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Total tin and organotin speciation in historic layers of antifouling paint on leisure boat hulls☆

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ABSTRACT

Despite their ban on small vessels in 1989 in the EU, organotin compounds (OTCs) are still being released into the environment due to their presence in historic paint layers on leisure boats. 23 paint samples scraped from recreational boats from three countries around the Baltic Sea were analyzed for total tin (Sn) and OTCs. Two antifouling paint products were also subjected to the same analyses. A new method for the detection of Sn in paint flake samples was developed and found to yield more accurate results compared to four different acid digestion methods. A new method was also developed for the extraction of OTCs from ground paint flakes. This endeavor revealed that existing methods for organotin analysis of sediment may not have full recoveries of OTCs if paint flakes are present in the sample. The hull paint samples had Sn concentrations ranging from 25 to 18,000 mg/kg paint and results showed that tributyltin (TBT) was detected in all samples with concentrations as high as 4.7 g (as Sn)/kg paint. TBT was however not always the major OTC. Triphenyltin (TPhT) was abundant in many samples, especially in those originating from Finland. Several other compounds such as monobutyltin (MBT), dibutyltin (DBT), tetrabutyltin (TeBT), monophenyltin (MPhT) and diphenyltin (DPhT) were also detected. These could be the result of degradation occurring on the hull or of impurities in the paint products as they were also identified in the two analyzed paint products. A linear correlation ($r^2 = 0.934$) was found between the total tin content and the sum of all detected OTCs. The detection of tin can therefore be used to indicate the presence of OTCs on leisure boats.

1. Introduction

With their introduction in the 1960's, antifouling paints containing organotin compounds (OTCs) such as tributyltin (TBT) and triphenyltin (TPhT) became widely popular for application on ship hulls due to their high efficiency in preventing biofouling (Yebra et al., 2004). In the 1980's, severe adverse environmental effects were discovered, consequently leading to their ban (Abel et al., 1996). In the EU, organotin paints were firstly banned on boats <25 m in 1989 (Directive 89/677/EEC), followed by a prohibition of OTCs in antifouling paints in the EU in 2003 (Directive 2002/62/EC) and an international ban for ships by January 1, 2008 by the International Maritime Organization (IMO, 2001).

Despite the nearly 30 year old ban on leisure boats, there are ample investigations in Sweden showing that OTCs are still being released into the environment from historic paint layers on the hulls. This has been observed as fresh inputs to surface sediments in leisure boat harbours (Eklund et al., 2008, 2009, 2012), high concentrations of TBT in the collected sludge and outgoing water from wash pads (Ytreberg, 2012) and in sediments of collection basins of boat brushers (Eklund et al., 2008). Similar observations have also been made in other EU countries. OTCs have, for example, been detected in the wash water of a boat washing pad in Turku, Finland (Haaksi and Gustafsson, 2016). Turner et al. (2015). also report the detection of Sn, as an indicator for OTCs, in paint flakes collected from slipways and abandoned boats in England, Malta and Greece. The presence of old organotin paint layers on boats in the EU is the

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result of the legislation that was passed, requiring that the organotin paint be either removed or “bear a coating that forms a barrier to such compounds leaching from the underlying non-compliant antifouling system” (EU, 2003). The cited studies give evidence that many boat owners decided not to remove the organotin paint or that they were not successfully sealed. As TBT has been identified as a priority hazardous substance by the European Commission (Directive, 2000/60/EC) and should therefore be removed from the environment as soon as possible, it is important to address these sources.

Two different types of organotin coatings have been used historically: the early “conventional” also known as “free association” paints, introduced in the 1960's, and “self-polishing copolymer” paints, introduced in 1974 (Omae, 2003). In the free-association paints, the biocide is simply mixed into the paint and will leach freely from the paint matrix through diffusion. The lifetime of such paints was about 2 years, with biocides leaching exponentially with time (Champ et al., 1996). Due to their high and uncontrollable leaching rates, free association paints were the first to be banned in some European countries prior to the total ban on leisure boats <25 m in 1989 (Abel et al., 1996). The self-polishing coatings introduced during the 70's had several advantages over to the conventional paints. In these paints, the organotin is bound to a polymer, typically methyl methacrylate, through ester bonds which are hydrolyzed in seawater, leading to a controlled and constant release of the biocide from the paint film. As the outmost layer is depleted of biocides, it is eroded by the seawater, exposing a fresh layer of paint (Almeida et al., 2007). With paint lifetimes of 5 years or more, the self-polishing paints became widely popular (Anderson, 2000). Free association paints were however still commonly sold on the antifouling market: the products registry from Sweden shows that only 10 out of 39 organotin paints were of the copolymer type in 1987 (Linden, 1987). The principal OTCs used in the free association paints were bis-tributyltin oxide (TBTO) and tributyltin fluoride (TBTF) and, to a lesser extent triphenyltin derivatives such as TPhTF, TPhTCl and TPhTOH (Yebra et al., 2004; Omae, 2003; Lapp, 1976; Bennett, 1996). TPhT is on the other hand reported to have been more commonly used in Japan (Bennett, 1996; Blunden et al., 1987). For the self-polishing paints, TBTO was used for the production of the TBT copolymer (Bennett, 1996). No references to any organotins other than TBT for the use in self-polishing paints have been found. Sweden implemented restrictions in 1987 on the organotin content of antifouling paints, amongst others for copolymer TPhT paints (Linden, 1987). This suggests that such paints may also have existed on the market, although probably used to a lesser extent. Apart from organotin paints, OTCs may also be present in certain biocide-free silicone paints. The use of dibutyltin laureate as a catalyst during their production has led to the detection of low levels of DBT in the paint along with impurities of MBT and TBT (Watermann et al., 1997, 2005).

A method using XRF-technology (X-Ray Fluorescence) enables the detection of Sn through non-destructive measurements directly on leisure boat hulls (Ytreberg et al., 2015). Measurements on nearly 700 leisure boat hulls in Sweden showed that Sn was detected on the majority of the boats, with 10% having significant concentrations (>400 μg/cm^2) (Ytreberg et al., 2016). However, the XRF method will only provide the total Sn concentration and does not give any information about the speciation. Thus, the aim of the present study was to develop new analytical methods for total Sn and OTCs in paint flakes, and to investigate how much of the total Sn on leisure boats is in the form of OTCs and which species that could be present on the hulls. Though the literature suggests that the main organotin specie used in antifouling paint was TBT, other organotin species could also be present.

2. Materials and methods

2.1. Sample collection and preparation

Paint samples were scraped from the hulls of 23 leisure boats in Sweden, Finland and Germany and collected in zip-bags. Roughly 1/3 of the sampled boats were abandoned and were sampled prior to scrapping whilst the other boats were actively used (Table SI 3 in the Supplemental Information). All of the boats had multiple layers of antifouling paint. Two paint cans of old organotin antifouling paints manufactured by Hempel and International (samples 24 and 25) were also analyzed. In order to increase the sample surface and therefore the extraction efficiency for both the total Sn and OTC determinations, the collected paint flakes as well as dried aliquots of the two antifouling products were ground in a ball mill (Fritsch Pulverisette) and sieved (≤100 μm) to produce a fine and homogenous powder subsequent to analysis. In addition, a sediment sample (sample 26) from the collection basin located under a boat brusher in Stockholm, Sweden was also ground and analyzed. A boat brusher is a boat scrubbing machine placed in the water, allowing cleaning of the hull through the action of rotating brushes without having to lift the boat out of the water. The sample 26 was collected after one boating season (5 months) and approximately 600 boat hulls had been washed during this time period. Visually, the sample appeared to contain a lot of paint particles.

2.2. Determination of total tin

For the determination of total Sn in the paint powders, 4 different acid digestion methods followed by chemical analysis on ICP-MS were evaluated for their efficiency. 3 of the paint powder samples were sent to an accredited laboratory (ALS Scandinavia AB) for acid digestion according to: 1) HNO_3/H_2O_2 microwave digestion, 2) $HNO_3/H_2O_2/HF$ microwave digestion, 3) Aqua regia digestion in a heating block and 4) $HCl/HNO_3/HF$ digestion in a heating block. A method to analyze the total Sn concentration on a Field Portable X-Ray Fluorescence spectrometer (FPXRF, Innov-X DELTA-50 FPXRF, Olympus, equipped with a 4 W, 50 kV X-ray tube) was also developed. A series of 6 paint powder standards with Sn concentrations ranging from 0 to 15,000 mg/kg were prepared by mixing different amounts of pure Sn powder (99%, <10 μm, Sigma-Aldrich) into aliquots of a commercially available antifouling paint for leisure boats (Biltema, Antifouling BS, #30–634). The aliquots were left to dry, followed by scraping, grounding and sieving (≤100 μm). The final powders were collected in polyethylene zip-bags for measurement on the FPXRF. The total Sn content was determined by ALS Scandinavia AB according to Method 4 described above. A calibration curve for Sn (emission line Kα) was subsequently generated on the FPXRF. The curve obtained showed a linear response with an excellent fit ($r^2 = 1.000$) and the detection limit of the method was determined to 20 mg/kg (Fig. SI 1). The hull paint samples were measured 3 times each, directly in their zip-bags, with repositioning of the bag between each XRF measurement.

2.3. Determination of organotin compounds

Two different methods were evaluated with regards to the extraction efficiency of OTCs. Determination of OTCs was performed following the accredited sediment analytical method developed at Aarhus University (Jacobsen et al., 1997; Strand et al., 2003), hereon after referred to as the “*Sediment Method*”. 50 mg of paint powder was extracted in 5 mL of hydrochloric acid (1 M) for 30 min in an ultrasonic bath. 0.5 mL of a sodium acetate buffer (20% w/v) was added and the pH adjusted to 5 with drop-wise additions of sodium hyroxide or hydrochloric acid., This was followed by in situ derivatization with sodium tetraethylborate and extraction using pentane. The pentane phase was collected after centrifugation. The derivatization step was then repeated once more and the collected pentane phases were pooled. Tripropyltin (TPrT) in methanol was added to the paint powder as the internal standard prior to the extraction. To improve the extraction efficiency, a modified method (hereon after referred to as the "*Modified Method*") was developed where a pre-extraction step was added to the *Sediment Method*. An organic solvent mixture, whose formulation was inspired by those of commercially available cellulose thinners, was used for this pre-extraction step and constituted of 75% (v/v) toluene, 20% (v/v) acetone and 5% (v/v) 2-propanol. 3 mL of the mixture was added to the 50 mg of ground paint flakes and the samples were ultrasonicated for 30 min, after which the procedure for the *Sediment Method* was followed. All samples were analyzed for the following OTCs: monobutyltin, dibutyltin, tributyltin, monophenyltin, diphenyltin, triphenyltin, monooctyltin (MOcT) and dioctyltin (DOcT). Organotin determination was performed with a Varian CP-3800 gas chromatograph equipped with a Varian 1177 split/splitless injector and a dual channel pulsed flame photometer detector (GC–DC-PFPD). Separation was performed with a silica column ZB-5 from Zebron of 30 m length, 0.25 mm i.d. and 0.25 μm film thickness, using He as a carrier gas. 1 μl sample extracts were introduced into the 220 °C quartz frit splitter lined injector, operated splitless for 1 min. The detector was set to 350 °C with a BG-12 colour filter with sampling delay and sampling width set to 4.0 ms and 11.0 ms in channel A and 3.0 ms and 4.0 ms in channel B without the square root mode enabling to distinguish peaks assigned to Sn containing compounds from phosphorus and sulfur containing compounds. The column temperature program consisted of the following intervals: 60 °C for 3 min, an increase to 150 °C after 16 min and then an increase to 270 °C after 22 min and kept until 30 min, followed by a quick increase to 340 °C that was kept until the end of the program at 37 min. Limits of detection were determined to 5–10 μg Sn/kg, depending on the organotin (Table SI 1). Satisfactory performance according to both methods was validated with a certified reference material (BCR-646) for sediment (Table SI 1).

A comparison of the extraction efficiency between the two methods with regards to antifouling paint was carried out by extracting 3 paint powder samples (samples 4, 7 and 9) in triplicates according to both procedures. Differences between treatments were tested for statistical significance at $\alpha = 0.05$ using t-tests. The same 3 samples were also used to test if repeating the pre-extraction step from the *Modified Method* would improve the recovery of organotins. For this test, the pre-extraction step was carried out 1, 2 or 3 times, with the solvent mixture removed between each extraction. After the final repetition, the extracted liquid phases were pooled together before continuing with the regular procedure of the *Modified Method*. All samples were again extracted in triplicates. One-way ANOVAs with post hoc testing (Tukey HSD) were performed ($\alpha = 0.05$) to assess for statistical differences.

In order to compare the *Modified Method* to another organotin method for sediments, the ground sediment sample from the boat brusher basin (sample 26) was analyzed by ALS Scandinavia AB, accredited for organotin analysis in soil, sludge and sediment according to the standardized method ISO 23161:2011 (EN ISO, 2011). With the ISO 23161:2011 method, there is the option to subject the sample to either to acidic (1:1:1 mixture of acetic acid:methanol:water) or alkaline (25% potassium hydroxide in methanol) extraction. The acidic extraction was utilized for this sample.

2.4. *Quantification of unidentified organotin compounds*

Post-analysis, several unidentified peaks of significant size were discovered in the chromatograms (Fig. SI 2). These were identified as potential OTCs, firstly, given their characteristic tailing peak shape, which is the result of the formation of tin-oxides during the combustion (Jacobsen et al., 1997; Mueller, 1984). Secondly, to rule out the peaks being sulfur- or phosphorus-containing contaminants which are a common problem for organotin analysis (Staniszewska et al., 2008; Bravo et al., 2004), the peak height ratios to the internal standard measured at both channels of the GC-PFPD were compared. The good agreement suggested that there was good evidence that the unidentified peaks were OTCs. 8 different unidentified OTCs (labeled U1 to U8) were found to be present in many of the samples and/or contribute significantly to the total content of OTCs. The retention times of all compounds are listed in Table SI 2 of the Supplemental Information. In order to quantify U1–U8 approximately, a second degree polynomial curve was fitted to a plot of the retention time vs the response factor for the standard OTCs ($r^2 \geq 0.9$). An approximate response factor for the unidentified compounds was then calculated based on their retention times. Standards of tetramethyltin, tetraethyltin, tetrapropyltin, TeBT and tetraphenyltin (TePhT) were injected on the GC to see if their retention times could match any of the unidentified peaks. Only one match was found: U5 was identified as TeBT.

3. Results and discussion

3.1. *Total tin content*

The total Sn concentrations of three paint samples (samples 5, 7 and 9) were determined by four different acid digestion methods (Table 1). Method 1 was found to be the least successful as it resulted in the lowest concentrations for all samples. It is therefore not considered in the continued discussion. The remaining three methods yielded similar concentrations for two out of three samples (samples 7 and 9). However, a quite large variation between the methods is observed for sample 5. The concentrations for this sample ranged from 151 to 232 mg Sn/kg, i.e. a 54% difference between the lowest and highest concentration. The extraction degree of total Sn therefore seemed to vary from sample to sample. Residues of material were reported post-digestion for all acid digestion methods evaluated here. Due to paint consisting of a complex matrix of solvents, additives and pigments with varying chemical properties, it is difficult to solubilize completely through wet digestion techniques (Silva et al., 2016). Turner et al. (2015). digested paint flakes in aqua regia and compared the concentrations of Sn with those obtained through screening by FPXRF using the factory-installed "plastics mode" of the instrument. For some samples they found that the FPXRF yielded higher values than the chemical analysis and suspected this was the result of incomplete dissolution of the paint samples during acid digestion. Furthermore, they also hypothesized that it may be more difficult to fully extract Sn through acid digestion if it is bound to polymers in the paint (see further discussion about types of organotin paints manufactured). To avoid these issues, a method to measure the total Sn in paint flakes by FPXRF was developed (see 2.2 M & M). Compared to the highest achieved concentrations from the chemical analysis, the XRF method yielded a similar concentration for sample 9, but 40–50% higher concentrations for samples 5 and 7 (Table 1). These results show that the measurement of total Sn in paint samples through chemical analysis may substantially underestimate the Sn concentrations. FPXRF measurements are not affected by the speciation of Sn and do not require solubilization of the sample to achieve an accurate measurement and is therefore a

Table 1
Total Sn concentrations (mg/kg dw) in 3 selected paint powder samples. Four different digestion methods were tested: HNO_3/H_2O_2 microwave digestion (Method 1), $HNO_3/H_2O_2/HF$ microwave digestion (Method 2), Aqua regia digestion in a heating block (Method 3) and $HCl/HNO_3/HF$ digestion in a heating block (Method 4). The results from the measurements with the FPXRF (average of 3 measurements) are shown in the last column.

Sample #	Method 1 HNO_3/H_2O_2	Method 2 $HNO_3/H_2O_2/HF$	Method 3 Aqua regia	Method 4 $HCl/HNO_3/HF$	FPXRF ($n = 3$)
5	140	169	151	232	351
7	1530	4670	5340	4840	7553
9	64.3	106	114	103	102

more suitable analysis method. Thus, all antifouling paint samples ($n = 25$) were analyzed for total Sn concentration according to this method (Table SI 3). With the exception of samples close to the detection limit of 20 mg/kg (samples 1 and 2), the precision of the triplicate measurements was $\leq 7\%$, indicating a high degree of homogeneity. The samples spanned over a wide range of total Sn concentrations from 25 to 18,214 mg/kg. The concentrations for two of the antifouling products (samples 24 and 25) are similar and very high at around 70000 mg/kg. It should be noted that their concentrations exceed that of the highest standard (15,000 mg/kg) in the FPXRF calibration curve and so should be interpreted with some caution.

3.2. Organotin speciation in paint flakes – method development

For parts of the following discussion, butyltins (MBT, DBT and TBT), phenyltins (MPhT, DPhT and TPhT) and unidentified OTCs (U1 – U8) have been summed together to simplify the data presentation. See Supplemental Information for the concentrations of the individual species (Table SI 4, 6 and 9) and all p-values from the statistical tests (Table SI 5, 7 and 8). MOcT and DOcT were not detected in any of the samples and are therefore not discussed.

3.2.1. Comparison of the sediment method and the modified method

The concentrations of butyltins were significantly higher for 2 of the 3 samples with the *Modified Method* (Fig. 1) and on average, 1.2 times higher compared to the original *Sediment Method*. Only samples 7 and 9 contained phenyltin compounds and for both samples, the *Modified method* resulted in statistically higher concentrations by factors of 2.4 and 7.5, respectively. This is mainly due to an increased recovery of TPhT which constituted all or the great majority (>90%) of the total phenyltin concentration for these samples. The measured concentrations of the unidentified OTCs were also significantly higher for 2 out of the 3 samples by about a factor of 4. Consequently, for the total sum of OTCs, the recovery was on average almost twice as high with the *Modified Method* although statistical significance was only achieved for samples 4 and 9 (Table SI 5). These results suggest that the added pre-extraction step of the *Modified Method* greatly enhances the extraction yield when it comes to paint flakes, The *Modified Method* is therefore more suitable for this type of sample matrix. Additionally, the results indicate that the concentrations of known butyl- and phenyltins in sediment samples containing paint particles may be underestimated with the *Sediment Method* and other similar methods.

3.2.2. Repeating the pre-extraction step of the modified method

For the *Modified Method*, the effect of repeating the pre-extraction step with the cellulose thinner-like mixture was tested on the same three samples, i.e. samples 4, 7 and 9 (Fig. 2 and Table SI 6). Repetition showed no significant effect for the butyltins as a group but differences could be detected for TBT. For samples 4 and 9, significantly higher concentrations with 2 and 3 repetitions of the pre-extraction step compared to just one were displayed. For the phenyltins, the average concentrations increased substantially between 1 and 2 repetitions. These differences were however not significant for either of the samples due to the large variation in concentration between the replicates. The unidentified OTCs were also affected by the number of repetitions, with average concentrations decreasing with increased repetitions for U1–U6. The

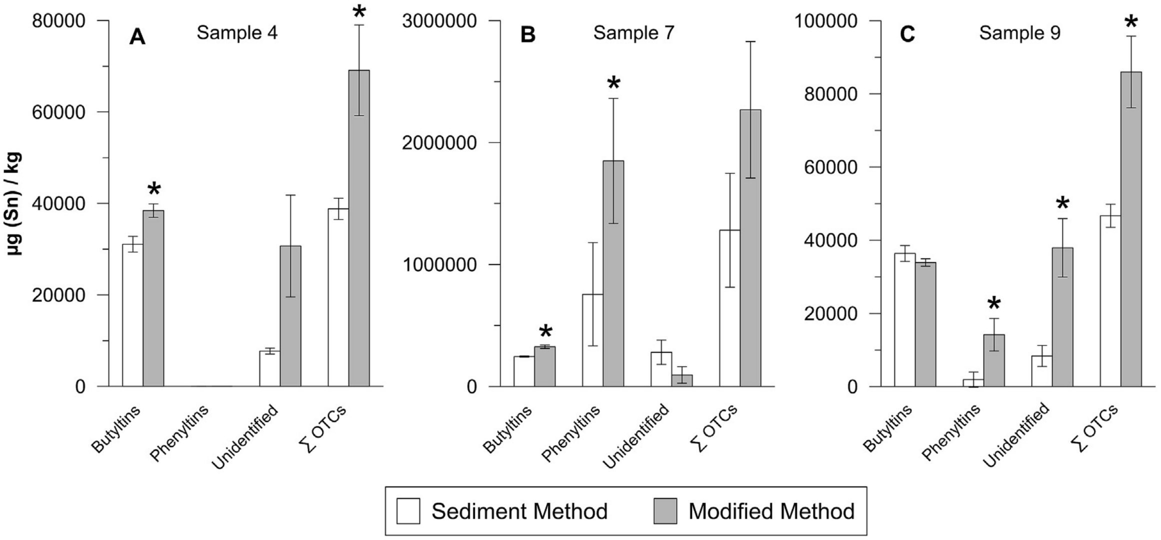

Fig. 1. Concentrations (µg/kg as Sn) of butyltins (MBT + DBT + TBT), phenyltins (MPhT + DPhT + TPhT), unidentified OTCs (U1–U8) as well as the total concentrations of OTCs (∑ OTCs) for paint flake samples 4 (A), 7 (B) and 9 (C) extracted according to the two different methods. Error bars show the standard deviation of triplicate measurements. Statistically significant differences ($p < 0.05$) between the two methods are indicated by asterisks.

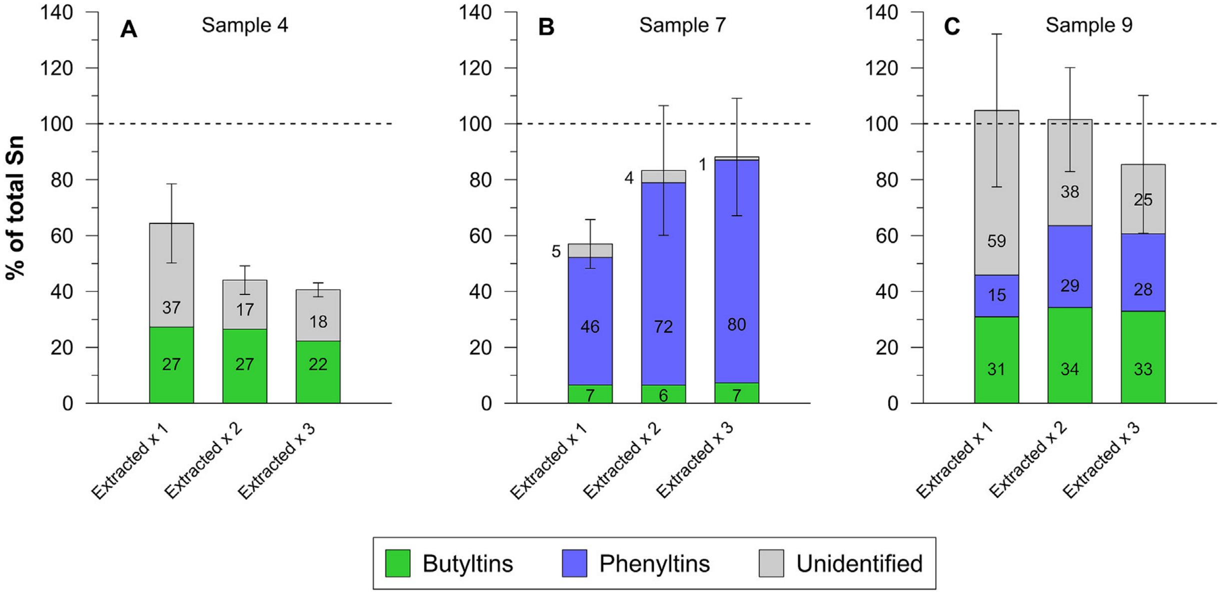

Fig. 2. Percent of total Sn extracted as butyltins (MBT + DBT + TBT), phenyltins (MPhT + DPhT + TPhT), and unidentified OTCs (U1–U8) for paint flake samples 4 (A), 7 (B) and 9 (C) with the pre-extraction step in the Modified Method repeated 1, 2 or 3 times. Error bars show the standard deviation of the average total recovery of OTCs for the triplicate measurements of each sample.

decrease was only statistically significant for some samples and species (see Table SI 5) but the general tendency of a decrease in concentration may nonetheless indicate that these compounds are more reactive and perhaps more prone to degradation than the other OTCs.

In order to get the best recovery of all species, the 26 samples were subjected to the pre-extraction step both once – to get the best recovery for the unidentified species – and three times – to potentially increase the recovery of TBT and phenyltins. The best recovery for the unidentified species was again found with one pre-extraction step: paired t-tests performed for each of the unidentified OTCs, showed that for several of these species (U1, U2, U5 and U6), concentrations were significantly higher with one pre-extraction step compared to three. The concentrations of the unidentified OTCs obtained with 1 pre-extraction step were therefore exclusively used for all samples. No significant difference was however found for the TBT concentrations ($p = 0.7209$), or the other butyl- or phenyltin species (see Table SI 8 for all p-values). An average of the results from 1 and 3 pre-extraction steps for these species was therefore used as the final concentrations.

3.3. *Speciation of OTCs in antifouling paint products (samples 24–25)*

The Hempel paint (sample 24) was labeled to contain both TBTO and TBTF and is therefore most likely a free association paint. For the International paint (sample 25), the can was only labeled "tin-based" and no speciation information could be obtained from the paint manufacturer upon inquiry. As both the total Sn concentration and the OTC speciation in both paints were very similar (Table 2), the International paint may also be of free association type.

For both paints, TBT constitutes the vast majority of the OTCs, with the purity of the Hempel paint being somewhat higher than that of International. Both MBT and DBT were present in the two products along with several unidentified OTCs and TeBT (U5). These compounds may be impurities from the production of the paints. TBT and TPhT used in antifouling paints were produced through an indirect route of manufacture involving the intermediate synthesis of TeBT and TePhT (Blunden and Evans, 1990). The tri-substituted compounds were then manufactured through reaction with tin (IV) tetrachloride (Bennett, 1996). For the synthesis of TBTCl and TPhTCl according to this procedure, yields of 95% and 72–87%, respectively, have been reported (Thoonen et al., 2004). TBTCl was then used as the precursor in the manufacture the biocides TBTO or TBTF for use in antifouling paint (Bennett, 1996). Suzuki et al., 1999 (Suzuki et al., 1999) investigated the purity of technical grade TBTCl and found that the product consisted of 96% TBT, 2.1% DBT, 0.5% TeBT, MBT (0.06%) and traces of various isomers of DBT and TBT. These impurities are similar to those reported in commercial grade 95/97% TBTO: TeBT, DBT derivatives and dibutylalkyl tin compounds (Bennett, 1996; Dobson and Cabridenc, 1990). Oddly, the International paint also contained MPhT, which in relation to the total OTC content only represents 0.6% (w/w). The actual concentration is however far from negligible at 290 mg Sn/kg. No DPhT or TPhT were detected in this paint, suggesting that the MPhT is perhaps not a by-product of the TPhT synthesis.

Table 2
Concentration (in µg/kg) and distribution of organotin species in antifouling paint products expressed as % of the total sum of all OTCs.

Sample #	Brand		Total Sn	MBT	DBT	TBT	MPhT	DPhT	TPhT	U1	U2	U3	U4	U5 (TeBT)	U6	U7	U8
24	Hempel	mg/kg	70,079	70	613	51,711	–	–	–	–	305	191	–	–	626	–	1341
		%		0.1	1.1	94.3	–	–	–	–	0.6	0.3	–	–	1.1	–	2.4
25	International	mg/kg	73,209	148	2081	41,916	290	–	–	–	223	179	–	409	380	–	1701
		%		0.3	4.4	88.6	0.6	–	–	–	0.5	0.4	–	0.9	0.8	–	3.6

3.4. Speciation of OTCs on leisure boat hulls

3.4.1. Distribution of OTCs in the hull paint samples (samples 1–23)

The distribution of OTCs in the 23 paint samples scraped from leisure boat hulls varies greatly (Fig. 3). In common for all samples is that at least one butyltin species and at least one unidentified OTC were found. Phenyltins are, on the other hand, only present in 13 of the samples, including all the Finnish samples. This suggests that paints containing phenyltins were perhaps more widely used in Finland. More samples from Finnish boats would need to be analyzed to confirm this theory.

Overall, the butyltin species dominate the pool of OTCs in 8 samples whereas the phenyltin and unidentified species are the dominant groups for 8 and 7 samples, respectively. TBT is the prevailing butyltin species for 18 samples with DBT being the main butyltin for the other 5. Furthermore, all three butyltin species (MBT, DBT and TBT) were present in 21 of the samples. TPhT constitutes the vast majority ($\geq$96%) of the phenyl species, with the exception of sample 6 where only MPhT and no DPhT or TPhT was detected (note that this is similar to the International paint, sample 25). The almost complete lack of mono- and di-substituted phenyltins suggests perhaps that TPhT is more resistant to degradation than TBT and/or that the original paints containing TPhT may have been produced with less by-products than the TBT-based paints. Amongst the unidentified OTCs, U3, U4 and U7 are each only present in $\leq$5 samples and each constitute a small portion of the total sum of OTCs when detected. The other unidentified OTCs are much more abundant, with U5, later identified as TeBT, being the most frequently detected (present in 20 samples), followed by U1 (18 samples), U2 (15 samples), U6 (12 samples) and U8 (12 samples). After DBT and MBT, TeBT was the most abundant impurity measured in the technical grade TBTCl by Suzuki et al. (1999). This is consistent with TeBT (U5) being not only the most frequently detected in the samples but also the most abundant compound amongst U1–U8 for 15 out of the 23 sampled boats. Even though TeBT is less toxic than its di- and tri-substituted counterparts, it may be degraded in the environment to form TBT and could therefore pose a risk long-term (Landmeyer et al., 2004; Gajda and Jancsó, 2010).

The presence of MBT and DBT in the Hempel and International paints analyzed could explain their detection in the samples of paint layers from leisure boat hulls. Additionally, all unidentified compounds found in the hull paint samples, except for U4 and U7, were also detected in the paint products. The varying degree to which these different compounds are found on the hulls could therefore reflect the purity of the organotin products used to manufacture the original paints. The possibility of degradation of TBT and TPhT, as well as that of TeBT, occurring on the boat hulls can nevertheless not be ruled out. It could explain why some samples had higher concentrations of DBT than TBT. There is a practice within risk assessment to assess the degradation degree of TBT in sediments by calculating the degradation index i.e. the ratio between TBT and its “degradation products” MBT and DBT (Díez et al., 2002). If MBT and DBT were already present in the original paint such a ratio could be misleading.

In terms of risk assessment and potential toxicity to aquatic organisms, TBT and TPhT are of highest interest as these tri-substituted OTCs are known to be endocrine disruptors and more toxic than their mono- and di-substituted counterparts (Sunday et al., 2012; Horiguchi et al., 2001). Of the two, most of the focus has so far been on TBT, both in scientific studies and when it comes to regulation and environmental monitoring as TBT has been known as the main OTC used in antifouling paints. TPhT has also been used in antifouling paints but more commonly used as a fungicide (Fent and Konstantinou, 2006). Hence, most guideline values for water, sediments and soils in European countries with regards to OTCs exist only for TBT. For sediments, for example, the only exceptions are Great Britain and Ireland that have guideline values for MBT + DBT + TBT and Finland with guideline values for TBT + TPhT (Swedish, 2009). In this sample set, however, 10 of the 23 hull paint samples contained more TPhT than TBT (Fig. 3), with 6 of those samples originating from Turku in Finland and the remaining 4 from Stockholm and Västerås in Sweden. For one sample from Gothenburg in Sweden (sample 14), TBT is only marginally higher (38% of total OTCs) than TPhT (37%). These results indicate that the occurrence of TPhT in antifouling paint products may have been more widespread than previously thought. It would be valuable to analyze more samples to confirm this hypothesis.

3.4.2. Identities of the unidentified OTCs

Only U5 could be positively identified upon injection of additional standards with tetraalkylated or –arylated OTCs. The retention times of the other unidentified compounds may however give some hints as to their identity since they are determined by the

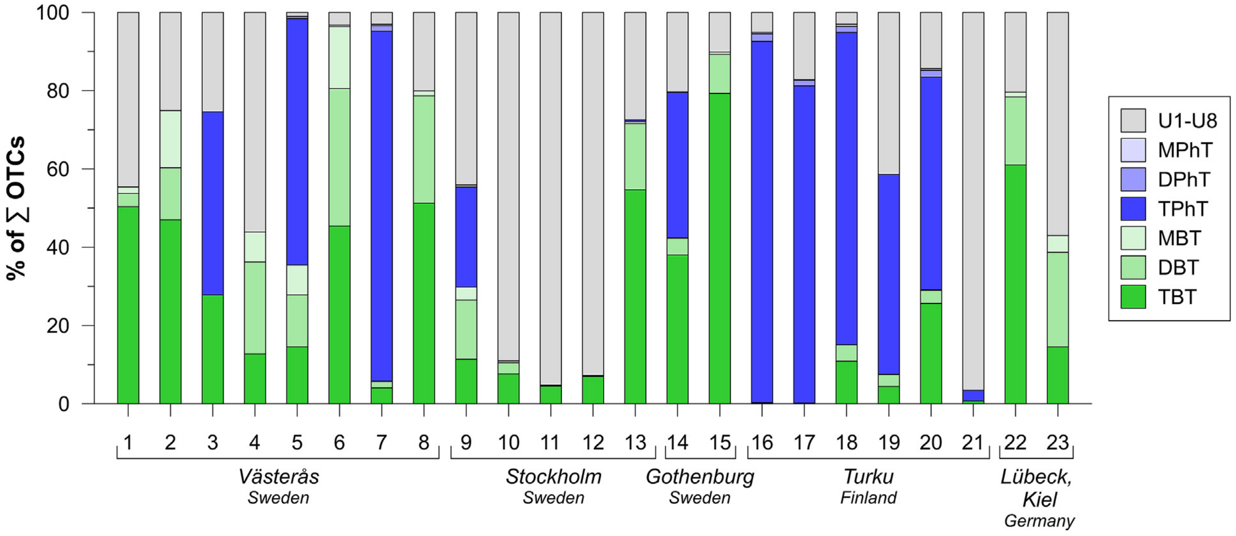

Fig. 3. Distribution of butyltins (MBT, DBT, TBT), phenyltins (MPhT, DPhT, TPhT), and unidentified OTCs (U1–U8) as % of the total sum of OTCs for the 23 hull paint samples.

Table 3
Possible identities of the unidentified OTCs based on impurities found by Suzuki et al., 1999) in technical grade TBTCl.

Impurities in TBTCl	Number of C atoms after derivatization	Potential matches
n-butylisobutyltin dichloride (DBT isomer)	12	U1
n-butyl-*sec*-butyltin dichloride (DBT isomer)	12	U1
di-*n*-butylisobutyltin chloride (TBT isomer)	14	U2 or U3
di-*n*-butyl-*sec*-butyltin chloride (TBT isomer)	14	U2 or U3
n-butyl(2-ethylhexyl)tin dichloride	16	U4, U6 or U7
di-*n*-butyl(2-ethylhexyl)tin chloride	18	–
di-*n*-butyl-*n*-octyltin chloride	18	–

volatility of the compound and, therefore, indirectly its size. In Table SI 2, the number of carbon (C) atoms for the derivatized standard compounds are listed next to their retention times, in order of elution. A linear regression was fitted to the two parameters showing a clear relationship ($r^2 = 0.93$). Based on this relationship, the following number of C atoms were assigned to the unidentified compounds: 12 (U1), 14 (U2 and U3), 16 (U4, U6 and U7), and 17 (U8). The number of carbon atoms was calculated for impurities other than MBT, DBT and TeBT that have been found in technical grade TBTCl (Suzuki et al., 1999), if derivatized with sodium tetraethylborate. Amongst the impurities, possible matches were found for all unidentified compounds except for U8 (Table 3).

3.5. Correlation between total Sn and OTCs

The majority of the Sn in the paint samples consisted of OTCs: on average, 69% (SD = 38) of the total Sn was in organic form. The large variation is due to four samples displaying especially low organotin contents at <30% of the total Sn (Fig. SI 3). For three of these (samples 3, 19 and 21), TPhT was detected, hence the low recoveries may be due to an underestimation of TPhT due to the issues with instrument performance. Poor sensitivity for TPhT during the analysis of the 26 samples led to uncertainties in the TPhT concentrations on the order of 50% for some samples. It is also possible that TPhT was present but not detected in some samples. This may have been the case for the fourth sample with low recovery (sample 6). The uncertainties in TPhT quantification would however not alone explain the large Sn "deficit" for these particular samples. One must therefore consider whether other OTCs than the ones analyzed here or inorganic Sn could additionally be present. Also contributing to the large variation is sample 17, with an organic tin content exceeding its total Sn concentration (171%). This high recovery of OTCs is due to TPhT being overestimated and exceeding the sample's total Sn by 39%. When excluding the mentioned deviating samples, the percentage of the total Sn as OTCs becomes 75% (SD = 24).

Linear regressions were fitted to investigate the correlation between total Sn and the OTCs (Fig. 4). The relationship to the sum of the butyl- and phenyltins and the unidentified OTCs, yielded coefficients of determination of 0.841 and 0.673, respectively, but the best fit was obtained with the sum of all OTCs (Fig. 4C), with $r^2 = 0.934$. It also has the slope closest to "1" and the fit with the narrowest 95% confidence interval. Hence, Sn detected on a boat hull, for example by XRF (Ytreberg et al., 2015) is a good indicator for the presence of OTCs.

3.6. Quantification of OTCs in sediments containing paint flakes

The comparison between the *Sediment* and *Modified Methods* with ground paint flakes, showed clear tendencies of underestimation for the former. To investigate whether this was isolated to the *Sediment Method* alone, a ground sediment sample containing a lot of paint flakes (sample 26) was analyzed according to ISO 23161:2011 and the *Modified Method*, for comparison. Although only one sample was used for this comparison, the results (Table 4) reflect the same findings as the previous comparison to the *Sediment Method*. The *Modified Method* has a superior recovery of butyltins and phenyltins by factors of 1.5 and 7.7, respectively, suggesting that the ISO method may not be efficiently extracting all OTCs from paint flakes. However, more samples would need to be analyzed to confirm this.

Soil and sediment samples collected at boatyards and harbors are very likely to contain paint particles (Singh and Turner, 2009). Utilizing the soil and sediment methods studied in this work, the concentrations of organotin compounds, and of TPhT in particular, would probably be underestimated in such samples. For both the

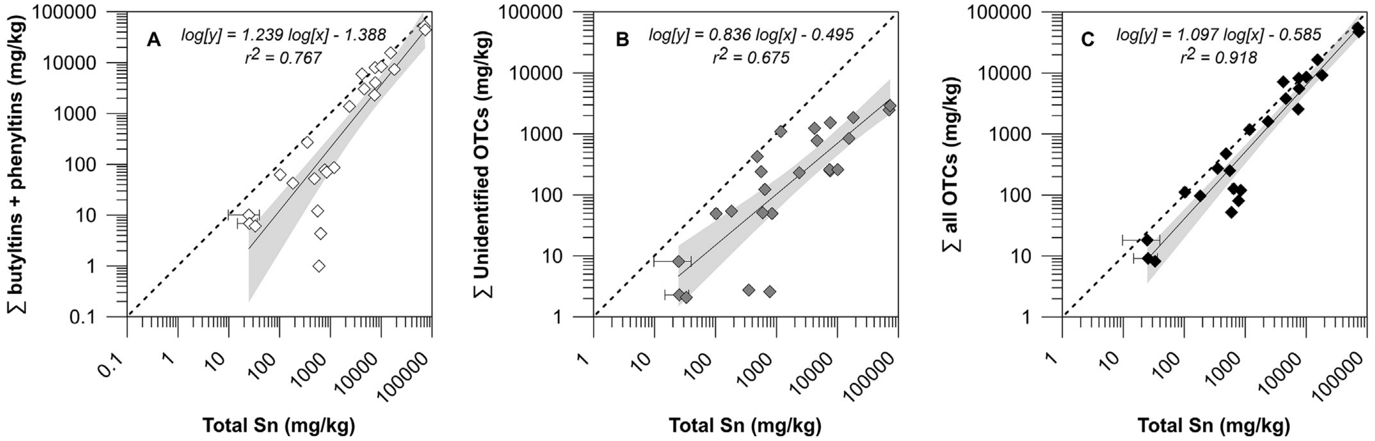

Fig. 4. Regression plots of ∑ butyltins + phenyltins (A), ∑ unidentified OTCs (B) and total OTCs (C) against the total Sn concentration in mg/kg. Error bars show the standard deviation of triplicate measurements of total Sn. The dashed line shows the 1:1 correlation. The shaded grey areas display the 95% confidence intervals of the linear regression fits.

Table 4
Analysis results for the sediment sample with paint flakes (sample 26) by two different methods: ISO 23161:2011 and the *Modified Method*.

OTC	ISO 23161:2011 (μg/kg as Sn)		Modified Method (μg/kg as Sn)	Factor of difference compared to ISO 23161:2011
	Reported value	Reported uncertainty		
MBT	3167	1276	644	0.2
DBT	2461	973	8351	3.4
TBT	44,613	14,448	64,840	1.5
MPhT	6851	2940	1855	0.3
DPhT	2301	948	2961	1.3
TPhT	37,646	15,465	355,800	9.5

Sediment Method and the ISO method, a mixture comprising of an acid and polar solvents were used for the extraction. In contrast, the “cellulose thinner” extraction mixture of the *Modified Method* consists mainly of non-polar solvents. This could perhaps explain the improved recovery. Both TBT and TPhT have low solubility in water. The solubility range from 4.5 to 50 mg/L for TBT, depending on the anionic ligand (e.g. Cl^-, F^-, OH^-). For TPhT, the solubility is even lower, ranging from only 1 to 5.2 mg/L (Blunden and Evans, 1990), which may explain the greatly improved extraction efficiency for this compound, in particular. What is also worth noting is that the concentration of TPhT in this sediment sample was 5.5 times higher than that of TBT. The OTCs in the sediments may reflect their occurrence on the 600 hulls washed in the boat brusher during the boating season. These results therefore indicate that TPhT may have been more prevalent than TBT on these particular leisure boat hulls.

4. Conclusions

This study highlights some analytical challenges in determining both the total Sn and the OTCs in antifouling paint flakes, with standardized methods underestimating their concentrations. The combined findings indicate that as a result, the concentration of OTCs, and particularly TPhT, in sediments will likely be underestimated, if they contain antifouling paint flakes. This issue needs further investigations as it may have implications on environmental risk management of matrixes such as soil and sediment. This is of particular concern for risk assessment of harbors and marinas as samples collected at such sites are likely to contain paint particles. The amount of OTCs stored in the sediment where they may act as long-term sources to the water phase could currently be underestimated.

OTCs were present on all the sampled leisure boat hulls, even at a total Sn concentration as low as 0.025% of the dry paint weight. Although TBT was detected in all samples and a substantial portion of the samples also contained TPhT, suggesting that this biocide may be more commonly occurring on leisure boats than previously thought. TeBT, which can degrade to TBT was also found to be present in large amounts. These combined findings show the need to monitor organotin species other than TBT. Recreational vessels have been shown to still be sources of OTCs, the recommendation to remove or seal layers of organotin paint has either not been followed or the sealers have not performed in a satisfactory manner. In order to phase out the priority hazardous substance TBT and other OTCs, boats with historical layers of organotin paint need to be identified and remedied. This study concludes that Sn can be used as an indicator to easily identify such boats.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2016.11.001.

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