Tributyltin Originates from Pleasure Boats in Sweden in Spite of Firm Restrictions

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Abstract: The temporal and spatial distributions of organic tin compounds, irgarol and metals in sediments from a marina and the harbor of a small town near Stockholm, Sweden were investigated as part of a study of the environmental impacts of anti-fouling paint. The upper (0-2 cm) sediment layer was collected at seven stations in the marina and eight stations in the small town harbor; two reference stations were also sampled. High levels of tributyltin (TBT) were detected in sediment that decreased along a spatial gradient moving away from the slipway in the marina. TBT was ten times higher in the surface sediment when compared to subsurface layers (10 cm deep). The highest concentrations of TBT were found at the slipways (up to 2000 µg TBT/kg DW) of the harbor. Analysis of accumulated sediments obtained from a collection basin situated beneath a boat washer revealed very high concentrations of TBT (63 000 µg/kg DW). These data provide persuasive evidence that TBT is still being released from pleasure craft even though it has been banned for use on such boats for 19 years. The source of the TBT is most likely from older paint that has been covered with newer coats. Our observations, together with other literature-based data, suggest that TBT is still being released into the environment and poses a serious ecological problem at marinas throughout the world.

1. INTRODUCTION

Through the middle of the 20th century, lead, copper and tar were commonly used as anti-fouling substances on the hulls of sea-going vessels [1]. Around 1960 tributyltin (TBT), an effective paint containing organic tin, was introduced. Because of its efficacy, TBT use spread rapidly [2]. Studies in the 1980's, however, identified deformities in oysters that were connected to TBT [3,4] Other researchers documented the extinction of snail populations due to dramatic physiological changes that were correlated to TBT from anti-fouling paint [5,6]. It was shown that female snails developed imposex (i.e. development of masculine attributes such as a penis) and eventually became sterile. The degree of imposex increased significantly at an exposure concentration of only 0.02 µg TBT/L [5,7,8]. Many Western countries, e.g., France, Britain, Sweden, USA and Canada, reacted quickly to this scientific evidence and prohibited the use of TBT-containing paint on pleasure boats less than 25 m long in 1986 to 1989 [9-11]. This prohibition targeted these smaller boats since they tended to be present in near-shore waters, which are important reproduction areas for a large number of organisms.

1.1. Regulations in Sweden

The realization that biocides used in anti-fouling paints can spread throughout aquatic environments and pose a risk to non-target organisms prompted the Swedish chemical authority to evaluate the anti-fouling paints sold on the Swedish market first in 1992 [12] and then in 1998 [13].

1.1.1. Regulations for Pleasure Boats

The first evaluation, concerning pleasure boats less than 12 m in length, resulted in the prohibition of diuron, a known carcinogen, and isothiazoline. The paints marketed after 1992, were based on copper and irgarol as active antifouling compounds. A risk/benefit analysis conducted in 1998 resulted in the qualified approval of these post-1992 paints in coastal waters of the northern and the southern Baltic Sea and the west coast of Sweden. The precautionary principle was used when it was determined that the environmental risks in the brackish waters of the Baltic Sea were considered higher than the benefits provided by anti-fouling paints containing copper and irgarol. These paints were, therefore, prohibited for use on pleasure boats in 1998, with full enforcement beginning on 1 January 2002. In the marine environment (relatively constant ocean salinity) on the west coast, the fouling problem was considered worse and therefore copper-containing paints were allowed. The permissible paints were determined to have lower copper leaching rates, i.e. less than 200 µg/cm^2 during the first 14 days and not more than 350 µg/cm^2 during the first 30 days [13]. The reason for the firmer restriction in the Baltic Sea is the higher vulnerability of this area due to its brackish conditions [14]. This sensitivity of aquatic ecosystems in the Baltic Sea was acknowledged when the Baltic Sea was designated a particular sensitive sea area (PSSA) by the International Maritime Organization (IMO) within the UN in 2004 [15]. The organisms living in the Baltic Sea had either invaded from the ocean or from freshwater limnetic environments, meaning the few species that inhabit the Baltic Sea live at the limit of their distribution. This makes Baltic Sea organisms more susceptible to pollutants (e.g. [14,16]). The lower number of indigenous organisms also means that there are fewer taxa that cause hull fouling. For example, of the genus, *Balanus*,

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which is identified as the worst culprit, only one species is found in the Baltic Sea compared to four off the West coast. The 1998 decision on anti-fouling paint restrictions became fully effective in 2002 and meant that no copper- or irgarol-based paints could be used on Swedish pleasure boats in the Baltic Sea.

1.1.2. Regulations for Ships

Because TBT can be released into the environment from paint on a long-term basis (although rates may change over time), the chemical is transported and distributed *via* routine commercial or recreational traffic. In Sweden use of TBT also on ships longer than 25 m was prohibited in 1998 [17]. In 2001, the International Maritime Organization (IMO) proposed the AFS convention for prohibition of TBT paint on all ships, with a total ban in 2008 [18]. According to the convention, enforcement will begin one year after 25 countries representing more than 25% of the world tonnage have ratified it. The European Union ratified the convention in 2003 [11] and when Panama signed in September 2007, the criteria of the convention were fulfilled, establishing an enforcement date of September 2008. Europe has taken an even more aggressive step by barring any ships painted with TBT from European harbors as of 1 January 2008 [11].

Higher loss rates are allowed from ships than from pleasure boats. According to the latest decision in 1998, with a 1 January 2002 enforcement date, paints on ships longer than 12 m are allowed to lose 55 µg copper/cm^2 per d. This is the limit for both the Baltic Sea and the North Sea. For ships traveling primarily in the open ocean, higher loss rates are allowed [17].

1.2. Study Objectives

The primary study object was to investigate the spread of substances related to boat activities in small harbors in Sweden. Emphasis was placed on TBT, which has been prohibited from use in the Baltic Sea as an anti-fouling agent on pleasure boats and ships for 19 years and five years, respectively. An additional goal was to determine the distribution of copper in Baltic Sea harbors where copper-containing paints have been prohibited for seven years by Sweden for use on pleasure boats < 12 m. Finally, the third project goal was to study the dispersion of toxic substances (from anti-fouling paints) that may have been mobilized through the use of a boat washer situated in a harbor.

1.3. Study Hypothesis

Since TBT has been prohibited for 19 years from use on pleasure boats, buried sediments should contain higher concentrations of the chemical than recent surface layers. Assuming the restrictions on TBT have resulted in reduced amounts being released to the environment, the concentrations of TBT degradation products, i.e. DBT and MBT, should be higher than TBT. The same pattern of vertical distribution in sediments may be expected for copper, but to a lesser extent since copper-containing such paints have been banned from use on pleasure craft for only seven years.

2. MATERIALS AND METHODOLOGY

2.1. Sampling Sites

To evaluate the occurrence of chemical constituents related to boat activities, two locations were studied. At all stations samples were collected with a core sampler; the top 2 cm of sediment were used in the analysis. The sampling sites were the harbor in the small town of Trosa, with around 1000 boats, 100 km south of Stockholm (Fig. **1**), and a marina with 250 boats, in Stockholm (Fig. **2**).

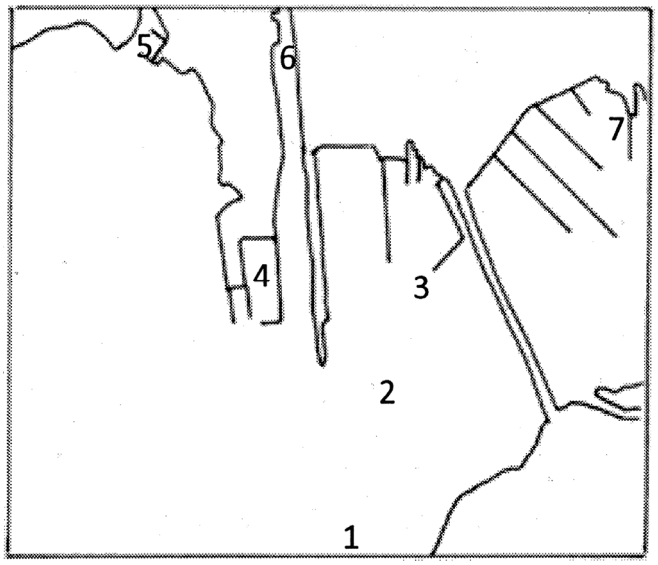

Fig. (1). The harbor at Trosa and location of sampling stations.

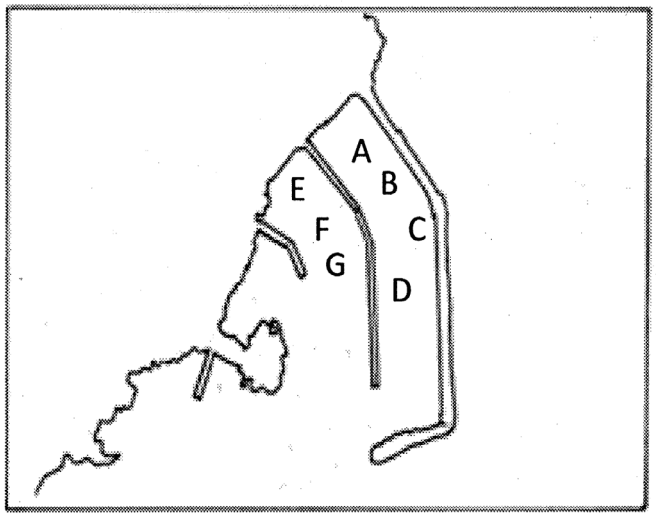

Fig. (2). The marina in Stockholm and location of the sampling stations.

In Trosa most of the moored vessels are pleasure boats, 5 to 10 m in length. Only about 20 vessels could be regarded as ships. The marina near Stockholm has been home to sail boats (primarily) for the last 50 years.

Two reference samples were collected in the middle of the Stockholm archipelago in an area with no proximal harbor and little boat traffic.

Samples were collected in Trosa in July, August and October 2006. The stations were located 1) in front of, and behind, a boat washer (station 3 S and 3N), 2) away from the boat washer (stations 2 and 1), 3) in the harbor of a boat club (station 4) and 4) three sites which are used as boat removal areas (stations 5, 6 and 7) (Fig. **1**). Two core samples were taken at each station on each of the three sampling occasions in Trosa. The boat washer was equipped with a containment basin (4 x 9 m) to collect material washed off the boats. The precipitated sediment in this basin was sampled in October 2007 after 200 boat washes. All sediment in the basin was collected, the supernatant was decanted and the amount of remaining sediment was estimated, which allowed for calculation of the total quantity of chemicals scrubbed off the boats. Two samples of the precipitated sediment were taken for chemical analysis.

The marina in Stockholm was sampled in February 2007. The marina consists of one harbor area where four samples were taken (stations A-D) and another part where the slipway is situated. In this area, three samples were collected at 20, 30 and 40 m from the shore (stations E-G) (Fig. **2**). At each site two core samples were obtained. These samples were pooled and the composite used for all chemical analyses. In addition to the surface samples, sediment was collected at discrete sediment depths at two sites in the marina at 20 (station E) and 40 m (station G) from the slipway. Exact sampling coordinates are shown in Table **1**.

2.2. Chemical Analysis

Dry weight and loss on ignition of the sediment was conducted according to standardized procedures (SS 028113-1). Concentrations of metals in sediment were determined using ICP-MS (SS-EN-ISO 17294-2) after nitric acid digestion (SS 028150). Determination of organic tin compounds and irgarol was performed by ALS Scandinavia AB. The laboratory is accredited for organic tin analysis but not for irgarol, however, all established quality assurance procedures were followed to ensure representative results. For determination of organic tin compounds, the sediment was digested in potassium-hydroxide, derivatisation was made in sodium tetraacetylborate before extraction in hexane and measurement with GC-FPD (DIN 19744). Irgarol was extracted with an acetone/hexane/cyclohexane (1:2:2) solution and quantified with GC-MS. Many chemical analyses were made on pooled samples and thus no statistics can be presented for these.

Table 1. Locations and Characteristics of the Sampling Points and Sediments

Stations	Latitude	Longitude	Depth m	Salinity PSU	DW %	LOI %
Reference						
Site 1	N59°24'22	E18°42'93	8 - 10	4.9-5.4	28 ± 5.4	8.3 ± 0.65
Site 2	N59°24'22	E18°42'27	8 - 10	4.9-5.4	38 ± 1.1	5.5 ± 0.92
Town harbour of Trosa						
Outer part, stn 1	N58°53'03	E17°33'10	3 - 4	1.5 - 4	22 ± 5.7	9.3 ± 0.85
Middle part, stn 2	N58°53'22	E17°33'20	3 - 4	1.5 - 4	22 ± 3.7	9.6 ± 0.51
In front of boat wash, stn 3S	N58°53'36	E17°33'30	3 - 4	1.5 - 4	24 ± 3.7	8.9 ± 0.28
Behind boat wash, stn 3N	N58°53'36	E17°33'28	3 - 4	1.5 - 4	19 ± 2.2	10 ± 0.12
Boat club, stn 4	N58°53'34	E17°33'06	2 - 3	1.5 - 4	25 ± 1.5	9.2 ± 0.98
Uptake area, stn 5	N58°53'52	E17°32'93	2 - 3	1.5 - 4	22 ± 1.1	11 ± 0.13
Uptake area, stn 6	N58°53'51	E17°33'09	2 - 3	1.5 - 4	31 ± 10	9.1 ± 1.3
Uptake area, stn 7	N58°53'47	E17°33'55	1 - 2	1.5 - 4	14 ± 0.45	11 ± 0.30
Small marina, 250 boats						
Harbour basin, stn A	N59°32'83	E18°15'31	4 - 5	1.5	14	12.2
Harbour basin, stn B	N59°32'81	E18°15'35	6 - 7	1.9	10	14.1
Harbour basin, stn C	N59°32'79	E18°15'41	5	2.2	6.6	14.3
Harbour basin, stn D	N59°32'75	E18°15'38	7 - 8	2.2	6.4	14.5
Pooled samples, A-D						
20 m from up-take area, stn E	N59°32'80	E18°15'23	3	2.3	19	7.3
30 m from up-take area, stn F	N59°32'78	E18°15'26	3	2.2	17	7.9
40 m from up-take area, stn G	N59°32'77	E18°15'27	3	2.3	24	6.8

Table 2. Concentrations of Organic Tin Compounds and Irgarol in the Surface Sediment (0-2 cm) in a Small Marina in Stockholm and in the Harbor of Trosa 100 km South of Stockholm

Stations	Monobutyl-tin MBT µg/kg DW	Dibutyl-tin, DBT µg/kg DW	Tributyl-tin TBT µg/kg DW	Tetrabutyl-tin µg/kg DW	(MBT+DBT)/ TBT	Irgarol mg/kg DW
Reference						
Site 1	23	25	10	< 1.0	3.7	< 0.1
Site 2	10	28	2	< 1.0	19	< 0.1
Town harbor of Trosa, 1000 boats						
Outer part, stn 1	60	26	7.1	< 1.0	12.1	Nd
Middle part, stn 2	37	22	11	< 1.0	5.4	< 0.05
In front of boat wash, stn 3 S	76	150	500	< 1.0	0.5	0.23
Behind boat wash, stn 3 N	58	54	45	< 1.0	2.5	Nd
Boat club, stn 4	44	22	9.4	< 1.0	7.0	Nd
Uptake area, stn 5	130	370	2000	< 1.0	0.3	Nd
Uptake area, stn 6	70	77	78	< 1.0	1.9	Nd
Uptake area, stn 7	76	120	120	< 1.0	1.6	Nd
Small marina, 250 boats						
Pooled samples of stn A-D	250	410	689	24	0.97	< 0.1
20 m from slipway, stn E	990	1400	1300	39	1.84	< 0.1
30 m from slipway, stn F	710	850	850	29	1.84	< 0.1
40 m from slipway, stn G	620	790	1100	8	1.21	< 0.1

The samples from Trosa harbor are pooled from three occasions in 2006 (July, August and October). The samples from a small marina in Stockholm were taken in February 2007 and the four samples from the harbor basins were pooled together.

3. RESULTS

3.1. Tin-Organic Compounds

TBT, dibutyltin (DBT), monobutyltin (MBT) and tetrabutyltin were detected in surface sediment samples (Table **2**). The concentrations of six other organic tin compounds (monooctyltin, dioctyltin, tricyclohexyl-tin, monophenyltin, diphenyltin, triphenyltin) were below detection limits and are not discussed in this paper.

The highest concentrations of TBT, DBT and MBT were present near the slipways, i.e. station 5 in Trosa harbor, with 2000 µg TBT/kg DW, and station E, with 1300 µg TBT/kg DW, in the marina in Stockholm. The lowest TBT values (2-10 µg/kg DW) were detected at the reference sites. In the outer part of Trosa harbor the surface sediment TBT concentrations were 7 to 11 µg/kg DW. Elevated concentrations of TBT were detected in front of the boat washer, with 500 µg TBT/kg DW (station 3 south). Although the highest TBT concentration was found in Trosa, the overall sediment TBT concentrations in the marina in Stockholm were much higher, ranging from 680 to 1300 µg/kg DW.

TBT concentrations were about equal to, or higher than, the DBT and MBT levels in all samples from the marina, the slipways and in front of the boat washer in Trosa. The ratio of the degradation products is shown in Table **2**. The lowest ratios of the TBT degradation products to TBT ((DBT + MBT)/TBT) were 0.3, which was found in one of the slipways (station 5) in Trosa, and 0.5, in front of the boat washer at station 3S. The highest ratios (19 and 12.1) were seen at one of the reference sites (site 2) and in the outer part of Trosa harbor (station 1), respectively. This same distribution pattern is reflected as the percentage of TBT compared to the total amount of TBT + DBT + MBT (Fig. **3**).

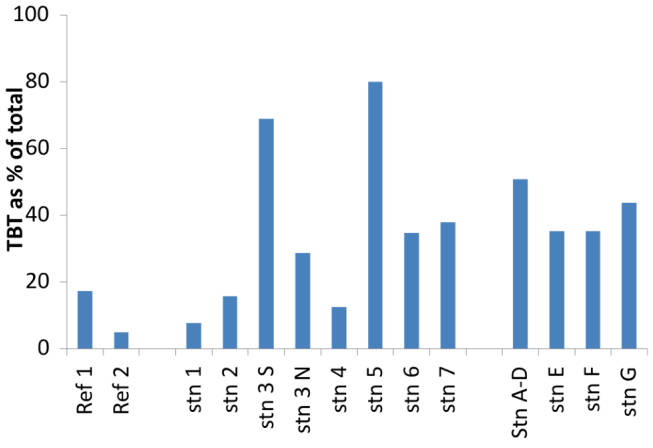

Fig. (3). TBT as a percent of the sum of TBT + DBT + MBT.

The highest percents of TBT were evident at stations 5 and 3 S, where more than 60% of the measured organic tin was TBT. This ratio suggests that these areas received the most recent inputs of TBT.

Table 3. Concentrations of Metals in the Surface Sediment (0-2 cm) in a Marina in Stockholm (250 Boats) and in the Harbor of Trosa (ca 1000 Boats) 100 km South of Stockholm

Stations	Cu mg/kg DW ± stdev July	Cu mg/kg DW ± stdev August	Cu mg/kg DW ± stdev Oct/Feb	Zn mg/kg DW ± stdev July	Zn mg/kg DW ± stdev August	Zn mg/kg DW ± stdev Oct/Feb	Pb mg/kg DW ± stdev July	Pb mg/kg DW ± stdev August	Pb mg/kg DW ± stdev Oct/Feb
Reference (2006)									
Site 1	11.8	33.9	24.3	44.4	95.6	84.6	10.6	21.6	13.4
Site 2	4.7	29.3	23.6	39.2	84.8	73.0	3.8	16.3	14.3
Town harbour of Trosa (2006)									
Outer part, stn 1	43 ± 1.0	44 ± 0.9	48 ± 0.3	142 ± 2.0	152 ± 4.2	177 ± 0.7	23 ± 0.3	23 ± 0.6	26 ± 0.1
Middle part, stn 2	46 ± 1.4	48 ± 2.8	47 ± 0.2	158 ± 5.7	173 ± 7.8	164 ± 10.1	24 ± 0.1	24 ± 1	24 ± 1.1
In front of boat wash, stn 3 S	34 ± 0.3	44	65 ± 1.1	117 ± 1.4	156	218 ± 3.5	21 ± 0.2	21	23 ± 0.5
Behind boat wash, stn 3 N	53 ± 9	46	52 ± 2.6	206 ± 64	160	175 ± 3.5	24 ± 2.6	24	25 ± 0
Boat club, stn 4	51	52	54	189	195	200	26	26	27
Uptake area, stn 5			304 ± 223			1160 ± 380			30 ± 0.4
Uptake area, stn 6			64 ±13			145 ± 7.8			53 ± 26
Uptake area, stn 7			104 ± 9.9			351 ± 6.4			45 ± 20
Small marina, (Feb. 2007)									
Harbour basin, stn A			138			298			101
Harbour basin, stn B			128			306			102
Harbour basin, stn C			107			305			83
Harbour basin, stn D			126			312			99
20 m from uptake area, stn E			207			353			114
30 m from uptake area, stn F			134			227			94
40 m from uptake area, stn G			102			198			73

The samples were taken with a core sampler at three occasions in 2006 (July, August and October) in Trosa and at one occasion in the small marina in Stockholm in February 2007. In Trosa two samples were taken at each station and in the marina one.

3.2. Irgarol

This compound was below the detection limit of 0.1 mg/kg DW in all measured samples except in front of the boat washer where 0.23 mg/kg DW was measured (Table **2**). It was also found in the sediment from the collection basin, at a concentration of 46 mg/kg DW (Table **5**).

3.3. Metals

The concentrations of copper, zinc and lead in surface sediments in the Stockholm marina were more than twice those in the Trosa harbor (Table **3**).

At both locations the highest concentrations of copper and zinc were found near the boat removal areas. In the marina in Stockholm there was a clear spatial gradient. Metals concentrations decreased with increasing distance from the removal area (Table **3**). Of the three sampled slipways in Trosa, the highest concentrations of copper and zinc (at least three times higher than any other site) were found at station 5. Lead was also elevated at station 5 in the Trosa harbor, although concentrations at stations 6 and 7 were higher. There were no significant differences between the stations in Trosa harbor (excluding the uptake areas) during July and August. However, in October, there were significant (t-test, $p<0.001$) increases in the sediment copper concentration (from 35-45 to 65 mg/kg DW) and zinc concentration (from 120 to 230 mg/kg DW) in front of the boat washer in Trosa harbor (station 3 S) when compared to the two outer stations (stations 1 and 2). There were not any differences in lead concentrations. The October copper and zinc levels in front of the boat washer were also significantly (t-test, $p < 0.01$) higher than concentrations from behind the boat washer (station 3 N).

3.4. Depth Profiles

The concentrations of all measured metals, as well as MBT, DBT and TBT, decreased with increasing sediment depth in samples collected from stations E (20 m from land) and G (40 m from land) (Table **4**).

The levels of organic tin decreased by at least an order of magnitude at 20 m and somewhat less at 40 m distance from the shore. The copper concentration in the deepest (8-10 cm) sample at 20 m also decreased by a factor of 10. Zinc and lead levels showed dramatic drops as well.

Table 4. Concentrations in Depth Profiles of Organic Tin Compounds, Irgarol and Metals in a Small Marina in Stockholm and in the Harbor of Trosa100 km South of Stockholm

Depth Profiles	MBT µg/kg DW	DBT µg/kg DW	TBT µg/kg DW	Irgarol mg/kg DW	Cu mg/kg DW	Zn mg/kg DW	Pb mg/kg DW	Sn mg/kg DW
Small marina, 250 boats								
20 m from slipway, stn E, 0-2 cm	990	1400	1300	< 0.1	207	353	114	7
20 m from slipway, stn E, 2-6 cm	640	910	700	< 0.1	93	141	70	3.8
20 m from slipway, stn E, 8-10cm	90	85	99	< 0.1	20	56	19	0.89
40 m from slipway, stn G, 0-2 cm	710	850	850	< 0.1	134	227	94	6.1
40 m from slipway, stn G, 10-12cm	190	97	97	< 0.1	50	81	23	0.98

Analyses are performed on two pooled samples from the respective stations.

3.5. Anti-Fouling Substances in the Collection Basin Beneath the Boat Washer

The sediment containing the highest concentrations of all the measured compounds was found in the collection basin beneath the boat washer. Copper and zinc concentrations were approximately 5000 and 16 000 mg/kg DW, respectively, and TBT was present at 63 000 µg/kg DW (Table **5**). Based on these measurements, the total amount of TBT produced at the end of the summer season, after 200 boat washes, was 0.8 g, or 4 mg per boat wash. The (MBT+DBT)/TBT ratio was 0.2 for both samples from the collection basin. In addition to TBT, the total amounts of copper, zinc, lead and tin were calculated to be 60 g, 200 g, 0.7 g, 1.4 g and 0.8 g respectively, after washing 200 boats.

4. DISCUSSION

4.1. Concentrations of TBT in Sediments in Ports and Open Seas

Data collected for this study indicate that the concentrations of TBT, DBT, MBT, copper, and zinc are elevated in the sediment in areas of concentrated boat activity, with particularly high concentrations in a marina where only pleasure boats are moored, as well as in areas where boats are removed from the water. The highest measured concentration of TBT, almost 2000 µg/kg DW, is comparable to concentrations found in large ports that experience traffic from much larger vessels. In a recent study of two large ship harbors, Oslo and Drammen in Norway, TBT concentrations of 420-1900 and 300-2700 µg/kg DW were measured, respectively [19]. Similar high TBT levels have been found in ports around the world, including up to 3000 µg/kg DW in Auckland, New Zealand [20], nearly 1000 µg/kg DW in Osaka harbor, Japan [21], and a mean of 4500 µg/kg DW in Barcelona, Spain [22]. TBT is not only a harbor and near-shore problem, but has also been detected in open ocean sediments. In an investigation of TBT in sediments around Denmark and the Swedish west coast, concentrations were found to decrease gradually from 19 to 1 µg/kg DW along the shipping lanes from the Öresund Sound, through Kattegat and into the Skagerack [23]. Cato [24] reported a TBT concentration of 110 µg/kg DW, offshore in the Baltic Sea.

4.2. Reduction of Organic tin Substances in the Environment

The recognized high toxicity, widespread occurrence and persistence of TBT has prompted many countries and international organizations like EU and IMO to adopt prohibitions and restrictions on TBT, with a goal of significantly reducing environmental concentrations (e.g. [15,18,11]).

After enforced restrictions of TBT, levels of organic tin compounds have been decreasing in many parts of the world. Regulations established in the Mediterranean region in 1991 have been effective in marinas, but significant TBT contamination is still present in commercial and fishing harbors [25]. In Auckland, New Zealand TBT measurements made a few years after the regulations were implemented showed a decrease in surface concentrations and the authors concluded that the restrictions were beneficial [20]. A marked decrease in concentrations of TBT in oysters and mussels occurred in the years after the 1987 ban in the UK [26]. A comparison of the TBT content in fish muscle tissue from 1985 to 1993 in the German North Sea and the river Elbe showed that levels had dropped by a factor of 3.5 and 6.5, respectively [27]. A study on archive fish samples collected from German rivers from 1998 to 2003 revealed decreasing concentrations at all sampling sites [28]. However, other studies in many other regions have indicated no recovery after 10 years of TBT

Table 5. Means and Total Amounts of Organic Tin Compounds, Irgarol and Metals from Two Samples Taken in the Containment Basin Beneath a Boat Washer in Trosa Harbor

Concentrations/Amount	MBT	DBT	TBT	Irgarol	Cu	Zn	Pb	Sn
Concentration, mg/kg DW	2.0 (±0.07)	13 (±0.2)	63 (±12)	46 (±7)	4 900 (±170)	15 900 (±490)	51(± 2.2)	108(± 6)
Total amount collected, mg	25	160	800	3	63 000	200 000	660	1 400
Amount per washed boat, mg	0.13	0.80	4	2.9	300	1 000	3	7

restrictions [29 and references therein]. No earlier data exist from the two study sites described here and therefore no direct historical comparisons can be made.

4.3.TBT in Marinas and Small Harbors

The high TBT concentrations identified in our study, both at the slipways and in the marina, are not exceptional. Comparable TBT concentrations have been observed in marina sediments from several locations around the world. Often the concentrations are similar to, or higher than, the levels from major harbors that cater to large, sea-going vessels. For example, in Hong Kong no significant differences in sediment TBT levels between shipyards and marinas were found, leading researchers to conclude that small boats may still be a significant source of TBT [30]. Biselli and coworkers [31] reported that marinas in Germany, on the coast of the Baltic Sea, had sediment concentrations of TBT up to 17 000 µg TBT/kg DW. At nine sites in the St. Lawrence in Canada, the highest TBT concentrations were found at three marinas, the highest value was 2200 µg/kg DW [32]. In a study of harbor sediments by the Swedish Geological Survey, elevated levels of TBT were measured in several marinas along the Swedish coast. In fact, some of the highest concentrations, up to 8000 µg/kg DW, were found in marinas [33].

The snail, *Nassarius nitidus*, has recently been investigated for the degree of imposex at several sites along the Swedish west coast. All of the investigated marinas or harbors were affected and impacts were even found in areas that had been expected to be free of imposex [34]. Data showing that 7 to 89 % of *Buccinium undatum*, and 100 % of *Neptunea antiqua*, in Danish waters have developed imposex indicate that TBT-contaminated sediments in open waters are adversely impacting mollusk populations [35]. Altogether, contrary to the common understanding that TBT is mainly a problem associated with its use on large ships (e.g. [23,36]), our study and several others (e.g. [30-33,37]) provide evidence that a substantial portion of the current problem stems from the use of TBT-containing anti-fouling paints on pleasure craft.

4.4. TBT in Depth Profiles, Degradation and Spills from Boat Washing

All data from the marina, the slipways in Trosa and in front of the boat washer are consistent in showing very high concentrations of TBT in all surface sediments. The two depth profile studies revealed the highest concentrations in the surface sediment, with approximately 10x lower concentrations at a depth of 10 cm. These data are in contrast to information collected from other locations where maximum levels of TBT have been found in subsurface layers, which suggests a recovery following implementation of enforced restrictions (e.g. [38-40]). When the highest TBT concentrations are in the surface sediments, as they were in the investigated marina, ongoing deposition of TBT, originating from recent sources, is indicated.

The ratio of degradation products, DBT and MBT, to the parent substance, TBT, ((MBT+DBT)/TBT) can be used as an indication of when the measured TBT was released [25,40,41]. In the town harbor of Trosa, data revealed a gradient from the outer part of the harbor to the middle of the harbor, with ratios of 12, 5 and 2.5 (Table **2**). In the most contaminated boat removal area the ratio was 0.3; in the least contaminated reference site the ratio was 19. While a ratio of <1 is indicative of recent TBT contamination [41], this is just a general guideline and it is not possible to accurately determine when TBT contamination occurred without site specific information on degradation rates of TBT. The relatively high concentrations of DBT and MBT in most sites in both the Trosa harbor and the Stockholm marina, with ratios around 2, indicate that TBT degradation has been ongoing for many years and that TBT release is decreasing.

Both the high value of 500 µg TBT/kg DW, and a low MBT+DBT/TBT ratio of 0.5 in front of the boat washer suggest episodic spills and/or an ineffective containment system. Some material washed off the boats is entering the water, either during washing or when the boat is moved after washing. Other contaminants associated with anti-fouling paints, i.e. organic tin compounds, irgarol, copper and zinc, were also present at elevated concentrations. It is likely that a significant portion of the TBT entering the water at the boat washer is coming from old paint layers. Residue from recent and historical paint layers is loosened and washed off the boat's hull. The comparably low quantity of the daughter products (DBT plus MBT) relative to the parent material, with a ratio of 0.2, indicate that TBT is recalcitrant, experiencing no appreciable degradation as long as the chemical remains incorporated into paint on the hull.

The total amount of TBT+DBT+MBT in the collection basin beneath the boat washer, following the washing of 200 boats, was slightly more than 1 g (Table **5**). This is comparable to the mass found in half a liter of TBT paint. The substantial mass of TBT, accompanied by high quantities of irgarol, copper and zinc, emphasize the importance of having a collection device underneath the boat washer. As long as boats still carry residual toxic paint on their hulls, which will probably continue for many years, boat wash water should be collected and every practical effort made to prevent discharge of the wash water back into the adjacent water body. At the time of this writing, the basin has been lengthened to better collect wash water and accompanying suspended and dissolved materials.

Despite the fact that antifouling paints containing TBT have been banned from use on pleasure boats since 1989, data from our study show higher TBT concentrations near removal areas, surface sediment concentrations that are an order of magnitude higher than subsurface (10 cm) levels and very high concentrations in the collection basin under a boat washer (63 000 µg TBT/kg DW). This evidence implicates ongoing release of TBT from the paint on pleasure craft. After the prohibition of the use of TBT paint on pleasure boats in 1989 [13], only professionals at ship yards were legally allowed to use paints containing organic tin compounds for use on ships > 25 m length. Application of these paints on Swedish ships was banned in 2003 [17]. In the five years since implementation of the complete ban, large and small watercraft should be receiving only non-TBT paints.

The most likely explanation for the high TBT concentrations found in the marina and especially at the launching and boat removal areas is that the chemical originates from older paint layers that are exposed when hulls are cleaned mechanically and by high-pressure washing. Since scraped-off paint flakes are usually left on the ground, much of it will eventually end up in drainage water that is flushed to the harbor. That these compounds are spread by way of such activities is further confirmed by the distribution patterns in the sediment; this is especially true of copper. There was a strong correlation between TBT and Cu ($r^2 = 0.8$) when all data points are included, indicating the source of the chemicals is the same, i.e. anti-fouling paints used on pleasure boats.

4.5. Future Aspects

The degradation rate of a chemical is a critical factor in determining the extent of potential environmental toxicity. Estimates of TBT half-life are very different. De Mora (1989) [38] reported a TBT half-life of 1.85 years in Auckland, which is similar to an estimated 2.1 year half-life, determined over a 14-year period, in marina sediments in the UK [42]. A half-life of up to 87 ± 17 years was determined in sediments collected in western Canada [43]. Cornelissen and co-workers [19] reported values of >10 to 20 years in Oslo harbor. Since degradation usually is temperature-dependant, degradation rates in Stockholm should be similar to Oslo harbor, which is at the same latitude. Therefore, elevated TBT concentrations in marina sediments will likely remain for many years in the absence of any remediation activities. Since boat owners usually want to have their boats nearby, many marinas and small harbors are found along the coast, which means the total impacted area might be relatively large. To reduce the further spread of TBT, several solutions might be needed, such as dredging of the most contaminated sediments, aggressive removal of hull paint on boats that have been painted with TBT in the past, vigorous enforcement of rules regarding containment of debris removed from hulls during cleaning, installation of rinse plates in connection to slipways where the spills can be collected, installation state-of-the-art collection systems in boat washers and more dry docking of vessels to reduce hull fouling and water exposure.

TBT is considered as one of the most potent environmental toxins and threshold values suggested by an expert group setting environmental quality standards for TBT within the Water Framework Directive (2000/60/EC), were 0.0002 µg TBT/L for water and 0.02 µg TBT/kg DW for sediment [44]. This means that the concentrations found in sediment in marinas and harbors in many parts of the world, are about 200 000 times higher than the currently recognized environmentally-safe levels. Our observations and data from the literature provide substantive evidence that TBT contamination is wide spread and that the concentrations in marinas often are as high as in large ports. Currently, only few countries have criteria for safe levels (e.g. [45]) and we suggest that such levels should be decided upon by environmental authorities in all countries.

5. CONCLUSIONS

- Tributyltin (TBT) is still being released to the environment from pleasure boats in spite of a 19-year old prohibition, and the concentrations may be substantial in some marinas.
- TBT originates most likely from older paint layers, which are scrubbed off when boats are cleaned and removed in the end of the season.
- Release of effective substances in anti-fouling paints in connection with the use of a boat washer occurs and should be addressed since the quantities released can be very high.
- Consistent and effective dredging rules should be established for all countries.

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