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Development of an integrated approach for the removal of tributyltin (TBT) from waterways and harbors:
Prevention, treatment and reuse of TBT contaminated sediments

TBT CLEAN

Task 3545
Release of TBT

Kris Pynaert and Lode Speleers

ERC
Environmental • Research • Center
Hekkestraat 51, Hofstade-Aalst
B-9308, Belgium

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EXECUTIVE SUMMARY

The results of report 3546 on sediment characterization have revealed that sediment in the Port of Antwerp is indeed contaminated with tributyltin (TBT), with average concentrations ranging from 50 to 4000 µg/kg DW. However, much higher concentrations were found close to the ship repair site, up to more than 40000 µg/kg DW. In task 3545, we have tried to evaluate the risk of TBT remobilization in the water phase when contaminated sediment particles are resuspended by dredging or other activities.

In lab-scale simulation experiments, different amounts of the highly contaminated sediment were resuspended in harbor water, and TBT release was monitored by taking samples of the water phase during a certain time interval. Initial experiments, where sediment was resuspended without pH control in the vessel, showed that increasing the amount of suspended solids caused a decrease in TBT release. This was contradictory to what we expected, and further experimentation showed that mixed liquor pH has a significant effect on the release of TBT to the water phase. Due to the lower sediment pH (7.74) compared to the harbor water pH (8.29), increased sediment suspension caused a larger pH drop, and consequently a lower TBT release. In detailed experiments with a pH controller, the critical pH for TBT release was found to be 8.1. At lower pH, TBT is strongly adsorbed to the sediment particles (pH 6-8.1), but desorption readily starts and steadily increases at higher pH. Increasing the amount of suspended particles at a constant pH also increased the TBT release. Salinity did not affect the extent of TBT release around pH 8, but at higher pH (10) less TBT was remobilized when the salt concentration was increased. These lab-scale findings were roughly confirmed during an on-site dredging operation. Peaks of more than 500 ng TBT/L were measured in the water column during dredging. These concentrations are not acute toxic, but certainly warrant the use of an appropriate dredging technique that minimizes turbidity (as a measure for suspended solids). It should however be noted that these on-site measurements will be repeated for confirmation during the next dredging campaign. In the near future we will also try to develop a better simulation set-up, one that better reflects the on-site (re)suspension mechanism.

The results of this task are only applicable to the specific situation in the harbor of Antwerp. This type of research should be performed for each harbor or waterway where resuspension is expected, because grain size distribution, organic matter content, salinity, buffering capacity and many other conditions will have a significant effect on the critical pH for TBT release. Comparing the actual harbor or waterway pH conditions (water + sediment) with the experimentally determined critical pH value should give an idea on the possible risk of TBT remobilization.

The task will be completed in the future with an estimation of the direct TBT release from painted surfaces, an experiment that has already started in which we have submerged 30 TBT-painted square steal surfaces (200 cm²) at different depths in the harbor and where we will follow up the TBT concentration in the paint.

1. GENERAL INTRODUCTION

1.1. Recapitulation of conclusions of task 3546 and link with task 3545

In the report prepared for task 3546 (Sediment characterisation), the use of organotin compounds (e.g. tributyltin, TBT) as wood preservatives, PVC stabilizers, catalysts, biocides, … is described in detail. As a consequence of their applications, organotin compounds were and still are directly released in the environment (see Figure 1). From an ecotoxicological viewpoint, TBT is the most harmful, because of its specific biocidal properties (used for that particular reason in antifouling ship paints) and adverse affects on non-target organisms present in rivers, harbours and oceans. Due to the extensive use of TBT paints for over 25 years, this chemical has found a way to accumulate in certain parts of the environment, especially in harbours and marinas with high shipping activity. Once released in the environment, the physico-chemical properties will determine how the contaminant is partitioned between water/sediment/air (see Figure 1). Due to the chemical characteristics of organotin compounds (see further), sediment has acted as a sink for these chemicals and has become a reservoir for possible remobilisation of TBT in the environment either through diffusion of TBT out of the sediment bed or release of TBT during resuspension of contaminated sediment particles. Next to a more stringent legislation on the primary release via TBT-containing antifouling paints, which are banned from 2003 onwards, remediation of historically contaminated sediment could thus be considered equally important.

Sediment samples at different locations in the port of Antwerp were characterized for their grain size distribution and a number of important environmental parameters like organotin compounds, PAHs, mineral oil, EOX, TOC and heavy metals. A “TBT-blackspot” was found close to the Antwerp ship repair site, with a TBT concentration of over 40 mg/kg DW. These high concentrations were most likely due to paint chippings and were very local. Other sites in the port were less contaminated with TBT, with concentrations varying between 0.05 and 2 mg/kg DW. In case highly contaminated sediments need to be dredged for maintenance or for ex-situ treatment/remediation, this inevitably causes resuspension of TBT-sorbed sediment particles. The aim of this task was to determine the physico-chemical properties of TBT-desorption from sediment to water phase, and determine a limit for resuspended solids concentration (turbidity) in order to minimize TBT-release in the water during dredging operations. Therefore, lab-scale simulations of dredging and disposal activities were carried out, both with heavy contaminated as with lower contaminated sediment samples from the port of Antwerp. The influences of important environmental conditions (mainly pH and salinity) on TBT-desorption were examined.

1.2. Environmental organotin partitioning

In Fig. 1, a general overview is shown of input, phase transitions and possible degradation of organotin compounds in the environment. Possible sources are described in the report of task 3546, while the processes of photochemical and biological degradation are described in the 'Screening of technologies' report and will also be discussed more in detail in later task reports. Of particular importance in the framework of this task, is the partitioning of the organotin compounds between the water, sediment, air and animal/plant tissue phases. This partitioning is mainly determined by the chemical features of the compounds involved (hydrophilic/hydrophobic character, charges, …).

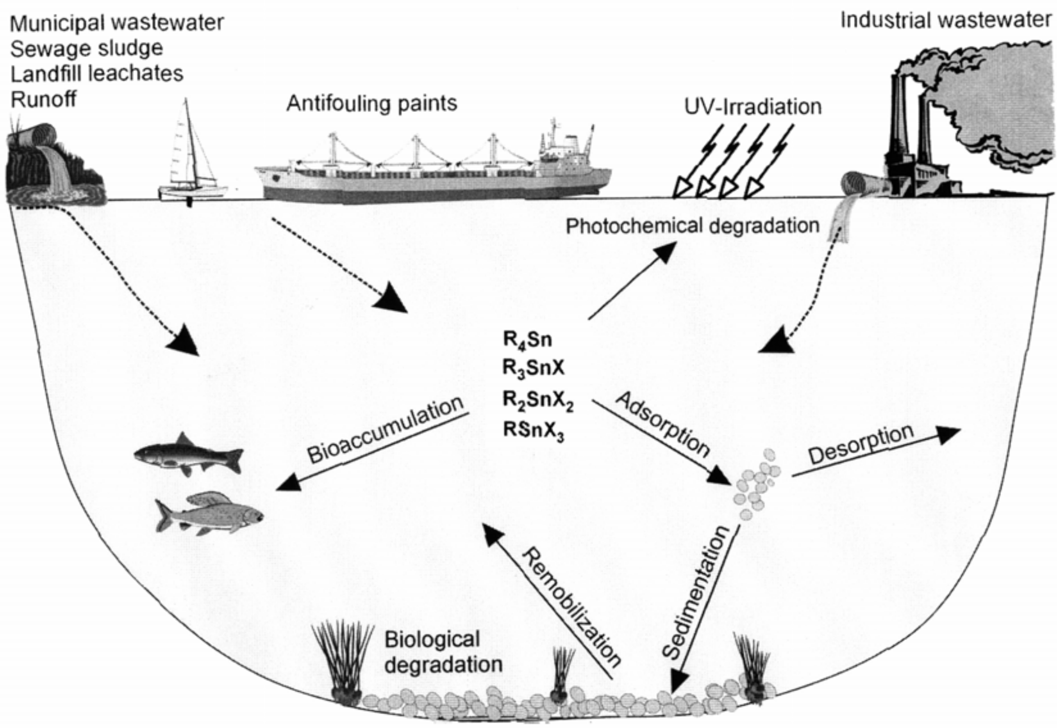
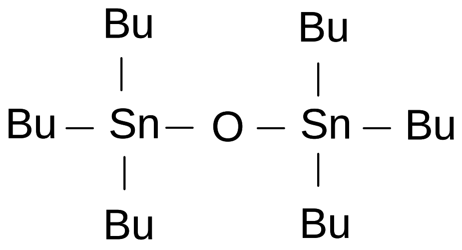


Figure 1. Schematic representation of organotin input, degradation and transition between environmental phases.

Organotin chemicals are compounds containing one (mono-), two (di-), three (tri-) or four (tetrasubstituted) carbon groups bound to a central tin (Sn^{4+}) atom. Figure 2 shows the chemical structure of TBTO (bis-tributyltinoxide), the active ingredient in many ship paint formulations. Depending on the environmental conditions, these chemicals can behave as hydrophobic compounds (due to their alkyl side chains) or as metal ions (due to the central tin ion). In the following, the partitioning behaviour of organotins is discussed more in detail.



$$\begin{array}{ccccccccc} & & \text{Bu} & & & & \text{Bu} & & \\ & & | & & & & | & & \\ \text{Bu} & - & \text{Sn} & - & \text{O} & - & \text{Sn} & - & \text{Bu} \\ & & | & & & & | & & \\ & & \text{Bu} & & & & \text{Bu} & & \end{array}$$

Figure 2. Chemical structure of bis(tributyltin)oxide, the active compound of many antifouling paints (Bu = $C_4H_9^-$).

1.2.1. Aqueous solubility of organotins

The behaviour of tri-n-butyltin biocides (Bu_3SnX), where X is the anion (e.g. hydroxide, sulphide, acetate, fluoride, chloride), may be described by the following equation for the undissociated (neutral) compound and for the dissociated (positively charged) cation upon reaction with water:

$$Bu_3SnX + H_2O \rightarrow Bu_3Sn(H_2O)^+ + X^-$$

Toxicity of TBT is attributed to the cation, and not to the anion associated with the biocide in the neutral compound. In a study by Inaba et al. (1995), the aqueous solubility of TBT and triphenyltin (TPhT) was studied at different conditions of pH, temperature and salinity. The results of that study are summarized in Table 1.

Table 1. Aqueous solubility of TBTs and TPhTs in various solutions at different temperatures (from Inaba et al., 1995)

Chemical	Temperature (°C)	Solvent	Solubility (mg_{Sn} L^{-1})		
			pH 5[a]	Minimum[b]	pH_{min}[c]
TBTCl, TBTO	25	Distilled water	70	15	7,9
TBTCl, TBTO	25	ASTM seawater	2	1,0	7,3
TBTCl	10	Distilled water	*ca* 30	7,9	7,6
TBTCl	10	ASTM seawater	*ca* 1	0,5	7,0
TPhTCl, TPhTO	25	Distilled water	4	0,8	7,2
TPhTCl, TPhTO	25	ASTM seawater	1	0,3	7,0
TPhTCl	10	Distilled water	2	0,4	7,5
TPhTCl	10	ASTM seawater	*ca* 1	0,2	7,5

[a] Value of solubility at pH 5

[b] Minimum value of solubility

[c] pH value at which minimum solubility was obtained

Several conclusions can be drawn from the results obtained by Inaba et al. (1995). First of all there is a significant pH effect on solubility of organotin species. Around neutral pH (7-8), solubility is minimal, while it increases at decreasing pH values. This pH effect is more pronounced in distilled water than in seawater, probably due to a salting-out effect on cationic species of the chemicals. In seawater, the hydrated TBT cation, tributyltin chloride, bis(tributyltin) carbonate, and tributyltin hydroxide are in equilibrium. At pH 8, the normal pH of seawater, the major species are tributyltin hydroxide and bis(tributyltin)carbonate. Solubility clearly decreases with increasing salinity. These observations imply that use of these organotin chemicals in freshwater may cause higher pollution than in seawater environments. Temperature also has an effect, with solubility increasing at increasing temperature. This difference in solubility may also influence the physico-chemical behaviour of organotins, such as the leaching rate and the distribution ratio between water and sediment (see next paragraph).

1.2.2. Adsorption behaviour of organotins

The fate of xenobiotic compounds in the aquatic environment is closely linked to their partitioning between aqueous media and particulate matter. Soluble pollutants are more mobile and available than particle-associated pollutants and are consequently more likely to undergo bioaccumulation, especially in pelagic organisms. The two major phenomena that affect the distribution of metal species between dissolved and particulate phases are adsorption onto particulates and flocculation in which the species are trapped by newly formed particulate matter. Because the two mechanisms are not easily distinguishable, the term ‘sorption’ is usually used to describe the cumulative effect of both processes. Sorption is considered one of the most important processes responsible for reducing the concentration and toxicity of butyltin compounds in the water column and is also the principal pathway for tributyltin accumulation in sediments. The determination of the (ad)sorptive behaviour of TBT is therefore necessary in order to understand its fate in freshwater and estuarine environments. The adsorption behaviour of TBT and butyltins in general has been well-documented in literature. However, experimental results vary significantly depending on the conditions used during the tests. Crucial parameters in the experimental set-up are: pH, T, suspended solids concentration, salinity, type of suspended solids and organic matter content. Each of these parameters will influence the adsorptive behaviour of butyltins in a particular way, which is discussed in the following paragraphs.

As already shortly discussed in report 3546, the partition coefficients indicate the occurrence of the substance in the various environmental compartments under equilibrium conditions. This can be expressed by means of different equilibrium constants, depending on the type of substrate used. Three constants are considered:

1) The particle-water partitioning coefficient, K_d

$$K_d\ [\mathrm{L/kg}] = (\text{chemical in sediment phase})\ [\mu\mathrm{g/kg}]/(\text{chemical in aqueous phase})\ [\mu\mathrm{g/L}]$$

Table 2. Reported particle-water partition coefficients for TBT (from Harris et al., 1996)

K_d (L kg^{-1})	*Salinity (g L^{-1})*	*Particle concentration (mg L^{-1})*	*Organic carbon (%)*	*Circumstances*	*Reference*
$60 \pm 30 \times 10^3$	Seawater	-[a]	-	Mesocosm	Adelman et al., 1990
71000	Seawater	0,68	-	Mesocosm	
39352	Seawater	1,6	-	In situ	Valkirs et al., 1987
38919	Seawater	3,0	-	In situ	
4608	Seawater	8,6	-	In situ	
3278	Seawater	5,8	-	In situ	Valkirs et al., 1986
3918	Seawater	6,7	-	In situ	
929	Seawater	14	-	In situ	
340	Seawater	50	-	In situ	
400	0	60	-	Laboratory	Harris and Cleary, 1987
140	32	60	-	Laboratory	
200	0	60	-	Laboratory	
100	32	60	-	Laboratory	
2180 ± 350	41[b]	10000	2,4	Laboratory	Maguire and Tkacz, 1985
800	0	3000-30000	4,2	Laboratory	Unger et al., 1988
130	24	3000-30000	2,9	Laboratory	
600	24	3000-30000	0,34	Laboratory	
110	35	3000-30000	0,90	Laboratory	

[a] Indicates no information availlable

[b] Calculated from reported ionic strength

The particle-water partition coefficient (K_d) of TBT has been determined a number of times under a variety of conditions, both in the laboratory and under natural circumstances. Values obtained are generally of the order of 1000 L kg^{-1}, but may vary between 100 and 70000 L kg^{-1}. The compound is generally considered not very mobile and will thus concentrate in soil sediment (Unger et al., 1988). In Table 2, an overview is given of some reported particle-water coefficients for TBT. Such wide variation, over nearly three orders of magnitude, is clearly significant in any general calculation of the environmental uptake of TBT on particles.

The disparate conditions under which partitions were observed give ample scope for a range of sources for this variation; particle concentration and organic carbon content, salinity, and pH have all been considered (Randall and Weber, 1986; Valkirs et al., 1986; Harris and Cleary, 1987; Unger et al., 1988; Harris et al., 1991; Huggett et al., 1992).

2) The organic carbon binding coefficient, K_{oc}

Another way of predicting mobility is to determine its binding to organic material. K_{oc} is an indicator for the tendency to associate with organic material (humus), which is usually common in dredged material.

$$K_{oc} = K_d \,/\, \%\ \text{organic carbon in sample}$$

Mobile chemicals would have K_{oc} values < 0,5. TBT has K_{oc} values typically >> 1. K_{oc} values for silty clay soils of 25000 L kg^{-1} are not uncommon. K_{oc} is much more representative for the behaviour of complex organic compounds than K_d.

3) The octanol-water partitioning coefficient, K_{ow}

The potential of a substance to concentrate in the food chain is indicated by the Hansch coefficient K_{ow} (or the octanol-water partitioning coefficient):

$$\text{Log } K_{ow} = \text{Log } [X]_{octanol} \,/\, [X]_{water}$$

The K_{ow} coefficient gives an indication whether a preference exists for the substance to concentrate in cell lipids (body fat). A Hansch coefficient > 3 indicates a high probability that the substance concentrates in body fat. As shown in Table 3, the K_{ow} value varies depending on the type of ligand associated with the cation. The value for all species is however >3, and TBT is thus likely to concentrate in cell lipids of the (marine) fauna and may be a candidate for bioaccumulation. In Figure 3, a schematic overview is given of the presence of triorganotin substances in water and in an organic phase.

Table 3. Equilibrium constants for TBT and TPhT

	TBT (pK_a = 6,25)		**TPhT (pK_a = 5,2)**	
Ligand	Log K_{ow}	Log K_i	Log K_{ow}	Log K_i
Cl^-	4,76	0,60	4,19	0,66
ClO_4^-	4,18	0,09	3,61	0,10
NO_3^-	3,49	0,62	2,97	0,26
OH^-	4,09	7,75	3,53	8,80

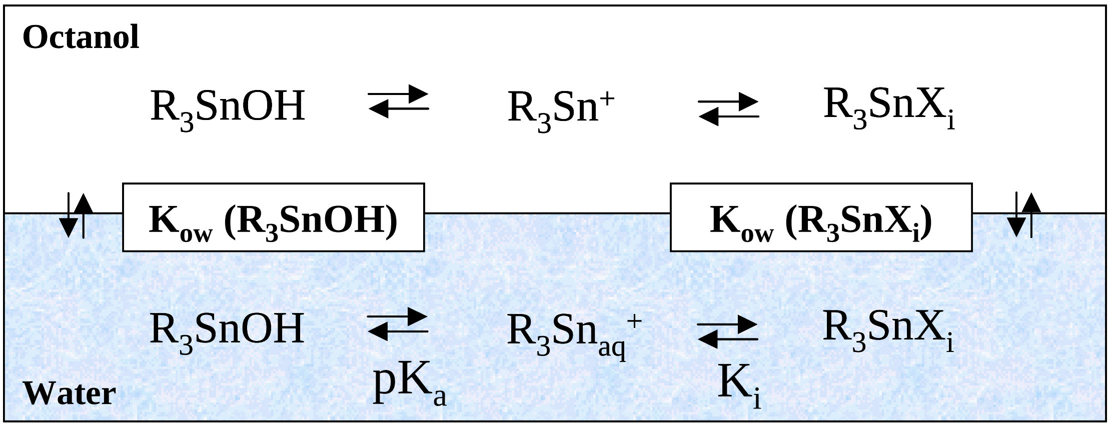


Figure 3. Schematic representation of the inter- and intraphase partitioning of triorganotin compounds in a water/organic phase system

The relatively low K_i values for Cl^-, ClO_4^- and NO_3^- compared to the high formation constant for the hydroxy-form is worth mentioning. Contrary to TBTOH, TBTCl will behave like a salt when present in the water phase. According to the acidity constant (pK_a) values, R_3Sn^+ will be dominant at low pH (hydrated as $R_3SnH_2O^+$), while R_3SnOH will dominate at high pH (Arnold et al., 1997).

1.2.3. Factors influencing the adsorption-desorption (or particle-water partitioning) of organotins

Sorption behavior of organotin compounds on sediments is governed by the constituents of sediments, and the composition of interstitial water in the sediments and overlying water, i.e. grain size distribution, clay minerals, organic matter, iron and aluminum (hydr)oxides and carbonate in the sediments; salinity, ionic composition, and pH of interstitial water in the sediments and overlying water. Sun et al. (1996) found that the adsorption of organotins varies greatly with molecular structure. The order of adsorption coefficient is Sn^{4+} > mono- >di- > tri-organotins. According to this study, the electronic properties of the Sn atom are the principal factors controlling the adsorption behaviour of organotins, which is mainly an ion-exchange process, with little lipophilic partitioning. However, the adsorption isotherm for all organotins followed both the Langmuir (typical for metals) as the Freundlich equation (used to describe the adsorption behaviour of non-polar organic matters). This is due to their central Sn atom and their organic substituent groups.

1.2.3.1. Sediment characteristics influencing the organotin partitioning

Results from Weidenhaupt et al. (1997) demonstrate that sorption of triorganotin cations to minerals (e.g. ***clay minerals*** such as kaolinite, montmorrillonite, …) may significantly contribute to the overall sorption of triorganotins to natural solid matrices. For clay particles, sorption was dominated by cation exchange, and was therefore proven to be pH dependent with maximum sorption at the maximum overlap of TBT and negative clay sites concentrations (pH ~ 7). TBT desorption increased both at higher and lower pH values.

In a study on the adsorption mechanism of MBT in clay minerals, Hermosin et al. (1993) conclude that the MBT adsorption process is a cationic exchange on these clay minerals, besides an additional adsorption of neutral $MBTCl_3$ attracted by the lipophilic moiety of the first MBT adsorbed. The expandable (swelling) minerals showed much higher adsorption capacity because MBT adsorbed in their interlayer spaces where MBT species make ‘aggregates’ or ‘clusters’ that propelled some montmorillonite layers from 14 to 22 Å.

In a study on the TBT adsorption to sediments from San Diego Bay, Kram et al. (1989) found a linear relationship between <63 µm size fractions and the capacity to adsorb TBT, suggesting that the sorption coefficient increases with increasing the amount of fine particles. The same study also revealed that the sediment adsorptive potential for TBT depends upon the expandable mineral percentage. A situation whereby expandable mineral-rich sediments would be exposed to high amounts of TBT would thus be a worst-case scenario, since TBT would persist in this environment for relatively long periods of time. Due to its high average <63 µm fraction (see report on Sediment Characterisation) and the high clay content (see Table 4 of this report), it seems likely that TBT is persistent in the sediment of the port of Antwerp. According to Hoch et al. (2002, 2003), the adsorption of both TBT and DBT was more pronounced when a higher percentage of high surface area/high cation exchange capacity clay minerals was present in the sediment.

It is to be expected that the partitioning of a relatively hydrophobic material such as TBT will depend upon the ***organic content*** of the particles concerned. In general this appears to be so, and this relation may be sufficient to account for the high-observed uptake of TBT in the biota. Based on data obtained from Maguire and Tkacz (1985) and Harris and Cleary (1987), an increased K_d value could be observed at increased organic carbon content. However, considerable variation remains unaccounted for by the organic carbon content of the particles concerned. Langston and Pope (1995) found that the partitioning coefficient is positively correlated with total organic material, as well as with humic substances, Mn, and high silt content. Their conclusion was that sediments are a major reservoir for TBT, particularly in organic-rich silts in sheltered areas. However, Unger et al. (1988) cautioned that organic carbon content alone was not a good predictor of TBT sorption. It has been remarked (Valkirs et al., 1986) that this partition coefficient appears to be inversely dependent on particle concentration, and this is also apparent in Table 3. It is not clear whether this appearance indeed reflects an inherent relation or if it is due to some additional factor with which the concentration of particulate material is confounded. Where vessel maintenance occurs, it has been suggested that extremely high partition coefficients observed in the field may simply reflect the presence of particles of antifouling paint within the particulate phase (Valkirs et al., 1987). The presence of paint particles, however, cannot explain the high partition coefficients reported in the relatively low turbidity mesocosm studied by Adelman et al. (1990). One suggested explanation for partition coefficients that decline as particle concentrations increase has been the presence of dissolved or colloidal organic material in concentrations proportional to those of the particles, which compete with them for the contaminant. The higher partition coefficients associated with low particle concentrations (Table 1), may in part reflect a higher proportion of planctonic algae or other organic material among the particles at lower overall particle concentrations. This is suggested by the high partition coefficient between green algae and water (~30 L g^{-1}, Maguire et al. (1984)). Other studies conclude that it seems very unlikely that TBT partitioning will be significantly affected by variations in suspended solids load, under normal estuarine conditions (Langston and Pope, 1995).

1.2.3.2. Interstitial and overlying water characteristics affecting organotin partitioning

- The effect of pH

TBT-species (TBTO, TBTCl) and TPhT-species (TPhTCl, TPhTO) have a maximum solubility at around a pH of 5 in distilled water. Lowest solubility was measured at around pH 7-8 (Inaba et al., 1995), however this was less significant in seawater, most probably due to interaction of ions. Several other reports mention the highest K_d-value at a near neutral pH, while this value decreases (TBT more soluble) for both a decreasing as an increasing pH (Langston and Pope, 1995). This again reflects the metal ion and hydrophobic materials characteristics of TBT. Arnold et al. (1997) reports that, depending on the pH, tri-organotins may exist in water as cationic and/or as various neutral species (see also Fig. 3) that may exhibit quite different partitioning behavior. They have investigated the influence of pH on the 1-octanol-water partitioning of TBT and TPhT and concluded that decreasing pH had a decreasing effect on the K_{ow} value, for both organotin compounds. Laughlin et al. (1986) showed that the equilibrium mixture of speciation products of TBT dissolved in seawater is composed of TBTCl, TBTOH, $TBTOH_2^+$ (as a function of pH) and a tributyltin carbonato species.

- The effect of ionic strength/composition and salinity

Wide variation in the values reported in Table 3 could also be due to the wide range of salinities of the water under observation. Salinity has a marked influence on the solubility of organotins such as TBT (see Table 1), the latter being less soluble with increasing salinity (Inaba et al., 1995). Salinity also proved to influence TBT sorption in several studies, although apparent disagreements can be found in literature. Some conclude that the adsorption coefficient decreases with increasing salinity (Unger et al., 1988; Weidenhaupt et al., 1997), while others state the opposite to be the case (Randall and Weber, 1986; Harris and Cleary, 1987). However, the latter were performed at extremely low sorbent-to-solution ratios (60 mg kg^{-1}), which could affect the adsorption process. A decreasing adsorption at higher salinities was explained in terms of ion exchange competition of seawater cations with sorbed TBT species, or in terms of changes in the nature of TBT species in solution due to formation of chloro-TBT complexes (Ohtsubo, 1999). Hoch et al. (2002, 2003) assessed the adsorption/desorption behavior of both TBT and DBT to clay-rich sediments under various environmental conditions, including salinity and found that a maximum of TBT and DBT adsorption occurred at a pH of 6 and salinity 0 ‰. The maximum desorption coincided with minimum adsorption and vice versa. TBT adsorption was strongest at salinity 0 ‰ and rapidly decreased with increasing salinity.

Depending on the type and concentration (10^{-3} to 1 M) of anions present, the formation of uncharged R_3SnX_i species leads to an increase in K_{ow} of between 1 and 3 orders of magnitude (Arnold et al., 1997). Laughlin et al. (1986) showed that the speciation equilibrium is influenced by [Cl^-], dissolved CO_2 and pH and is easily displaced by variation within the environmental concentration range of these substances. The octanol-water partitioning coefficient in their study was minimal at around 25 ‰ salinity (K_{ow} = 5500), and increased both at higher as at lower salinities (maximum of around 7000 in deionized water). Based on their data, these researchers concluded that partitioning behavior is affected by local chemical composition of seawater, and movement of TBT species and similar charge-forming organometallics may therefore be influenced strongly by covariant chemical factors in the environment. TBT sorption onto quartz sand was also shown to be strongly affected by pH and slightly by ionic strength in a study conducted by Bueno et al. (1998). Due to the low ionic strength used in this study (0,001 to 0,1 M), which was fixed by nitrate salts not forming a stable complex with TBT^+, the change in ionic strength did not affect TBT speciation at pH 8. Therefore, the TBT^+ behavior in their study is consistent with that of metal cations which compete with the electrolyte cation for the available adsorption sites. As a consequence, TBT sorption decreased with increasing ionic strength. Other studies, for example Langston and Pope (1995), report a sorption increase at high salinity concentrations, probably due to formation of the neutral TBTCl species, which may have another sorption behavior consistent with hydrophobic compounds.

1.2.4. Role of the sediment as a secondary source for organotins

The interaction between the hydrophobic organic moiety of TBT and its charge characteristics dictate that its environmental chemistry is highly dependent on the local chemical environment. As a result, its partitioning between dissolved and particle-adsorbed states depends on a wide range of factors, as described previously. This relatively complex environmental chemistry has resulted in observed K_d values that vary over nearly three orders of magnitude. These variations also have an influence on desorption rates of organotin compounds, as decreasing K_d values generally imply higher desorption. This means that the significance of the sediments as a secondary source for TBT will vary considerably from place to place. With this in mind, lab-scale experiments were conducted with sediment from the harbour of Antwerp, in order to estimate the adsorption/desorption behaviour of organotins present in the sediment.

2. TASK OBJECTIVES AND EXPERIMENTAL WORK

2.1. Task objectives

Literature data and the survey conducted in the port of Antwerp for task 3546 have shown that sediments can be major sinks for tributyltin and other organotin compounds. An important question that has to be answered is whether these organotin compounds can be remobilised to the aqueous phase, where they could have adverse effects on living organisms in the future. A possible event during which remobilisation can occur is dredging, an activity which causes resuspension of sediment and consequently brings adsorbed TBT in contact with TBT-poor overlying water. The objective of this task was to investigate whether organotins are indeed remobilised during disturbances of the sediment bed. Experiments were primarily conducted in lab-scale set-ups, simulating harbor conditions.

2.2. Lab-scale experimental work

2.2.1. Laboratory set-up

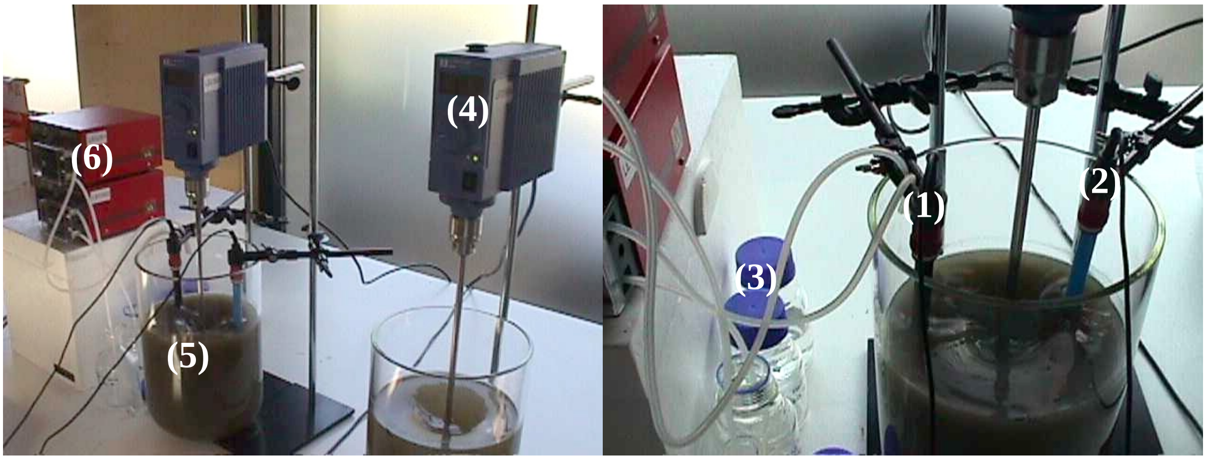


Figure 4. Photographs of the experimental set-up used for the sediment suspension simulations. (1) pH electrode; (2) temperature electrode; (3) acid/base; (4) electrical mixers; (5) reactor vessel with suspended sediment; (6) pumps for acid/base dosage.

All simulation experiments were conducted in a 6L glass reactor, equipped with an electrical mixer. A pH controller (Type Consort R305 with temperature correction) was installed to continuously monitor and maintain pH at a set value. A photograph of the set-up is shown in Fig. 4.

2.2.2. Sediment types used in the experiments

2.2.2.1. Location of the sediment types

We expected the TBT-release to be the highest at locations in the harbor where high concentrations of TBT were found in the sediment. That is why we selected two types of sediment: one from close to the Antwerp ship repair facility and one from a dock about 500 m from that location (see Figure 5). Both sediment characteristics were already described in detail in report 3546, but are summarized hereafter due to their importance for the discussion of the results presented in this report.

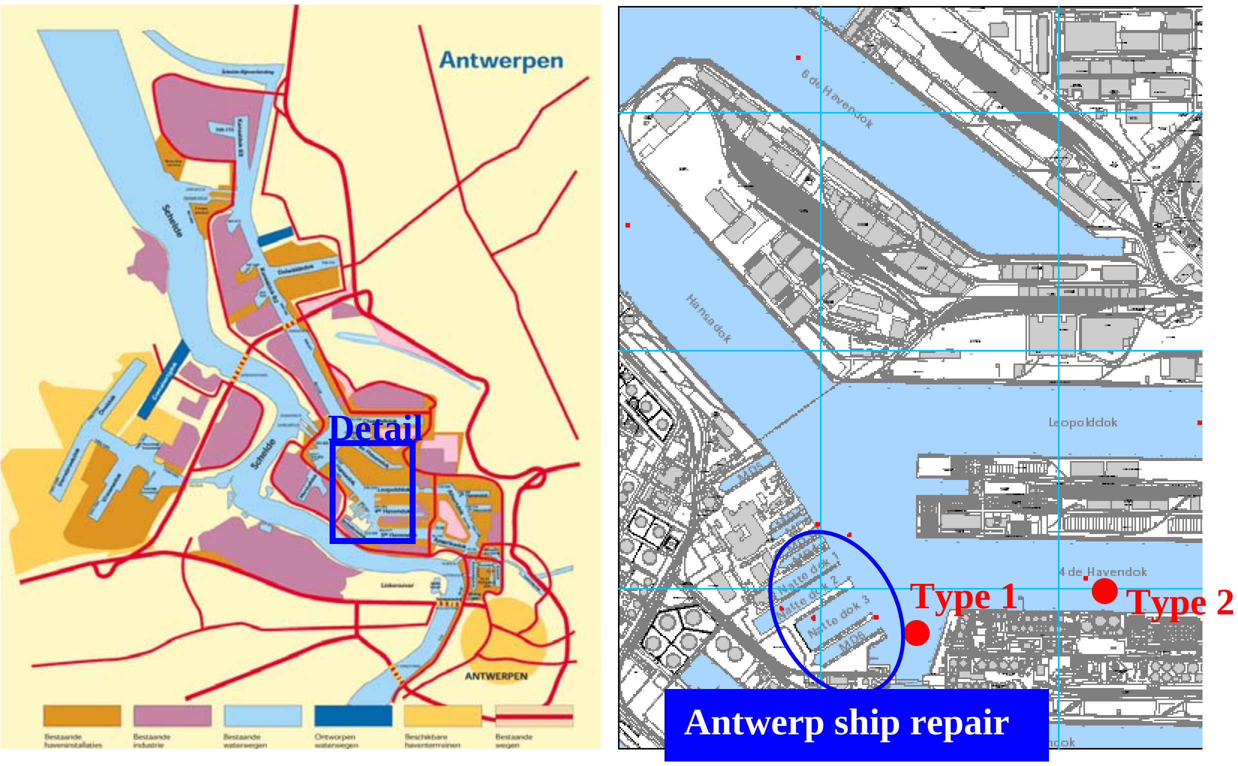


Figure 5: Location of the sediment types used in the TBT-release experiments (GIS-map kindly provided by Gemeentelijk Havenbedrijf Antwerpen).

2.2.2.2. Characteristics of the sediment types

In Table 4, an overview of the analyses results on both sediment types is given.

Table 4. Overview of important characteristics of sediment types in the simulation experiments.

	Type-1	**Type-2**
pH	7.74	7.69
Grain size parameters (% of dry weight)		
Fraction < 2 µm (clay)	33.1	21.9
Fraction <63 µm	59.9	44.3
Fraction 63-125 µm	12.6	10.9
Fraction 125-250 µm	24.8	33.8
Fraction > 250 µm	2.65	11.0
General parameters (on dry weight)		
TOC (%)	3.13	5.70
Mineral oil (mg/kg)	1020	680
Metals (Sum of Zn, Cu, Ni, Hg, As, Pb, Cr, Ca) (mg/kg)	1434	663
PAHs (Sum of 16 by EPA) (mg/kg)	5.10	4.29
EOX (mg Cl/kg)	65	5.2
Organotins (in mg/kg DW)		
Total TBT	43,0	1,58
Total DBT	1,37	0,25
Total MBT	0,87	0,22

2.2.3. Characteristics of the harbor water used in the experiments

Table 5. Characteristics of the harbor water used for the simulation experiments

Parameter	**Value**	**Parameter**	**Value**
Ammonium (mg/L)	<0.50	Minerals (mg/L)	
Total nitrogen (mg N/L)	7	Na^+	768
Total COD (mg O_2)	40	K^+	59
Aluminum (µg/L)	21	Ca^{2+}	111
Iron (µg/L)	39	Mg^{2+}	123
Cobalt (µg/L)	<3.0	Total solids (mg/L)	3646
Manganese (µg/L)	6.6	Volatile solids (mg/L)	897
Heavy metals (µg/L)		pH	8.29
As	6.8	Anions (mg/L)	
Ca	<0.30	Cl^-	1925
Cr	<3.00	NO_2^-	<0.1
Cu	3.3	NO_3^-	26
Hg	<0.20	PO_4^{3-}	<1.0
Pb	<5.0	SO_4^{2-}	277
Ni	4.6	Bicarbonate (mg/L)	183
Zn	26	Suspended solids (mg/L)	9

In order to correctly assess TBT release from sediment to water phase, we opted to use harbor water instead of synthetic water. Due to the proximity of the sea, the harbor water contained elevated levels of NaCl and other ions.

2.2.4. Effect of concentration of suspended solids (as a measure for turbidity) on TBT release

2.2.4.1. Low levels of suspended solids

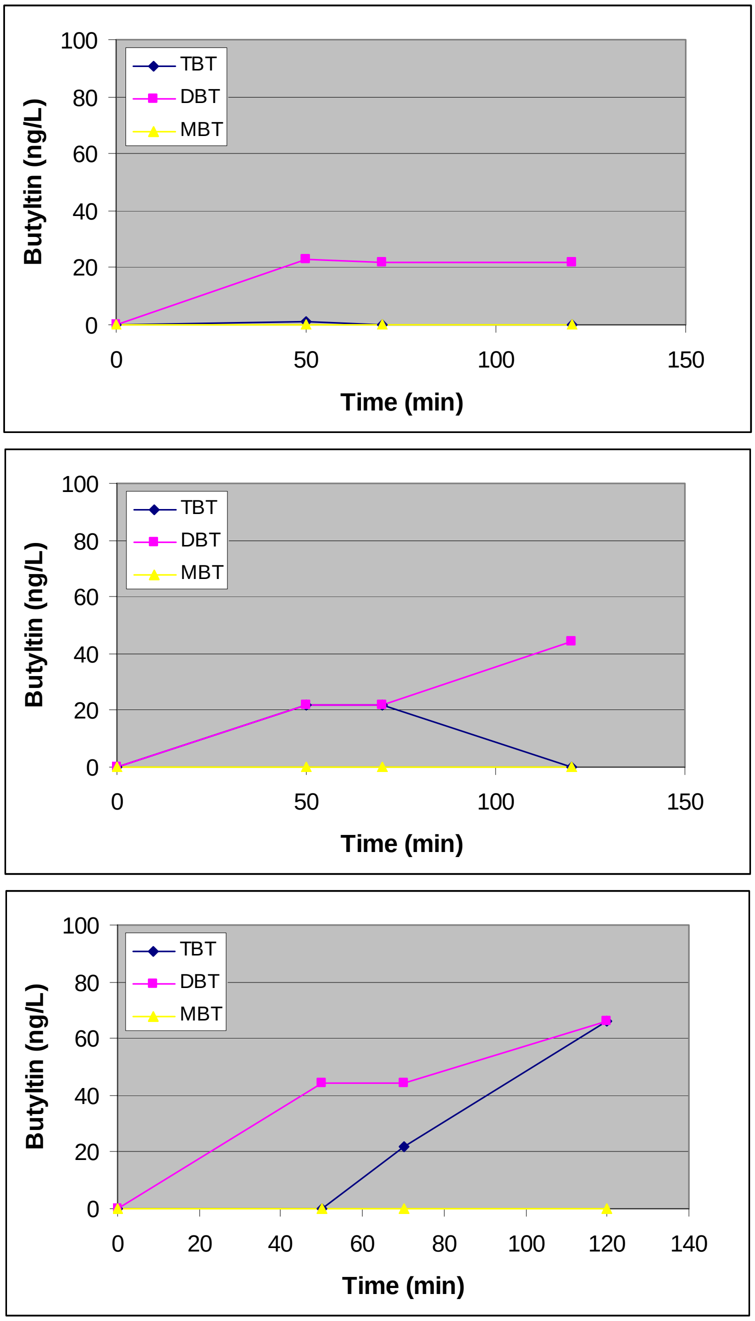


Figure 6. Release of butyltin compounds during a resuspension experiment in harbour water where type-1 sediment was mixed during 2h at 150 rpm. Top graph: 0.1 g SS/L, middle 0.2 g SS/L, bottom graph: 0.5 g SS/L.

The first experiments were carried out with low concentrations of suspended solids (SS): 0.1, 0.2 and 0.5 g dry weight/L of type-1 sediment, added as wet sediment (39% DW). These concentrations are typical in practice for low-turbidity dredging. pH control was used at this stage, but resuspension of these small amounts of sediment caused no significant change in the mixed liquor pH. The latter was about 8.3 and slightly dropped to 8.25 during the experiment. The temperature of the water was 19.8 ± 0.3. In Figure 6, the results of a release experiment with 0.1, 0.2 and 0.5 g SS/L are shown. The mixing time of 2 hours was chosen because it is a relevant time interval for on-site dredging on a particular spot in the harbor. The mixing intensity was set at 150 rpm to insure homogenous mixing of the sediment in the water and is difficult to relate to turbulence in the water phase during on-site dredging activities. Samples were taken with a syringe and immediately filtered (0.45 µm filter).

During the mixing experiment, DBT desorbed first, followed by a TBT release. For none of the three tested SS concentrations, MBT could be measured in the water phase. The extent of DBT and TBT release was only minor, with concentrations reaching just over 60 ng TBT/L after 2h at 0.5 g SS/L. However, there is a significant effect of SS concentration on the TBT release, the latter increasing at higher SS-concentrations.

In the same experiment, the sediment was allowed to settle during 19h, after which the mixer was switched on again (150 rpm) during 3 days. The results for the TBT release are shown in Figure 7.

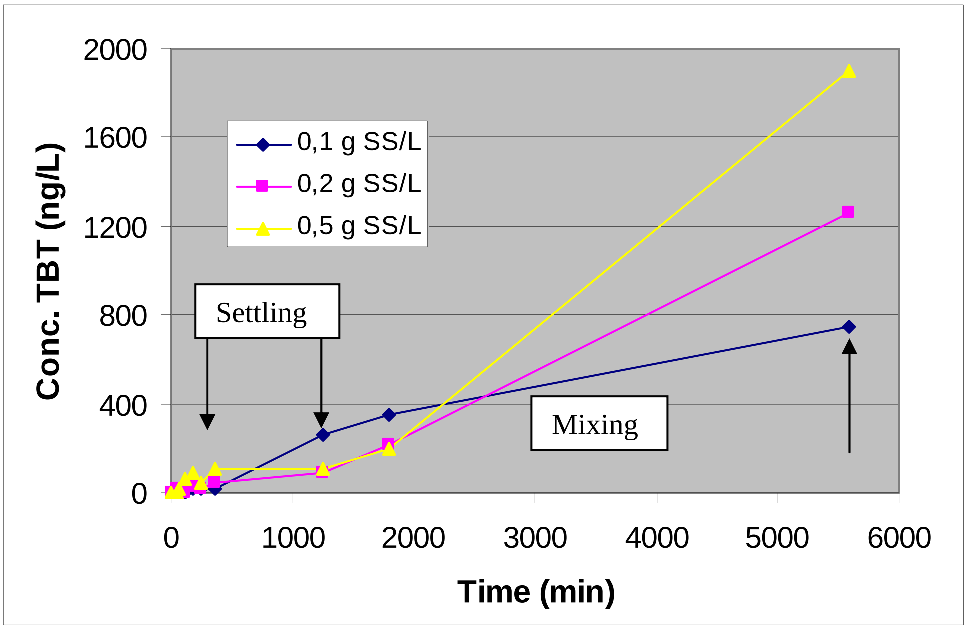


Figure 7. TBT release during a settling and long-term mixing experiment with 0.1, 0.2 and 0.5 g SS/L of type-1 sediment in harbor water.

During the 19h settling, a portion of the TBT sorbed onto the sediment was still released to the water phase, and this was particularly the case where only 0.1 g SS/L was suspended. The latter is strange at first sight, but is most likely due to the combined effect of desorption/sorption kinetics of TBT onto the sediment particles. This kinetics may be influenced by the amount of particles in suspension, and desorption may be favored over sorption at low particle/water ratios. However, this phenomenon was not characterized more in detail, and the explanation should thus be treated with caution.

In case of long-term mixing, the amount of TBT released in the water phase is however directly related to the amount of solids in suspension. After 3 days of mixing at pH 8.25, between 10 and 20% of the TBT sorbed onto the sediment was released to the water phase. Again, this confirms the earlier observation of increasing TBT release at higher suspended solids concentrations.

2.2.4.2. Elevated levels of suspended solids

A similar set of experiments was carried out with 1, 2 and 5 g SS/L of type-1 sediment, typical for dredging on-site with a suction hopper dredger. In this case, mixing was limited to 1 hour at 150 rpm (19.1 ± 0.5°C), followed by a settling period of 5 hours. No pH control was applied in these experiments.

A peculiar phenomenon was observed, MBT was apparently desorbed at the start of the experiment to about 100 ng/L, and was sorbed again during the mixing of the sediment. We could not find an explanation for this effect in literature, and conclude that this MBT must have originated from the water and pore water in the sediment sample that was added to the harbor water at the beginning of the experiment. A second observation is that DBT again rapidly desorbs from the sediment during mixing, while TBT-desorption is only observed in the settling phase. The latter again indicates slower release kinetics of TBT compared to DBT for this type-1 sediment under the given circumstances. The DBT release was only slightly affected by the amount of SS in the test, and reached an equilibrium state at about 150 ng/L. However, TBT release was affected by the suspended solids content, but not as we expected. For 1 g SS/L, a maximum TBT level of about 200 ng/L was measured, while this was only about 100 ng/L for 2 and 5 g SS/L. This apparent contradiction to what was found earlier and was also reported in literature was most likely caused by another system parameter like pH. Indeed, mixing of 1 g SS/L produced a mixed liquor pH of 8.24, while this was 8.14 and 8.02 for 2 and 5 g SS/L respectively. We concluded that pH and SS concentration had an opposing effect on the TBT release in these experiments. The next logical step in our experiments was thus to characterize the effect of pH on the release of the butyltins.

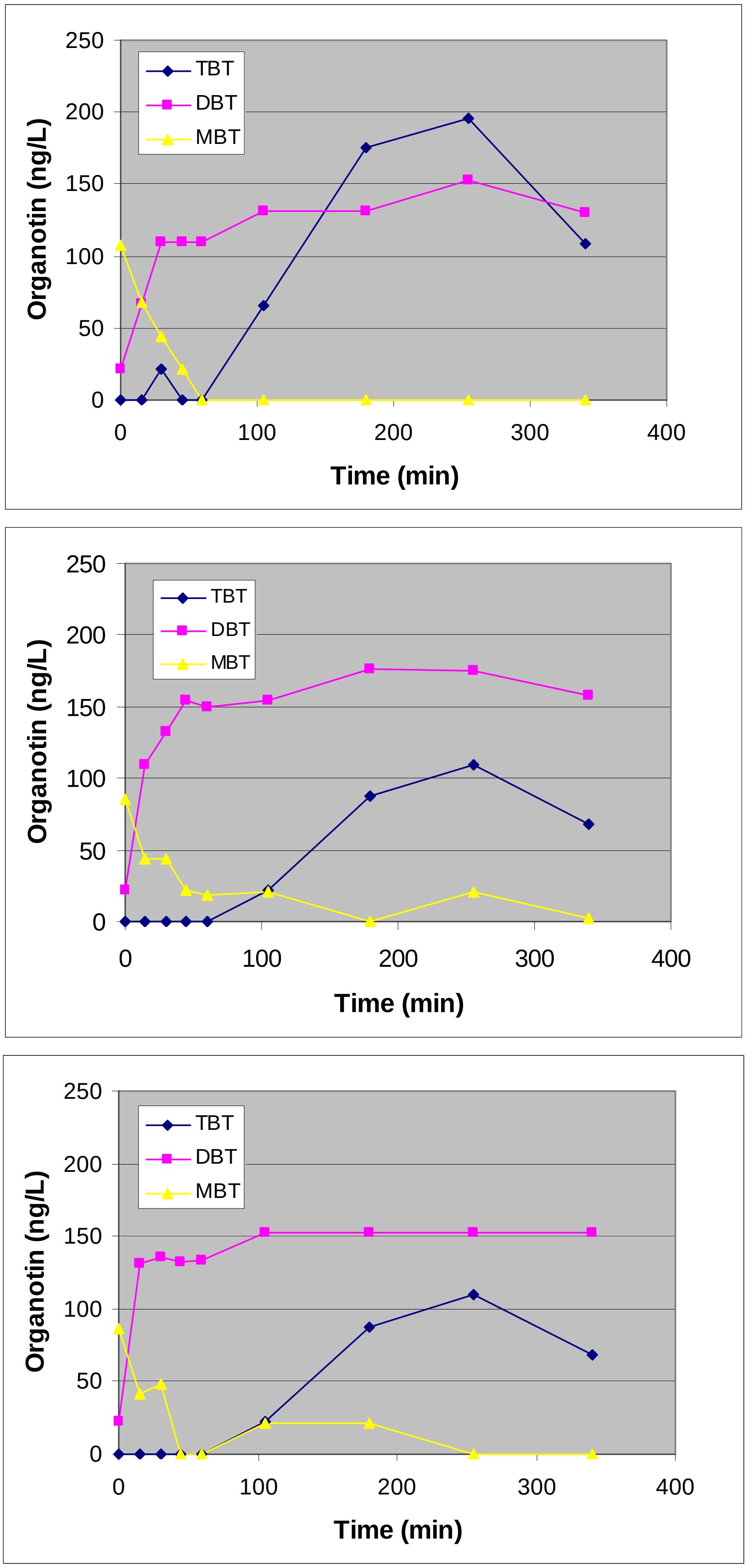


Figure 8. Results of the TBT release experiment with 1 (top), 2 (middle) and 5 (bottom) g SS/L.

2.2.5. Effect of pH on the release of TBT and other butyltins

A pH controller was installed on the reactor, in order to carry out experiments at a fixed pH. Correction was done with a 0.1 N HCl and a 0.1 N NaOH solution. Tests were carried out under the following conditions: 4 hour mixing at 150 rpm, temperature 18.4 ± 1.1 °C, 4L mixed liquor, 1 g SS/L of type-1 sediment. Samples were taken with a 10-mL syringe and immediately filtered over a 0.45 µm filter.

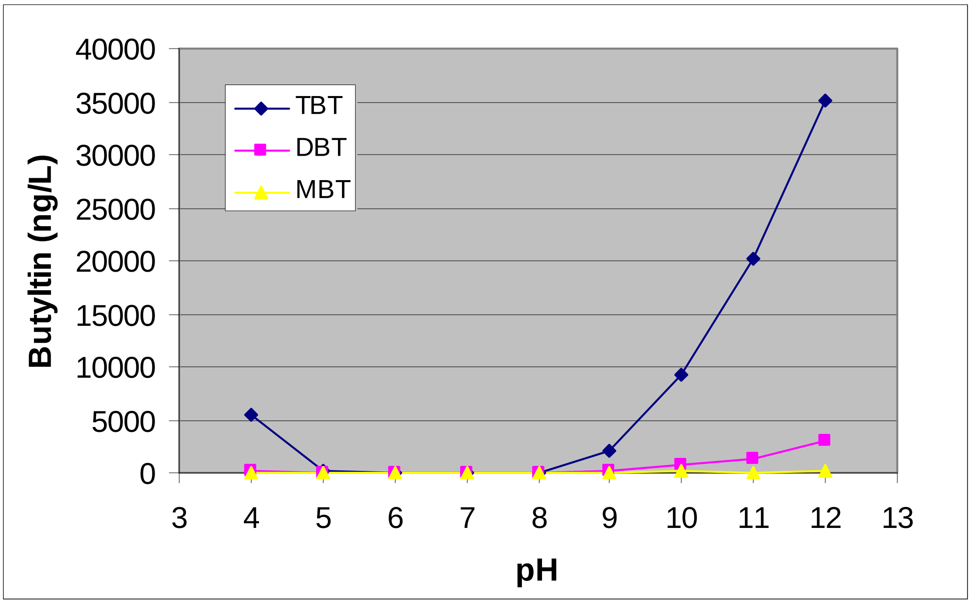
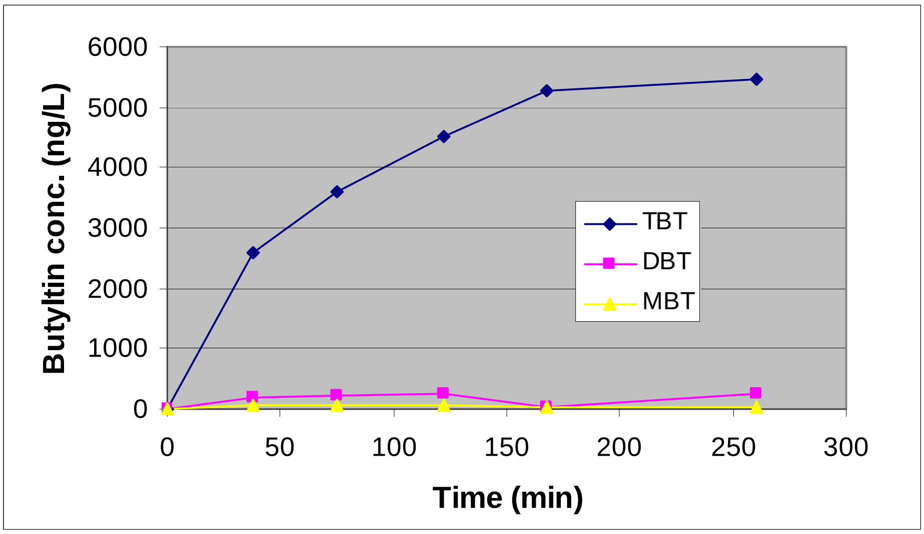


Figure 9. Effect of pH on the amount of butyl compounds present in the water phase after 4h mixing of type-1 sediment at 150 rpm.

In Figure 9, an overview is shown of the butyltin (TBT, DBT and MBT) concentrations that were present in the water phase at the end of the 4h mixing period. It is clear that maximum sorption (minimum release) occurs at near neutral conditions, over a range from pH 6 to 8. This is confirmed in literature, as is the fact that butyltins are desorbed both at higher and lower pH values. At pH 12, about 80% of the theoretical amount of TBT that was added with the sediment was desorbed and present in the water phase. A similar effect was obtained for DBT and MBT. The values obtained in our experiments are however also influenced by a change in ionic strength of the solution at different pH, due to the addition of acid and base for pH correction. Later in this report, the influence of salinity will be discussed more in detail. In Figure 10, a detailed graph is shown of the release of butyltin compounds at a specific pH value of 4 and 11.



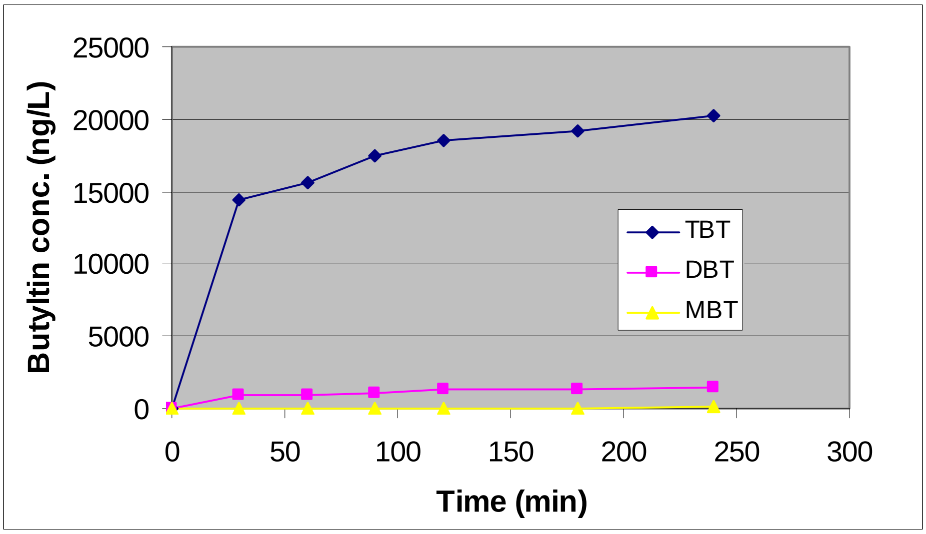


Figure 10. Detailed presentation of the release of TBT to the water phase during a mixing experiment at pH 4 (top) and 11 (bottom).

For both pH 4 and pH 11, the initial release is rapid and is followed by a period in which the equilibrium is reached asymptotically. From these experiments it was concluded that pH has a marked influence on the release of TBT, and should be taken into consideration when environmental conditions are determined.

Because we are most interested in the release of TBT in the harbor, we subsequently focused more on the pH region that is of interest for practical purposes. For harbor areas, the pH varies from about 7.5 to 8.5, depending on local conditions. As we have seen in Figure 9, the risk of TBT desorption is absolutely minimal below pH 8, but increases above pH 8. That is why we conducted additional experiments at pH values between 8 and 8.5. The results are shown in Figure 11, which displays the final TBT concentration after 4h mixing at the given pH (1 g SS/L).

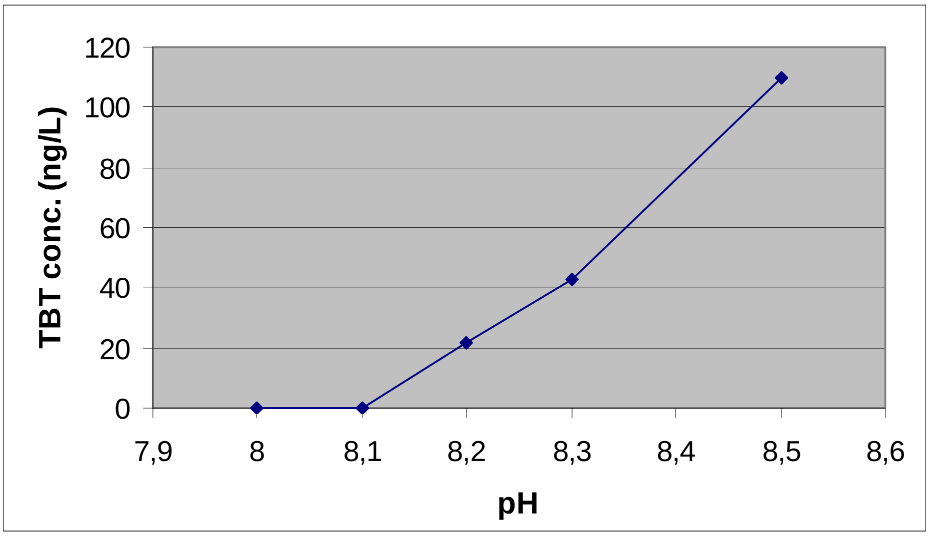


Figure 11. Final TBT concentrations in the water phase after 4 hours mixing of 1 g SS/L at a given pH.

Figure 11 shows an increasing desorption of TBT from pH 8.1 onwards. As the pH in harbors and seas can be 8.2-8.4, TBT remobilization under such conditions can be expected. The extent will depend on other parameters as well, e.g. salt concentration and amount of resuspended solids.

A similar pH/TBT-release relation was examined for type-2 sediment. This sediment was less contaminated, but was expected to have a similar behavior as type-1 sediment. Again, experiments were carried out with 1 g SS/L, at 150 rpm. The results are shown in Figure 12.

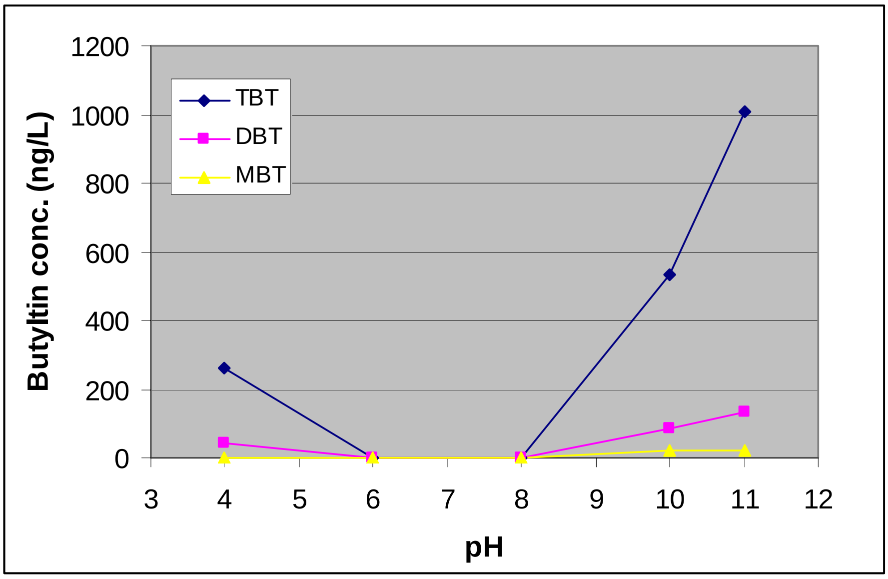


Figure 12. Release of butyltin compounds to the water phase after 4h mixing at 150 rpm of 1 g SS/L of type-2 sediment.

Despite the differences in sediment characteristics between type 1 and 2, the two curves in Figure 9 and 12 are highly similar. Also for the lower contaminated sediment, desorption was below detection between pH 6 and 8. Both at lower and higher pH, TBT was remobilized in the water phase.

2.2.6. Effect of suspended solids concentration at constant pH

Using type-1 sediment, we tested the TBT release at increasing SS concentrations at pH 8. In Figure 11 it is shown that no TBT is desorbed from the sediment at 1 g SS/L. In a similar set-up, we did not find any TBT in the water phase when resuspending 2 and 4 g SS/L of the same sediment. This experiment was also repeated for type-2 sediment. The results were identical to those obtained with the highly contaminated sediment: no detectable TBT in the water phase.

However, when suspending more of type-1 contaminated solids at a higher pH, more TBT was released. To illustrate this, the TBT release at pH 12 for 1 g SS/L and 10 g SS/L is shown in Figure 13.

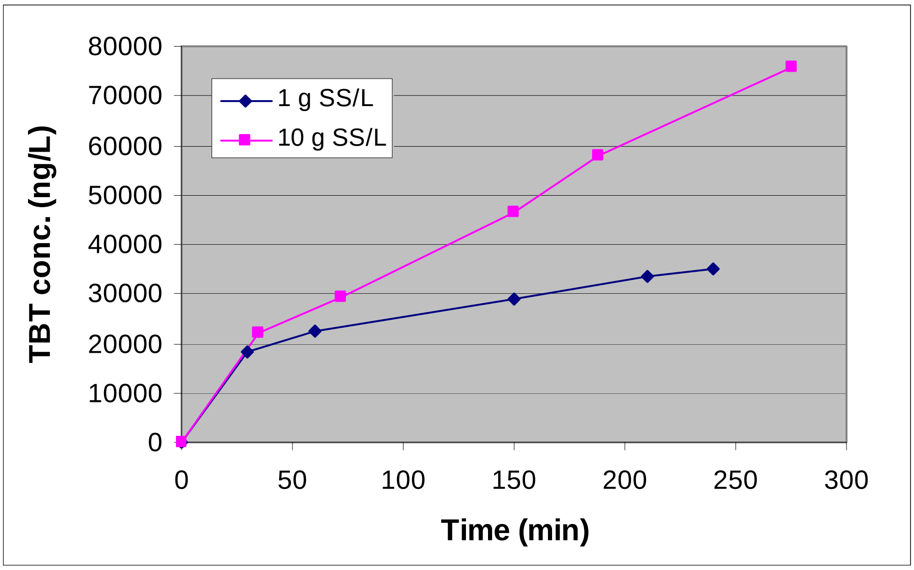


Figure 13. Release of TBT at pH 12, when mixing 1 and 10 g SS/L type-1 sediment at 150 rpm.

2.2.7. Effect of increased salt concentration

From literature, contradicting information can be gathered concerning the effect of salt concentration on TBT sorption/desorption. Some state that TBT is more easily desorbed in the presence of high amounts of salt, while others claim the opposite. Again, this seems to be a question on the conditions that were used during the experiments (type of sediment, clay content, organic matter content, pH, …). In our case, we used the highly contaminated type-1 sediment, suspended in harbor water as characterized in previous paragraphs. We worked at two different pH values, one relevant for harbor and sea conditions (pH 8), and a higher pH of 10.

At pH 8, we tested four salt concentrations: no salt (demineralized water), harbor water (HW), HW + 15 g NaCl/L and HW + 30 g NaCl/L. In none of the four experiments, TBT was measured in the water phase during a 4h mixing experiment with 1 g SS/L. This indicates a strong TBT bonding to the organic matter and clay particles at this pH.

At pH 10 however, TBT desorption was expected and a possible influence of salt would be more pronounced. In Figure 14, the results of an experiment in which we added 15 and 30 g/L NaCl to harbor water are shown. The initial release of TBT was comparable in all tests, but an increasing amount of salt clearly decreased the TBT desorption rate during the rest of the test.

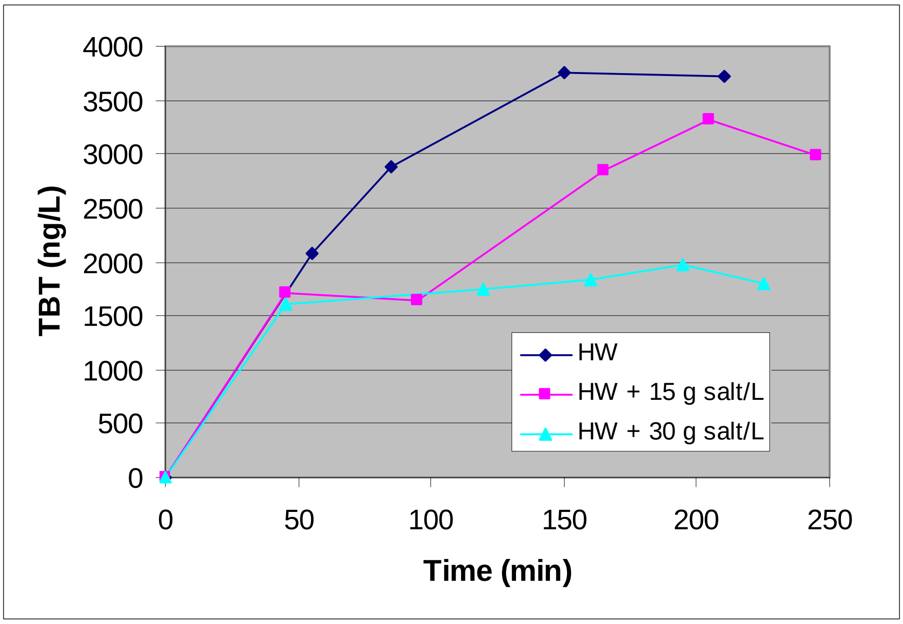


Figure 14. Effect of increasing salt concentration on TBT desorption to the water phase at an elevated pH of 10.

There are several possible explanations for this effect. Addition of the salt ions Na^+ and Cl^- will strongly influence the equilibria of TBT-species in solution. At pH 10 and low salt content, the largest part of the TBT in solution will most likely be in the hydroxy- or carbonato-form. When adding salt at a constant pH, this equilibrium will partly shift to the TBTCl form, which behaves quite differently compared to the other TBT forms. Increasing salt concentration also tends to strengthen the binding characteristics of organic matter, causing a decrease in release rate.

2.3. On-site experiments

2.3.1. On-site measurement of TBT release during sediment resuspension

On May 6th 2003, an on-site dredging operation by means of a grab dredger was carried out in order to obtain contaminated sediment for pilot-scale (bio)remediation experiments by DEC nv. Because this was an ideal opportunity to measure the TBT release on-site, we sampled the water phase during the dredging activities. Sampling was done at 4 and 8 m depth, with an Eyckelkamp peristaltic pump. On May 5th, a background measurement of the water column was performed, where samples were taken at one-meter intervals up to 10 m depth. This profile is shown in Figure 15.

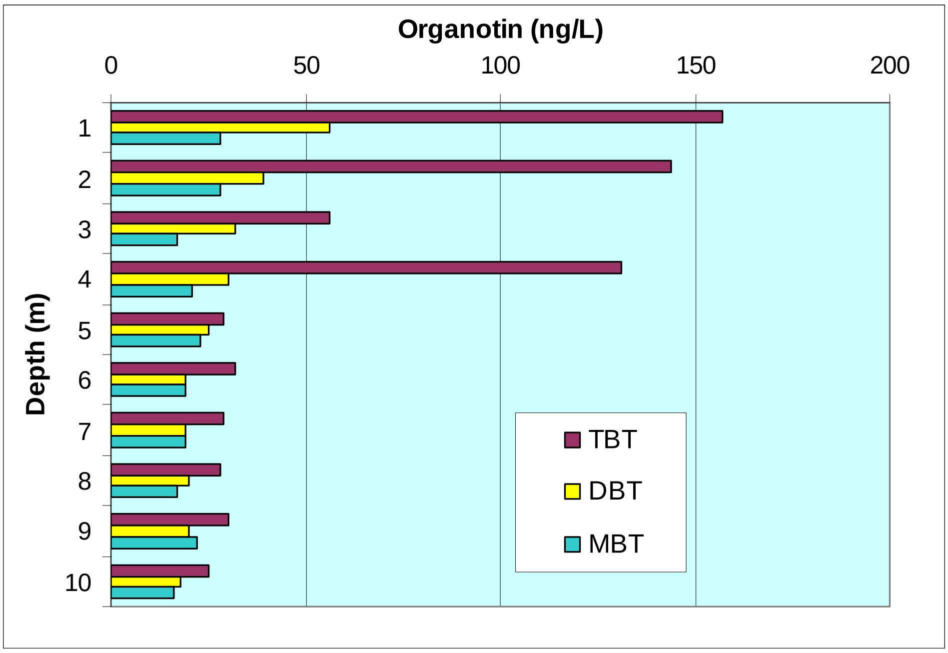


Figure 15. Background levels of butyltin compounds at the dredging site of sediment type-1.

Figure 15 shows that there are elevated levels of butyltins in the harbor water (background SS level was <20 mg/L at all depths), especially in the upper layers. This observed phenomenon cannot be explained, because we expected this profile to be the inverse. Literature points out that TBT is converted to DBT and MBT under UV light, that it can be converted under aerobic conditions by microbial breakdown, that this breakdown is faster at higher temperature, … so the expectation was that TBT concentration would be highest at the bottom, closest to the sediment bed from which TBT is leached, where it is dark, cold and least oxygenated. It is our intention to repeat this measurement during the next sediment dredging campaign.

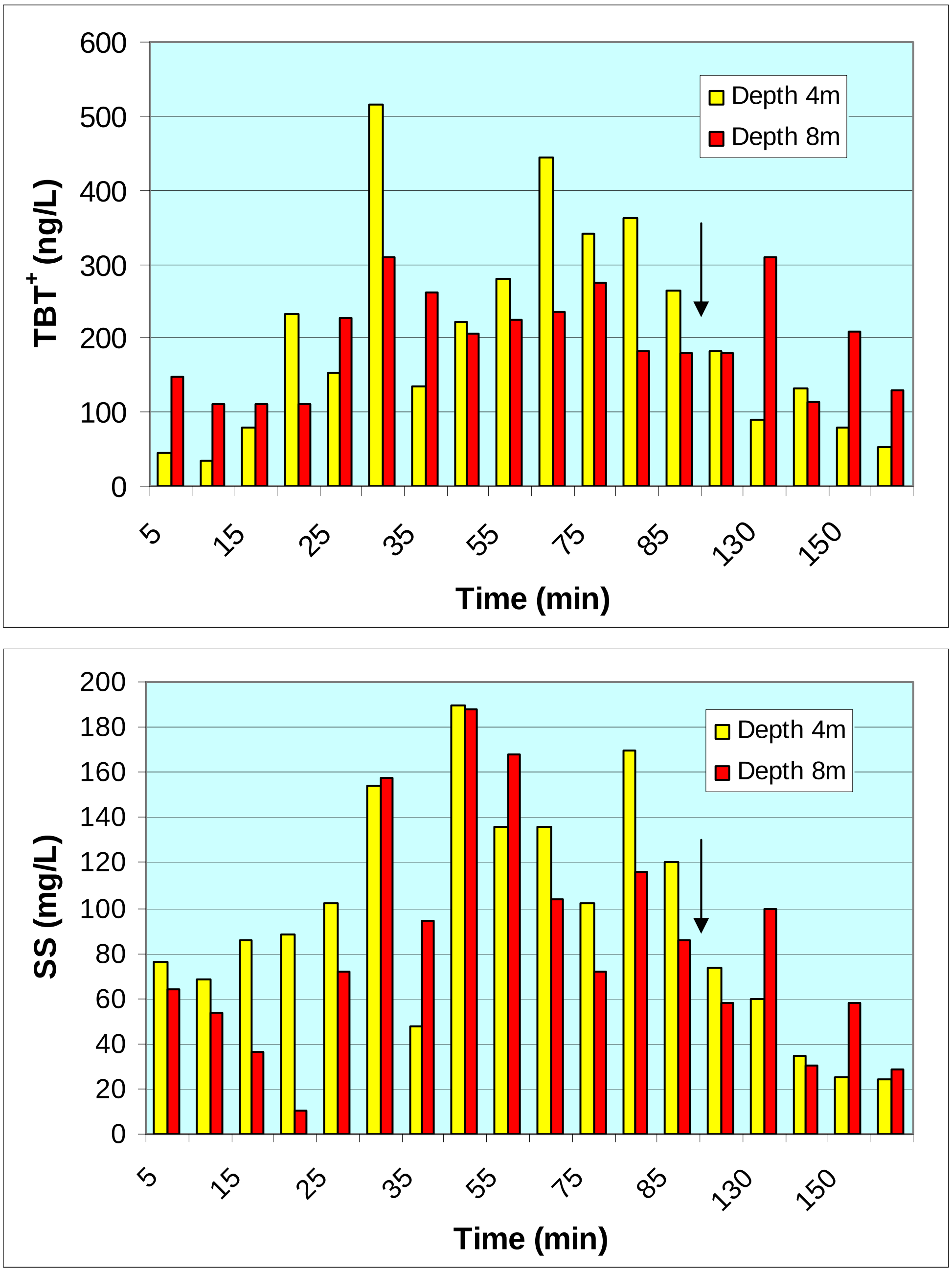


Figure 16. Tributyltin concentration over time at two depths in the water column during dredging (top), related to the suspended solids concentration measured in the samples at the same time (bottom). The arrows indicate the end of the dredging operations.

During the actual dredging operation, we took samples of the water column above the spot where sediment was dredged. However, due to the grab technique that was used to dredge, and the fact that the grab was moved under water over about 20 meter towards the container, no real suspension occurred right above the dredging spot. Therefore we moved our sampling point to where the grab was lifted out of the water and sediment fell into the water (after about 20 minutes dredging). There we took samples in the sediment suspension cloud at 4 and 8 m depth. The TBT and SS concentration started to rise simultaneously as soon as we moved our sampling spot, which indicates the direct relation between the two parameters. Peaks of over 500 ng/L were measured, which is high when compared to the chronic toxicity levels (see Table 6) but lower than the acute toxicity levels. Because we used a filter of 0.45 µm to remove the solids before TBT measurement, it cannot be ruled out that some TBT was bound to dissolved colloidal matter and was not present as TBT^+ in the water column. Because we did not follow up the changes in environmental conditions during the sampling period (mainly pH) it is very difficult to compare these results with our lab-scale simulations. This experiment will also be repeated in the near future, with all necessary measurements of other important parameters included, and a supplementary sampling point at 1 m depth will also be used.

Table 6. Overview of the ecotoxicity of TBT towards marine organisms

TBT conc. (ng/L)	**Effect**
< 10-100	Imposex in dogwhelks and molluscs Growth effects algae/oysters
100-1000	Growth effect (e.g. trout)
Threshold acute: 700	Acute toxic for marine algae, mussels, oysters and copepods
1000-10000	Acute toxic for trout, salmon, shrimp, Daphnia Acute toxic for ragworms

Due to the chemical nature of TBT, having a high affinity for particulate matter, and possible breakdown processes when TBT is dissolved (UV, biodegradation, …), these elevated concentrations are only expected to occur for a short period of time. Even in a relatively short after-dredging measurement, the TBT concentration already started to decrease along with the suspended solids concentration (Figure 16). Again, this phenomenon will be re-evaluated during the next dredging campaign, which will also include longer after-dredging sampling of the water phase.

2.3.2. Release of TBT from painted surfaces

A last objective of this task was to evaluate the actual release of TBT from ship paints. Together with the Port of Antwerp we installed 30 square pieces of steal (≈ 200 cm^2), painted with TBT-paint, in the harbor. One row of 10 is installed at the surface, a second row is at 1-m depth, and a last row is at 2-m depth. Over time, the amount of TBT present on the steal will be measured, and TBT release will be estimated. Results of this experiment will be reported at the end of the TBT-Clean project.

2.4. General interpretation and discussion of the results

The aim of this task was to determine a turbidity limit for resuspension of contaminated sediment, in order to minimize the release of the extremely toxic TBT to the water phase. The first set of experiments showed that there is indeed a direct relation between amount of resuspended solids and release of TBT, the latter increasing at higher suspended solids concentration at constant pH. However, this desorption mechanism is to a high extent determined by the environmental conditions at which it occurs, especially pH. The latter affects the solubility of TBT (more soluble at low and high pH) and all equilibriums in the water phase, and thus also the solid-water partitioning of TBT. At higher pH, more TBTOH is formed which is not electrostatically attracted to the negative clay sites. The main mechanism of adsorption is then the hydrophobic attraction, which is weaker and easily disturbed.

In our lab-scale experiments with a fixed volume of water, resuspension of wet sediment caused a drop in the water pH (8.29) because of the lower sediment pH (7.74). The higher the amount of solids suspended, the lower the pH of the mixed liquor. As a consequence, we concluded that suspending higher amounts of sediment decreases the TBT release because the pH is lower. However, this finding can not be extrapolated to on-site dredging, because there it is likely that resuspension of sediment will only cause very local and temporary changes in the water pH, and that desorption will mainly occur at the harbor water background pH, independent of the suspended solids concentration. Therefore, resuspension should be minimized at pH values higher than 8.1 to avoid TBT release. The limit for resuspension is mainly determined by the extent of the TBT release, which should in all cases be lower than the acute toxicity level of 700 ng/L. Because dredging activities are not continuous, higher concentrations of TBT during dredging are not supposed to occur over longer periods of time, lowering the risk for chronic toxicity. Background measurements of the water phase at the Antwerp ship repair site however show concentrations of about 150 ng/L, possibly having an adverse effect on sensitive organisms over longer periods of time.

Besides the pH, the composition of the sediment will also determine the extent of TBT release. The sediment samples we used for our experiments were taken with a Van Veen grab, sampling the top of the sediment bed, and were enriched in fine particles. The clay content was 33.1 and 21.9% for type-1 and 2 sediment respectively, and it could be expected that a big part of the TBT would be sorbed onto negative clay sites by strong electrostatic forces. This proved to be so, because between pH 6 and 8.1 no TBT was released to the harbor water phase, even at elevated suspended solids concentrations of 4 g/L. More detailed pH experiments however revealed that desorption starts to occur from about pH 8.1, and steadily increases with increasing pH. Fine silt and clay particles will settle much slower than larger particles, which increases the contact time of the particles with water and also increases the risk of TBT release at elevated pH. As such, the grain size distribution also has a marked effect on TBT release during and after dredging.

Finally, the salt content of the system in which particles are suspended does not have a significant influence on the TBT release at pH 8, but seems to have a negative influence at higher pH values. These results should however not be generalized to all sediment types, because the clay and organic matter content greatly affect the response to changing salt concentrations. This was already shown in literature, and expressed by the numerous contradicting research results that were published on this topic in the past.

3. CONCLUSIONS AND FURTHER RESEARCH PERSPECTIVES

1. Resuspension of contaminated sediment, either through dredging activities or any other activity (e.g. propeller of large ships), will always be a risk for remobilization of TBT to the water phase.
2. For TBT this remobilization process is very complex because it depends on both sediment characteristics (TBT-concentration, pH, grain size distribution, organic matter, …) as water characteristics (pH, salinity, …). As a consequence, each harbor case has to be evaluated separately.
3. The lab-scale experiments with sediment from the Port of Antwerp showed that the risk of remobilizing TBT is minimal when the pH of the water phase is lower than 8.1. At higher pH the risk of releasing TBT to the water phase increases, and the effect is more pronounced when higher amounts of solids are resuspended. The harbor water pH of 8.29 in the Antwerp port consequently poses a higher risk. However, in the lab-scale experiments we did not find acute toxic levels of TBT in the water phase, even with suspended solids levels up to 4 g SS/L.
4. In-situ measurement of TBT release during dredging showed higher levels of TBT than predicted from the lab-scale experiments, with peak values approaching acute toxicity levels. The harbor water pH (8.29 in the port of Antwerp) will presumably determine the extent of TBT release, which increases when resuspension increases. Because the harbor water pH in Antwerp is higher than 8.1, the highest pH at which no TBT was released under lab-scale conditions, caution is advised and a dredging technique that minimizes resuspension should be selected in areas with a high TBT content.
5. We propose a stepwise approach for dealing with the problem of TBT release in TBT contaminated harbors and waterways:
    a. Lab-scale determination of TBT release as a function of pH (see Fig. 9 and 10), to determine the critical pH for TBT release from the specific sediment (maximum pH of no release).

b. If the pH of the waterphase is lower than the critical pH, dredging will cause only limited TBT release and traditional dredging equipment can be used.
c. If the pH of the waterphase is higher than the critical pH, high TBT release is very likely and dredging will pose higher risks. In case the sediment has to be dredged, a technique that minimizes resuspension is advised. Otherwise, dredging is not recommended and should be avoided.

Because the lab-scale simulations did not reflect the real dredging conditions, we will try and work out another set-up to make more accurate predictions of TBT release on-site. This should allow any authority to make a risk assessment of TBT release, using their own sediment and harbor or river water. A possible set-up could be an aquarium filled with sediment, where a local disturbance of the sediment bed is induced (mixing) and where pH, TBT and suspended solids are followed in time. Results of these tests will be added to this report in the next report to the EU in six months.

In the near future, we will follow up the TBT concentration in the water phase during a second on-site dredging operation, together with the most important environmental conditions like pH and amount of solids suspended. The results will be compared to those obtained in the first dredging operation and also linked to the results from the lab-scale experiments. Results of these additional on-site measurements will be reported at the end of the TBT-Clean project.

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