consistent since about 1972. The reduction of TBT usage on the southern British Columbia coast in the years following 1989 has resulted in measurable decreases of TBT in biota and in the effects of TBT as indicated by the incidence of imposex in neogastropod whelks.[17] The major input of TBT is now primarily from large ocean-going ships. Thus, the deposition of TBT on deep sediments away from major harbors would be expected to reduce commensurately and would account for the reduction of butyltin levels in surface layers. Reductions of butyltin compounds in subsurface sediments may be ascribed to chemical and biological processes. In the Strait of Georgia sediments of this present study, sufficient degradation has occurred to reduce concentrations below the detection limits of current analytical methods. Similar decreases have been reported in other areas where TBT input has been severely retarded. Nevertheless, there remain strong indications that further reductions may be required to reduce inputs to major harbors and shipping corridors.

Prince Rupert harbor

Results of the analyses of 33 Prince Rupert harbor surface sediments (Fig. 2) for butyltin residues are shown in Table 1. With a few exceptions, TBT and DBT were detected in all samples, while MBT was detected in only six. Tributyltin values ranged from below the limit of detection to 1262 μgSn kg^{-1}, with most values below 100 μgSn kg^{-1} (dry weight). Dibutyltin concentrations ranged from less than the detection limit to 109 μgSn kg^{-1}, while MBT values ranged from below detection to 27 μgSn kg^{-1}. TBT/DBT ratios ranged from 0.2 to 62.

Samples from two stations (P2 and P23) had TBT values of 1262 and 647 μgSn kg^{-1}, respectively. Although anomalous in this data set, these con-

Table 1 Butyltin data from Prince Rupert harbor surficial sediments, 1995

Sample no.	Depth (m)	TBT (μg kg^{-1})	DBT (μg kg^{-1})	MBT (μg kg^{-1})	TBT/DBT
P1	60	33.8	9.0	ND[a]	3.8
P2	60	1262	20.2	ND	62
P3	50	12.4	3.82	ND	3.2
P4	50	73.4	ND	ND	—
P5	50	27.9	48.3	12.8	0.6
P6	62	ND	7.3	ND	—
P7	62	57.9	41.4	12.3	1.4
P8	37	188	19.9	ND	9.4
P9	38	38.5	40.6	ND	0.9
P10	45	ND	83.6	ND	—
P11	46	50.8	ND	ND	—
P12	32	19.0	17.0	ND	1.1
P13	45	ND	17.9	ND	—
P14	43	31.2	26.0	ND	1.2
P15	20	ND	4.5	ND	—
P16	36	27.8	11.0	ND	2.5
P17	36	38.6	12.6	13.1	3.1
P18	40	11.1	11.9	ND	0.9
P19	31	27.6	22.8	ND	1.2
P20	29	29.9	11.1	10.9	2.7
P21	40	14.3	22.8	36.6	0.6
P22	56	79.6	32.8	ND	2.4
P23	61	647	30.0	ND	22
P24	30	31.7	10.0	ND	3.2
P25	22	26.2	29.3	ND	0.9
P26	33	72.2	56.9	ND	1.3
P27	33	41.0	7.62	ND	5.4
P28	35	25.3	8.48	ND	3.0
P29	41	24.8	109	ND	0.2
P30	42	ND	58.8	ND	—
P31	38	38.8	47.8	27.0	0.8
P32	21	11.4	17.5	10.5	0.7
P33	43	ND	37.1	ND	—

[a] ND, not detected.

centrations are comparable with data reported for Vancouver harbor and two harbors on Vancouver Island[4,7,] but far below concentrations near shipyards in Vancouver reported in the mid-1980s.[2] Because they appear to be isolated, we suspect that they may be due to occlusion of hull paint particles from anchored ships.

In general, the somewhat random distribution of the butyltin compounds in these sediments suggests that their source is primarily ocean-going ship-bottoms, as this harbor is used for anchorage of large bulk carriers. The average depth of Prince Rupert harbor where samples were collected is 33 m with a range of 21–62 m. Unlike the shallow waters in Victoria and Esquimalt harbors, these depths are well beyond those where turbulent mixing from propellers might be expected to resuspend surficial materials. Mixing will be limited to that from tidal flushing, which is reported to be good,[18] due to the large tidal range. Input of TBT from shoreline industries in this city of approximately 30 000 population is also expected to be limited. There are no large commercial boatyards and only a limited number of marinas. The latter could have contributed TBT to the sediment column before the imposition of controls on TBT-based paint.[6]

Ratios of TBT to DBT for these samples (Table 1) suggest that only limited degradation is occurring, or input of new TBT from the water column exceeds the rate of degradation. Degradation, as mentioned above, is dependent upon a number of factors. In the present case, waters of this harbor lying on the north coast of British Columbia are cold, with the mean temperature not expected to exceed 4°C. Depths up to 62 m would preclude significant light infiltration. We have insufficient information on the bacterial organization of these sediments, but it is likely that they would be representative of coastal sediments. There is also little information on the sediment particle distribution and organic carbon loading, both of which can be important in the degradation process.[19]

The TBT/DBT ratio is an important indicator of the rate of input of fresh TBT, relative to its decomposition. In this study, the ratio was greater than unity in 17 of the 25 samples for which we were able to calculate the value. Ratios calculated from Environment Canada data for Vancouver harbor sediments in 1994 had a mean ratio of 2.4 ± 1.7 and a range of 0.8–6.2 ($n = 23$). Similar values were obtained for harbor sediments on the Atlantic coast of Canada.[4]

It has been shown in our work and that of others[7,8] that bottom conditions of this type can result in half-lives of years. The lack of detectable MBT in most of the samples examined here (an 18% occurrence) would also suggest that further degradation of DBT is limited. We have observed similar low MBT levels in previous studies of a sediment core from Esquimalt harbor.[7] Chau *et al.* recorded a 25% incidence of MBT in a 1994 survey of Canadian coastal sediments.[4] Saint-Louis *et al.* report measurable MBT in only three of 42 sediments from the St Lawrence estuary.[19]

CONCLUSIONS

We have examined butyltin residues in two areas of the British Columbia coastline. Sections to 40 cm in two deep cores recovered in 1995 and 1996 from the Strait of Georgia contained no detectable quantities of TBT, DBT or MBT. These results contrast with an earlier study where low to sub-μg kg^{-1} concentrations were found in a core collected in 1991. The decrease in butyltin concentrations demonstrates the effects of reduced input of TBT from coastal shipping and/or pleasure boating since 1989, as well as the slow degradation of butyltin compounds to concentrations below the limits of detection.

Concentrations of TBT and DBT ranged to over 1200 μgSn kg^{-1} in 33 surface sediment samples from Prince Rupert harbor. TBT/DBT ratios in most samples were greater than unity, suggesting strongly that fresh input from marine antifoulant coatings on large ocean-going vessels is continuing. TBT concentrations at Prince Rupert are comparable with those in larger harbors in southern British Columbia.

These results are similar to those reported elsewhere in most developed western countries. Controls on the use of TBT-based antifoulant coatings have resulted in reduced concentrations in sediments and biota, and the incidence of imposex in whelks has lessened. However, in spite of these promising indicators, the facts that TBT/DBT ratios in many sites are still high and TBT is measurable in the water column signify that controls may require strengthening in order to eliminate this persistent and pervasive chemical.

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