Master Thesis in Geosciences

Butyltin Compounds in Marine Sediments

Sorption and BC-inclusive models of butyltin compounds

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Abstract

TBT has been widely used for decades as the dominant composition of antifouling paints. The toxicity of TBT on aquatic life is very serious and many studies have shown that TBT can be lethal to aquatic organisms at quite low concentration. Imposex phenomena have been detected on some organisms such as dogwhelks and snails, which is an important reason for the sterility of some groups of organisms. TBT shows a strong tendency of bioaccumulation, which can be a threat to both aquatic organisms.

TBT can be broken down to less toxic butyltin compounds DBT and MBT mainly through biodegradation. It is a complicated process and difficult to control. But it is the most effective way to degrade TBT. As the metabolic substances of TBT, it is still necessary to pay attention to DBT and MBT. Sorption is an appropriate way to reduce the concentration of TBT as well. In this study, POM was used to do the measurement of organotin compounds in spiked artificial seawater. The sediment sample, from Hovedøya harbour, Oslo was extracted to find how much TBT, DBT and MBT there. The concentration of three compounds indicated a good degradation condition in the harbour.

Sorption models with BC were run using the concentration of three butyltin compounds, TBT, DBT and MBT. The results implied a strong sorption ability of BC to hydrophobic organic matter. With the increasing water concentration, the sorption went down. BSAF values were calculated with BC models. BSAF values considering of BC were apparently lower than those without BC, which indicates that BC could be a good sorbent for these three compounds, especially for TBT. However, the water concentration of TBT in Hovedøya harbour was 0.0137 ug/l that was not an ideal situation for BC sorption. DBT and MBT are more hydrophilic than TBT, BC sorption will not be so effective.

Keywords: antifouling paint; butyltin compounds; TBT; DBT; MBT; sorption; K_d; BSAF; BCF; bioaccumulation; imposex; BC

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List of Abbreviation

AC	Activated carbon
BC	Black carbon
BCF	Bioconcentration factor
BSAF	Biota-sediment accumulation factor
C_{BC}	Concentration in black carbon
C_{POM}	Concentration in POM
$C_{sediment}$	Concentration in sediment
C_{tissue}	Concentration in tissue
C_{water}	Concentration in water
DBT	Dibutyltin
DOT	Dioctyltin
DPhT	Diphenyltin
f_{bc}	Dry-weight fraction of black carbon in sediment
f_{lip}	Dry-weight fraction of lipid in tissue
f_{oc}	Dry-weight fraction of organic carbon in sediment
Ka	Acidity constant
K_d	Sediment-water partition coefficient
$K_{F,BC}$	Freundlich BC-water distribution ratio
Ki	Formation constant
K_{lipid}	Lipid-water partition coefficient
K_{oc}	Organic carbon-water partition coefficient
K_{ow}	Octanol-water partition coefficient
K_{POM}	POM-water partition coefficient
MBT	Monobutyltin
MOT	Monooctyltin
MPhT	Monophenyltin
n_{BC}	BC Freundlich exponent
OC	Organic carbon
OTC	Organotin compounds
PAHs	Polycyclic aromatic hydrocarbons
PCBs	Polychlorinated biphenyls

TBT	Tributyltin
TBT^+	Tributyltin cation
TBTCl	Tributyltin chloride
TBTO	Tributyltin oxide
TBTOH	Tributyltin hydroxide
TcHT	Tricyclohexyltin
TcHT	Tricyclohexyltin
TOC	Total organic carbon
TrPhT	Triphenyltin
VDSI	Vas deferens sequence index

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1. Introduction

1.1 Contaminated sediments

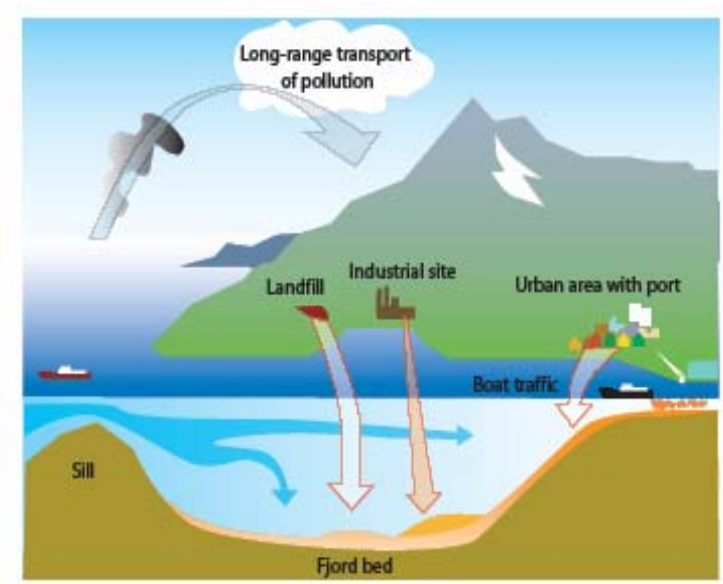


Figure 1.1 Ways that pollutants enter marine system

As shown in Figure 1.1, most pollutants enter the marine system through these four ways, boat traffic, industrial site, landfill and long-range transport. For different contaminants, the dominant way is not the same. Since butyltin compounds are mostly used in antifouling paints, the main source to marine environment is from boats. The principle will be explained in chapter 1.3.1.

In addition, butyltin compounds are used in some industries such as wood preservative and PVC products as well. Although this is an important source, the amount of butyltin from industry is much less than that from boats. Butyltin compounds from the landfill is not considerable nowadays because most pollutants are isolated well from the outer environment, but it could be a more and more significant source in the future if the isolating layer did not work well someday.

The sources mentioned above can be controlled, as they are local. But long-range transport of pollution is hard to control, and even difficult to measure how many pollutants are transported. This is a global problem for many contaminants, but it is negligible for most butyltin compounds.

When butyltin compounds enter the marine environment, the geographic characteristics have significant effects on the behaviours of compounds. As a fjord is not an open system, it is easier for compounds to concentrate and sink down to the sediments. The sill will prevent fresh seawater from entering the fjord and the compounds will stay in the fjord.

Then, the concentration in the fjord will be much higher than in open sea, which is a serious threat to marine ecosystem.

Due to the widely use of butyltin compounds, the effects of them on marine life were already apparent in the late 1970s. And since 1980s, more and more countries have recognized the impacts of butyltins on aquatic life. Investigations concerning butyltin compounds in the marine environment of Norway started as late as in 1993-1994. Figure 1.2 shows the levels of tributyltin (TBT) compounds along the Norwegian coast, which is the most toxic compound among butyltins. The highest concentration of TBT is in Bergen fjord. TBT exists in most areas and the concentration along the western coast is generally higher than that along the eastern coast probably because of the petroleum industries. The surprising thing is that even in northern Norway where there are much less industries and people; there are enough TBT to lead to imposex as Vas deferens sequence index (VDSI) values are high.

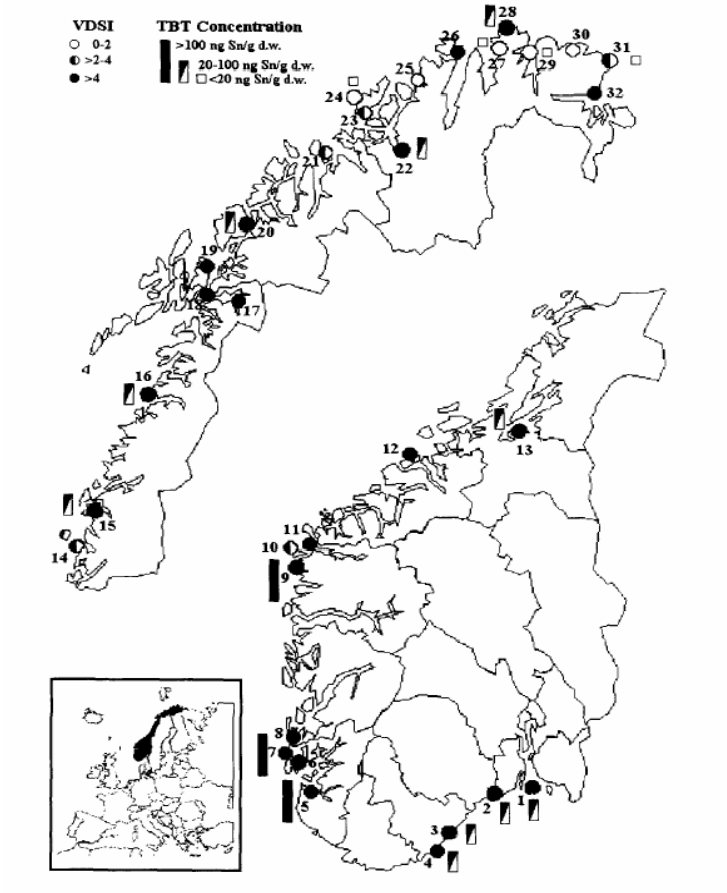


Figure 1.2 TBT levels along the Norwegian coast (Hølsvik et al., 1999)

Figure 1.3 Smaples taken in Hovedøya Harbour (NGI, 2007)

This thesis focuses on the sediment from Hovedøya harbour that is a small boat harbour close to Oslo city. The study in this area helps to know more about the status of butyltin compounds in Oslo harbour that is an important commercial port in Norway.

Sampling of sediment in December 2006 (NGI, 2007) showed the concentration of TBT, DBT and MBT in four stations (Figure 1.3) in the Hovedøya harbour (Table 1.1). The shipping yards in this harbour is the main source of butyltin compounds because these yards are used not only for small boat shipping but also for painting of boats.

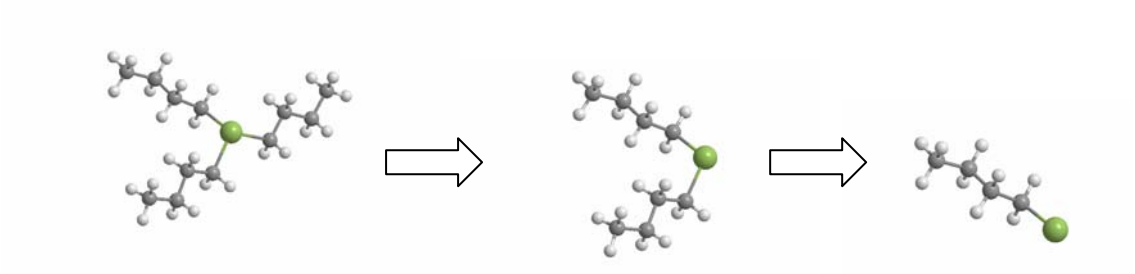
Table 1.1 Sediment concentration of TBT, DBT and MBT in Hovedøya Harbour (NGI, 2007)

Station	TBT (ug/kg d.w)	DBT (ug/kg d.w)	MBT (ug/kg d.w)
1	964	190	18.5
2	8.2	4.4	1.3
3	5.8	1.7	0.8
4	32.5	17.3	2.5

1.2 Butyltin compounds

Butyltin compounds are compounds consisting of one to four compounds attached to a tin atom via carbon-tin covalent bonds. They are a part of organotin compounds. When there are fewer than four carbon-tin bonds, the butyltin cation can combine with an anion such as acetate, chloride, fluoride, hydroxide, oxide or sulphide. Thus a species such as TBT is a cation whose formular is $(C_4H_9)_3Sn^+$. In seawater, TBT exists mainly as a mixture of the

chloride, the hydroxide, the aqua complex, and the carbonate complex (Laughlin et al. 1986a), because TBT^{+} is not statable. Dibutyltin (DBT) and monobutyltin (MBT) are the metabolites of TBT. The formulas of DBT and MBT are $(C_4H_9)_2Sn^{2+}$ and $(C_4H_9)Sn^{3+}$, respectively. Structures of TBT, DBT and MBT are shown in Figure 1.4, which shows the degradation process of TBT.



Tributyltin $(C_4H_9)_3Sn^{+}$ Dibutyltin $(C_4H_9)_2Sn^{2+}$ Monobutyltin $(C_4H_9)Sn^{3+}$

Figure 1.4 Structures of TBT, DBT and MBT (Rapport Analyses chimiques, 2004)

Table 1.2 Some characteristics of butyltin compounds

	Tributyltin chloride	**Dibutyltin dichloride**	**Monobutyltin trichloride**
Molecular formula	$C_{12}H_{27}Cl_1Sn$	$C_8H_{18}Cl_2Sn$	$C_4H_9SnCl_3$
Molecular mass (g/mol)	323.5	303.8	282.2
Appearance	clear, yellow liquid	clear, yellow liquid	Clear, brown liquid
Solubility in water (mg/l)	Practically insoluble	320	Soluble
Density	1.2	1.4	1.7
Melting point	-9°C	39-41°C	
Boiling point	171-173°C	135°C	93°C
K_{ow}	4.1 (Oen et al., 2006)	1.5 (O'Loughlin et al., 2000)	0.4 (O'Loughlin et al., 2000)

Values of these three butyltin compounds are from Chemblink (2007)

K_{ow} is Octanol-water partition coefficient

Since TBT^{+}, DBT^{2+} and MBT^{3+} are not stable, they have to exist as complexes. Table 1.2 conclude the characteristics of TBT, DBT and MBT chloride complexes. The solubility of monobutyltin is not available, but the sequence should be MBT>DBT>TBT.

1.3 Sources of TBT

Since TBT is the most toxic compound among butyltin compounds, it has caused wide concern. TBT compounds have been most widely used as a marine antifoulant on small boats, ships, and marine structures. They have also been used as disinfectants, fungicidal wood preservatives, textile disinfectants, and stabilizer in PVC resin. Paper and pulp mills, cooling tower, breweries, textile mills and leather-processing facilities may also use some forms of TBT. However, continued use of TBT on large ships is probably the main source for new TBT to aquatic environment.

In Norway, antifouling agents and wood preservatives are the two main sources of TBT compounds as shown in Table 1.3. However, the use as antifouling agents is dominant as shown by the release rate, 90% for antifouling agents and 5% for wood preservatives.

1.3.1 Antifouling paint

Antifouling paints are effective to prevent marine organisms from sticking to the hulls of boats and ships. This works by releasing small amounts of the biocide from the painted hull into the water, forming a thin envelope of highly concentrated TBT around the boat or ship. Two different types of antifouling paints are used.

Table 1.3 Estimated data for TBT (ton/ year) use and release to environment in Norway for 1998 and 1999 (SFT, 2002)

Sources	**Use (1998)**	**Released**	**Use (1999)**	**Released**	**Comments**
Antifouling agents	28.2	28.2	28.3	25.5	90 % of antifouling agents used is released to the environment.
Preservative for wood	6.6	0.3	5.0	0.25	5 % of used preservative for wood is released to the environment.
Other producers	25		0.1	0	Mainly painting products. These should be treated as special waste.

1. Free-association antifouling paint

In this paint, TBT is mixed with the paint matrix, which release to the marine environment by diffusion as Figure 1.5 implies. At first, the diffusion rate is quite high and slows down as time goes on. It is hard to control this kind of diffusion. The concentration around the ship body is very high and toxic for organisms near the ship.

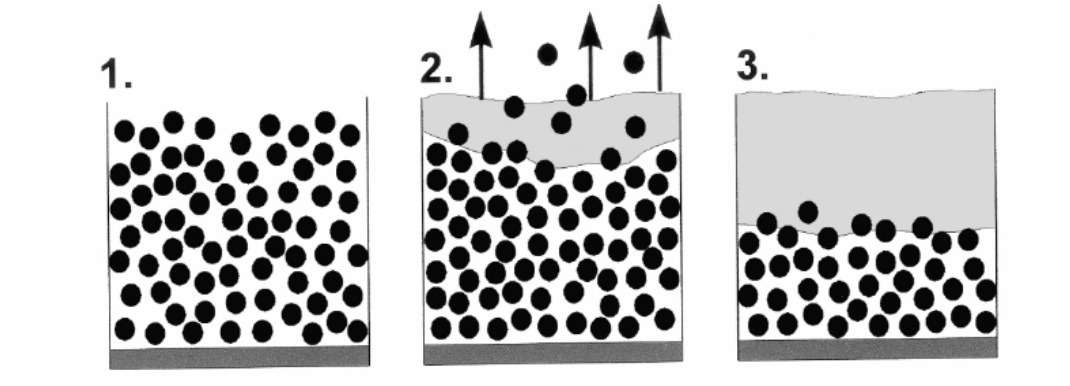


Figure 1.5 Free-association antifouling paint, the molecules of the biocide are leached by seawater percolating through the coat of paint (Anderson, 1986).

2. Self-polishing antifouling paint

In this paint, the toxic compounds are chemically bonded with a polymer causing a delay of TBT release to the marine environment. But due to the erosion of seawater, there will be reaction in the surface of the paint that releases TBT to the aquatic environment. In this way, TBT release to the sea gradually. The coat of paint is eroded back to the hull (Figure 1.6). Toxic compounds in self-polishing antifouling paint release to the water more slowly than that in free-association antifouling paint.

1.3.2 Wood preservative

In order to preserve wood well, butyltin compounds were used about 50 years ago. TBT leaching from wood that has been applied by a double vacuum treatment is considered to be negligible. After evaporation of the solvent the pollutants remain safely within the wood structure, due to their low vapour pressures (Hoch, 2001). But the TBT remaining in treatment facilities will release out and then pollute the environment. Moreover, the TBT remaining in the wood will be a problem in the future when the preserved materials are used.

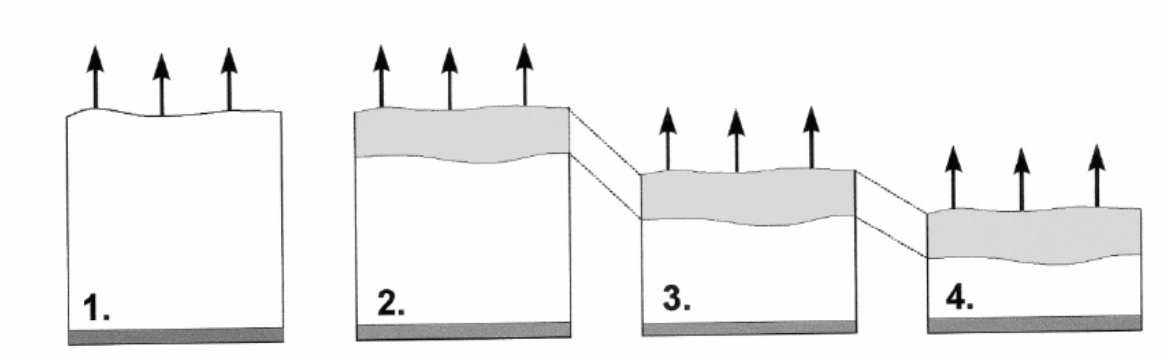


Figure 1.6 TBT is released from copolymer paints by chemical reaction with seawater. The coat of paint is gradually eroded back to the hull (Anderson, 1986).

1.3.3 Other butyltins leaking from PVC

The less toxic butyltin, mono- and dibutyltins (MBT and DBT) are used primarily as heat and light stabilizers in the production of PVC plastic. The organotins have been shown to leak from PVC and other materials leading to contamination of food, drinking water, municipal water, and sewage sludge.

1.4 Toxicity

1.4.1 General overview

The butyltin compounds are toxic and the toxicities are related to the number of organic compounds bonded to the tin atom and to the number of carbon atom in the organic compounds. Toxicity to aquatic organisms generally increases as the number of organic components increases from one to three and decreases with the incorporation of a fourth, making tributyltin more toxic than other forms (Hall and Pinkney, 1985; Laughlin and Linden, 1985; Laughlin et al., 1985).

As the most toxic butyltin compound, TBT can cause thickening of shells in sea oysters by the disturbance of calcium metabolism; it can lead to imposex in marine life that is the most sensitive effect on them. It has been reported that TBT reduces resistance to infection in fish such as flounder and other flatfish that live on seabed and are exposed to relatively high levels of TBT, especially around areas with silty sediment like harbours and estuaries.

Moreover, due to bioaccumulation of TBT, traces of TBT have been found in whales, dolphins and members of the seal family in the United States, south-east Asia, the Adriatic Sea and the Black Sea via the food chain (IMO, 2002).

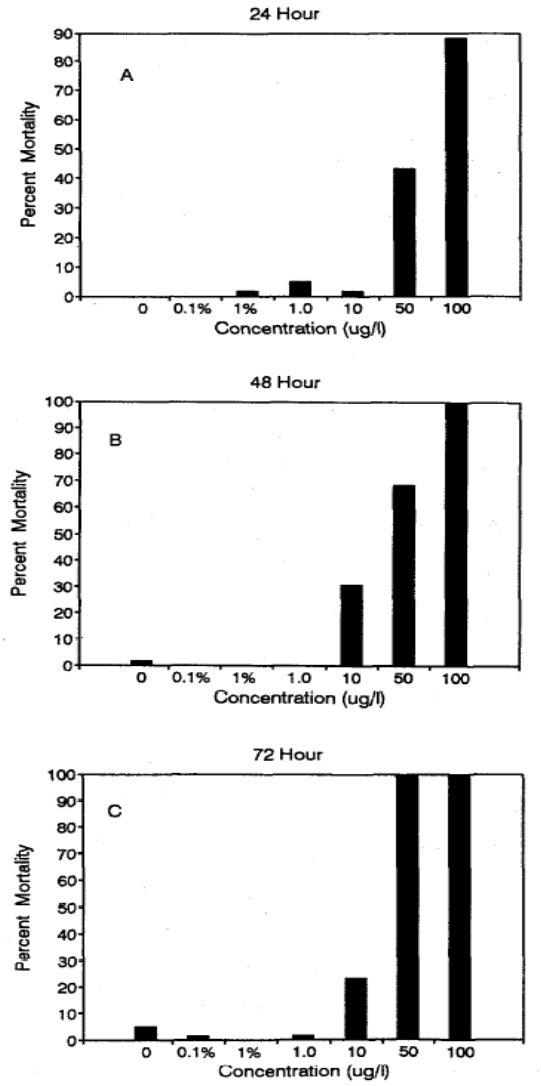


Figure 1.7 Percent mortality of *Limulus Polyphemus* embryos after (A) 24 hour, (B) 48 hour, (C) 72 hour exposure to TBT (Mark et al., 1998)

1.4.2 Effects on aquatic life

Tributyltin compounds are highly toxic to many species of aquatic organisms. TBT exposure to non-target aquatic organisms such as mussels, clams, and oysters, at low levels, may cause structural changes, growth retardation and death (Huggett et al., 1992). Molluscs, used as indicators of TBT pollution because of their high sensitivity to this chemical, react adversely to very low levels of TBT (0.06-2.3 ug/L). They release TBT very slowly from their bodies after it has been absorbed.

The effects of TBT can be shown by effective concentrations such as EC_p (effect concentration associated with p% reduction in growth), LC_p (lethal concentration associated with p% mortality), LOEC (lowest observed effect concentrations), or NOEC (no observed effect concentration). LC_{50} values for some aquatic life are shown in Table 1.4. The research data indicate that effects of TBT on aquatic life depend on concentrations, exposure time, and species. The effective concentration values are different from species to species. Generally, EC_{10} (effect concentration associated with 10% reduction in growth) or EC_{20} is recommended for ecological risk assessment (Chapman et al., 1998). As Figure 1.7 indicates percent mortality of aquatic life increases obviously with the increase of concentration. And the longer the exposure time, the higher the mortality will be.

For some species such as snails and dogwhelks, imposex phenomena have been observed all over the world. Imposex is known to be a sensitive endpoint for identifying biological effects of TBT. The phenomena are caused by exposure to organotin compounds and results in accumulation of male hormones (testosterone) in the body and eventually result in the endocrine disruption syndrome. Several stages of imposex at higher TBT concentrations can lead to female sterilization and death (Mensink et al., 1996b). Imposex has been recorded in 72 marine species. TBT concentration of just 2.4 ng/l is needed to produce sexual changes in dog-whelks, leading to sterility.

The specific principle of imposex is under debate nowadays, but laboratory and field experiments with dogwhelks which are the most effected species of gastropods, have shown that the phenomena of imposex, especially in areas with high shipping activities. In some area with high TBT concentration, the amount of dogwhelks reduces very fast and even extinction has been reported.

Plejdrup and co-workers (2006) examed the Norwegian dogwhelks whose population varied from having no incidence of imposex at all to a population where imposex had resulted in the sterility of 24% of adult females. The results are shown in Table 1.5. As the indicator of imposex, VDSI (vas deferens sequence index) is used for effect monitoring purpose. Between the VDSI stage 3.3 and 4, the TBT polluted population was over intermediate, and at the stage 4.3, the dogwhelks were severely polluted. At stage of 5 and 6 females were known to be sterile. Over 6, death of females appeared and even extincted. According to EPA criteria, a VDSI level higher than 3.0 is regarded as a high imposex incidence. Therefore, five of the examed places showed high imposex incidence. Highest incidence was found in Haugesund followed by the Oslo fjord (Table 1.5).

1.4.3 Bioaccumulation

TBT has shown a strong tendency for bioaccumulation. The octanol-water partition coefficient (K_{ow}) for TBT indicates a potential for bioaccumulation, as the log K_{ow} values range from 3.2 to 4.1. The K_{ow} value can be explained by the following formula:

$$\boldsymbol{K_{ow} = C_{octanol}/C_{water}} \qquad \boldsymbol{(1)}$$

where $C_{octanol}$ is the octanol concentration and C_{water} is the observed water concentration.

Table 1.4 LC_{50} values of TBT for some aquatic life

Species	LC_{50} (ng/g sediment)	LC_{50} (ng/l water)	Reference
Armandia brevis	902 (42 d)		Meador & Rice,2001 Meador & Rice, 1997
Corophium volutatot	2185 (10 d)	329 (10 d)	Stronkhorst et al., 1999
Echinocardium cordatum	4055 (14 d)	382 (14 d)	Stronkhorst et al.,1999
	1594 (28 d)	222 (28 d)	Stronkhorst et al., 1999
Rhepoxynius abronius		38700	Meador & Rice, 1997
Eohaustorius washingtonianus		4700	Meador & Rice, 1997
P. lividus		309	Bellas et al., 2005
C. intestinalis		7100	Bellas et al., 2005
P. serratus		22300 (24 h)	Bellas et al., 2005
		17520 (48 h)	Bellas et al.,2005
R. harisii		13000 (96 h)	Laughlin & French, 1989
P. japonicus		1000 (24 h)	Lignot et al., 1997

Table 1.5 Female sterility (%), vas deferens sequence index (VDSI) level and ±SE, and TBT tissue concentrations (±SE) in the *Nucella lapillus* populations (Green et al., 2002, Green et al., 2003, Green et al., 2004 and Green et al., 2005).

	Brashavn Kirkenes	Husvaagen	Haugesund	Gåsøy-Ullerø	Risør-Risøy	Oslofjord
Mean female sterility 2001–2003	0%	0.2%	24%	0.4%	0.1%	1.6%
(VDSI 2001–2003)	(0.017±0.076)	(3.687±0.134)	(4.307±0.145)	(3.656±0.157)	(3.314±0.166)	(3.97±0.054)
TBT tissue conc. (ug Sn/kg d.w.)	4.650[a] (±0.515)	15.170[b] (±1.014)	136.750[c] (±2.123)	25.370[b] (±1.252)	37.770[b] (±2.028)	32.900[b] (±1.747)

[a] Sampled in 2002–2003.
[b] Sampled in 2001–2003.
[c] Sampled in 2000–2003.

Studies with algae, aquatic invertebrates, and fish have confirmed that bioaccumulation of TBT in these organisms is substantial. The bioconcentration factor (BCF) is the coefficient used to indicate the equilibrium between tissues and water that can be explained by following formula:

$$BCF = C_{tissue}/C_{water} \quad (2)$$

Where C_{tissue} is the tissue concentration and C_{water} is the observed water concentration. High potential BCF>1000; Moderate Potential 1000>BCF>250; Low potential 250>BCF.

Another coefficient can be used to indicate the bioaccumulation from sediment, BSAF (biota-sediment accumulation factor). BSAF explain the equilibrium between tissue and sediment.

$$BSAF = (C_{tissue}/f_{lip})/ (C_{sediment}/f_{oc}) = K_{lipid}/K_{oc} \quad (3)$$

Where f_{lip} is the dry-weight fraction of lipid in tissue; f_{oc} is the dry-weight fraction of organic carbon in sediment and K_d is the sediment-water partition coefficient, which can be calculated by K_{ow}.

$$\log K_{oc} = 0.989 \log K_{ow} - 0.346 \quad (4)$$

$$K_d = K_{oc} * f_{oc} \quad (5)$$

$$K_d = C_{sediment} / C_{water} \quad (6)$$

Where K_{oc} is the partitioning between the organic carbon and water.

BCF values range up from 10 000 in periwinkles to 50 000 in fish, and 500 000 in clams. Although TBT does not appear to significantly biomagnify up the food chain in some studies conducted to date, it is found in the tissues of marine mammals and other organisms in open ocean areas. Alzieu and co-workers (1980) showed that in contaminated area tin levels in the flesh of oysters were 100 times higher than concentrations in the water, which indicates that contamination via food organisms was more important and more dominant than via water. The BCF values of some species are shown in Table 1.6, from which species such as *Rotifers*, *Mytilus adulis* and *Nucella lapillus* are more likely to accumulate TBT than others due to high values of bioconcentration factors.

Bioaccumulation of TBT in higher-level animals depends on what kind of organisms they eat as well. For example, Acadian redfish (*Sebastes fasciatus*) feeding preferentially on shrimps and small crustaceans rich in TBT showed a contamination level about three

times higher than eelpout (*Licodes vahlii)* which was living in contact with the sediment and feeding on worms and other burrowing species having a lower proportion of TBT in their tissues.

Table 1.6 BCF values of TBT for some aquatic life

Species	**BCF**	**Reference**
Gastropoda		
Adelomelon brasiliana	7.7-32.8	Cledon et al., 2006
Thais clavigera	5000-10000	Horiguchi et al., 1995
Nucella lapillus	29000	Bryan & Gibbs, 1991
Bivalvia		
Dreissena polimorpha	20-45	Stab et al., 1996
Nuculana pernula	138-404	Strand et al., 2003
Mytilus edulis	7400-19000	Zoulian & Jensen, 1989
Algae	4290	Sun et al., 1999
Rotifers	22000	Sun et al., 1999
Mysids	11900	Sun et al., 1999
Zooplanktons	1700	Sun et al., 1999
Mysids	1700	Sun et al., 1999
Swordfish	1800	Sun et al., 1999

1.4.4 Effects on mammals and human beings

TBT is moderately to slightly toxic to mammals. Human skin is sensitive to TBTO tributyltin oxide), although the extent of sensitivity is not known. TBT can cause eye irritation in humans exposed over a few hours (Occupational Health Services, 1987). Inhalation of TBT may interfere with breathing and cause headache, weakness, tremors and incoordination. The lowest concentration inhaled from the air that causes toxicity in humans is 10 ppm for three minutes and 20 ppm for five minutes (Occupational Health Services, 1987). The oral LD_{50} of TBT is 1,500 mg/kg for rats, 2,000 mg/kg for rabbits, and 900 mg/kg for mice (Occupational Health Services, 1987). The dermal LD_{50} of TBTO is 11,700 mg/kg for rats and 900 mg/kg for rabbits (Sax, 1984). The values mentioned above are acute effects. The chronic effects caused by the bioaccumulation will be a long-term threat to mammals and even to human beings, although there is no indicator that TBT is transferred to terrestrial organisms via food chains.

1.4.5 Regulations on use of TBT

With the realization of the harms of TBT all over the world, the antifouling paints with TBT on the vessels less than 25m were banned in 1980s in some countries (Table 1.7), which has improved the environmental conditions. Oysters and other aquatic life have recovered. But the TBT remaining in the aquatic body is still of environmental concern. Norway banned the use of organotin paints on vessels less than 25m in 1989.

Table 1.7 History of the ban on TBT

Country	Year of ban	Results	Reference
U.K	1987	Oyster culture has returned in the harbour areas where boat traffic is low and water exchange is good.	Dyrynda, 1992
Mexico	1988-1989	Tissue concentrations of TBT in oysters have decreased.	Wade et al., 1991
Canada	1989	reduction of imposex	Tester net al., 1996
Switzerland	1988	TBT concentrations were decreasing in the water, but declines were not seen in the sediment or in the zebra mussel.	Becker-van Slooten & Tarradellas, 1995
France		Some small ports have not seen a decline in imposex.	Huet et al., 1996
U.S	1987	A general decrease in tissue concentrations was measured on the west coast, and east coast sites showed mixed responses.	Uhler er al., 1989, 1993

An assembly Resolution in 1999 organized by IMO recommended a global ban on the use of organotins in antifouling paints by 2001. But it seems that the timeframe has been postponed. By 2008, EU legislation will ban the use of TBT on EU flagged vessels and any ship painted with TBT will be refused entry to EU ports. Considering the size of the European Union market this would hamper any shipping company's trade (WWF, 2006).

1.5 Environmental Fate

After TBT releases from sources such as boats, industries and landfill and enters the marine environment, it environmental fate is shown in Figure 1.8. TBT can be broken down in water under the influence of light (photolysis) and microorganisms

(biodegradation) into less toxic di- and monobutyltin. Half-life varies from a few days to several years. TBT also shows bioaccumulation in some aquatic life.

Sorption is an important process in the aquatic system. TBT sinks down to the sea bottom by sorption to organic matters and then combines with sediment. In sediments, microorganisms will be the dominant group to degrade TBT.

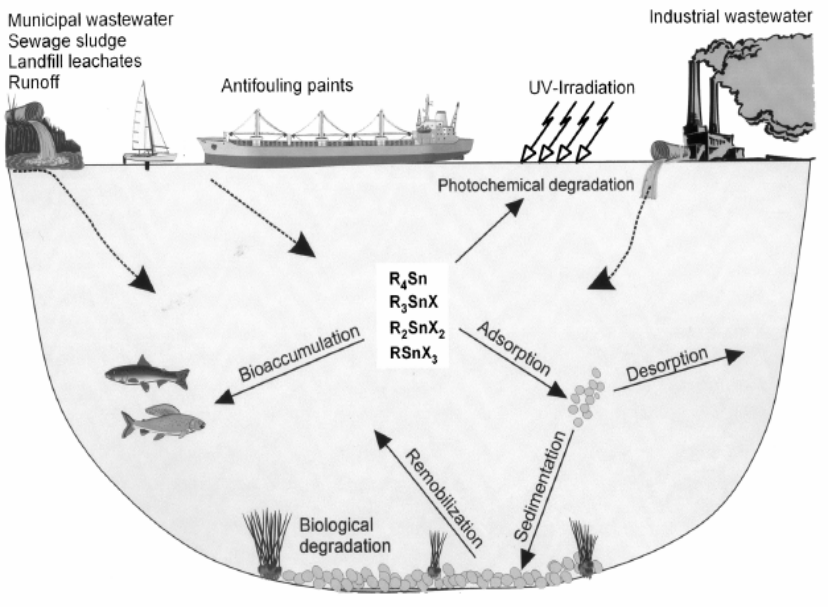


Figure 1.8 Distribution and fate of organotin compounds (OTC) and their general routes into the aquatic environment

1.5.1 Speciation

In seawater, TBT can exist as free cation, hydroxide or chloride complex. The neutral hydroxide (TBTOH) dominates as can be demonstrated by following calculations. The chemical characteristics of seawater and TBT are listed in Table 4.1 and 5.1. Concentration of TBT in the solution is assumed as 100 mg/l.

In seawater, there are two equilibriums.

$$TBT^{+} + Cl^{-} == TBTCl \qquad (a)$$

In Equilibrium (a), formation constant (logKi = 0.6 (Arnold et al., 1997)) is used for TBTCl. $Ki = [TBTCl] / ([TBT^{+}]*[Cl^{-}])$

$$TBT^+ + H_2O == TBTOH + H^+ \quad (b)$$

Equilibrium (b), acidity constant (logKa = 6.25 (Arnold et al., 1997)) is used for TBTOH.

$Ka = ([TBTOH] * [H^+])*[TBT^+]$

$$[TBT] = [TBT^+] + [TBTCl] + [TBTOH]$$
$$= [TBT^+] + Ki * [TBT^+] [Cl^-] + (Ka * [TBT^+] / [H^+])$$

The speciation graph is shown in Figure 1.9 that will be helpful to explain the pH effects on sorption of TBT.

1.5.2 Sorption

The sorption process is important to investigate the transportation of TBT in the aquatic system. The sorption of TBT to the sediments considerably depends on the pH, salinity of the aqueous phase and the sediment type. It has been noted that contaminant sorption to sediments may proceed at relatively slow rates for long periods of time after an initial rapid phase (Pignatello, 1996).

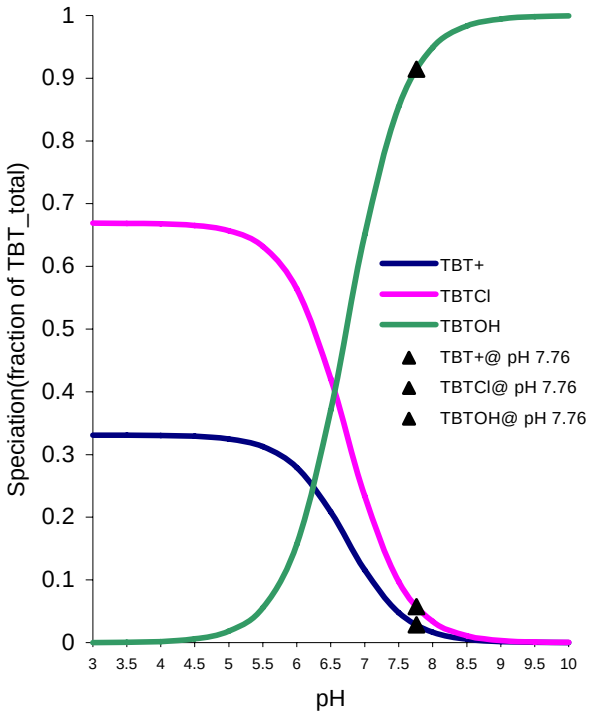


Figure 1.9 Speciation of TBT compounds in seawater

There is an important effect of pH on sorption of TBT in the sediment. Weidenhaupt (1995), Weidenhaupt and co-workers (1997), and Arnold and co-workers (1997) have shown that, for pH< pKa (= 6.25), TBT is mainly present as a cation in the aqueous phase in fresh water, whereas the neutral species are in the organic phase. In the seawater, however, it is coincidentally the opposite. TBTCl is the dominant partitioning in the aquatic phase for pH<6.25 (Figure 1.9). Sorption maximum is at pH 6 (Burton et al., 2004), which can be explained by Burton's (2004) hypothesis as follows.

$$\equiv S\text{-}OH^- + TBT^+ \leftrightarrow \equiv S\text{-}OHTBT$$

If sorption of TBT to natural sediments occurs predominantly via this reaction (where S includes organic surfaces), then maximum sorption around pH 6 is to be expected. This is because (1) at higher pH values the cationic TBT^+ becomes increasingly less abundant (Figure 1.9) and (2) as pH increases so too does the abundance of deprotonated surface ligands. Although the cationic TBT^+ species is relatively abundant at pH 4, the abundance of deprotonated surface ligands is less than at pH 6. Therefore, at pH values near pH 6 there is an optimal balance between the abundance of TBT^+ cations and the number of deprotonated surface ligands.

Under acidic conditions (i.e., pH<6), TBT is sorbed by both combination of TBT^+ and hydrophobic partitioning TBTCl into nonpolar organic matter. Under less acidic conditions, sorption can be attributed to hydrophobic partitioning of TBTOH into nonpolar organic matter (Burton et al., 2004).

Generally, the pH value of seawater is about 8, which means that the neutral TBTOH is the predominant species in marine system. As such, the main sorption mechanism is likely the TBTOH to organic matter.

The effects of salinity on the sorption of TBT are relatively clear. In general, TBT adsorption decreased with increasing salinity due to the growing competition with metallic cations (Ca^{2+}, Mg^{2+}, Na^+, and K^+) in the seawater to the surface site of the clay minerals. Only at pH 4, the TBT sorption onto kaolinite did not show any effect by changing the salinity (Hoch, 2004).

The sorption process depends on the characteristics of the sediments as well. Studies concerning sorption of TBT have involved a range of sorbents such as natural sediments (Unger et al., 1988, Langston and Pole, 1995, Ma et al., 2000, Hoch et al., 2002), quartz sand (Bueno et al., 1998), clay minerals (Weidenhaupt et al., 1997, Hoch, 2004), oxide minerals (Randall and Weber, 1986), organic matter (Poerschmann et al., 1997, Arnold et al., 1998), and municipal waste compost (Vassallo and Vella, 2002). And from their investigations, TBT exhibits a stronger affinity to clay material than quartz sand (Table 1.8). Hoch and co-workers (2004) concluded that for different clay types examed (kaolinite and montmorillonite), the highest TBT adsorption was found at salinity of 0%

and pH 6. And K_d values of different sediment types are shown in Table 1.9. K_d values increase with the increase of organic carbon.

According to the present survey, the proportion of organic matter in the solid phase is the most important parameter controlling TBT distribution in aquatic system. The strength of organotin compounds (OTC) adsorption correlated well with the carbon content and cation exchange capacity of the soil and was in the order mono->di->tri-substituted OTC. The OTC adsorption coefficient was much larger in organic soils (K_d>10^4) than in mineral soils (Huang and Matzner, 2004).

Table 1.8 K_d and percentages of adsorption of TBT onto montmorillonite (SWy), kaolinite (KGa), and quartz sand (Qz) at pH 6 (Hoch et al., 2004)

	SWy	**KGa**	**Qz**
K_d (l/kg)	89	51	25
TBT ads. (%)	65	55	36

Table 1.9 K_d values of different sediment types (Bioforsk, 2006)

	Olivin	**Rock**	**Sand**	**Clay**	**Sediment**
K_d (l/kg)	35	15.5	755	631	2194
TOC (%)	0.1	0.1	1.3	3.8	4.2

1.5.3 Abiotic degradation

1. Hydrolytic cleavage

The Sn-C bond can be attacked by both nucleo-phile and electrophile reagents. For example, mineral acid, carboxylic acid, and alkalimetals are agents that are able to heterolytically cleave of Sn-C bonds (Hoch, 2001). The process of cleavage of TBT is shown in Figure 1.4 in detail. Since the hydrolytic cleavage of TBT requires extreme pH or other conditions, it seldom happens in the natural environment. Studies in this field are under debate. Maguire and co-workers (1983) and Maguire and Tkacz (1985) pointed out that TBTO remain stable for 11 months in distilled or natural water at 20^{o}C, in a dark and sterile medium, whereas, Seligman and co-workers (1986a) claimed that slight

degradation of TBTO was apparent after 94 days in darkness in the presence of formalin as a sterilizing agent.

2. Photodegradation

Photodegradation of TBTO by ultraviolet light happens when wavelength of UV light is longer than 290nm that possesses energy of 300kJ/mol, because the energy required to break the carbon-tin bond is 190-220kJ/mol. The photolysis under natural light condition in distilled or natural water is limited, leading to a TBTO half-life in excess of 89 days. Due to the low transmittance of UV light, this breakdown process is expected to occur only in the upper few centimetres of water column. Because it is possible in only a limited portion of aquatic environment, photolysis probably is not a significant breakdown process of TBT (Maguire et al. 1983).

The main derivative of photodegradation of TBT is DBT, and MBT is very little. Field and laboratory measurements have shown that conditions of transmission of light and the presence of photosensitizing substances (acetone, humic acid, etc.) can considerably accelerate the process.

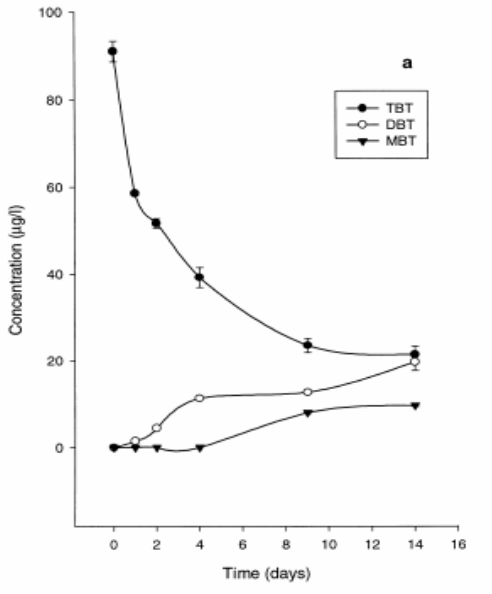


Figure 1.10 Residual concentrations of TBT, DBT and MBT in the incubation medium of *C. vulgaris* (Tsang et al., 1999)

1.5.4 Biodegradation

Biological processes are likely to be the most important mechanism for the decomposition of TBT in the marine environment, so the ratio of TBT to DBT and MBT can be the indicator for the degradation of TBT. In the experiments, some species such as *Chlorella vulgaris* can metabolize TBT to less toxic compounds DBT. But there are many conditions for the biological degradation such as species, temperature and light and so on. Temperature is quite important because it determines the degradation rate, the colder the slower.

Generally, biodegradation happens more often and more efficient in aerobic environment than in anaerobic environment. Decomposition is slower when TBT has accumulated in

sediment. If oxygen is completely excluded, TBT half-life may be several years. But this is not always the case. For some organisms, the anaerobic environment will be more suitable for decomposition. Biodegradation plays a role both in water and in sediment. However, degradation of sediment-bound TBT was found to be a slow process. In aerobic layers the half-life of TBT was between 4 and 5 month, whereas, in deeper anaerobic layers a half-life value was not obtained within 500 days.

Tsang and co-workers (1999) tested TBT degradation by *C. vulgaris*. The result is shown in Figure 1.10. After 16 days of incubation, TBT concentration went down to 21.4 ug/l, and DBT concentration went up to 20 ug/l. MBT concentration increased generally to 10 ug/l at the end. The research shows the importance and dominance of biodegradation in the removal of TBT.

The biodegradation of TBT is a complicated process. Although a few experiments have shown good results, it is hard to control and to be used as an engineering way of TBT remediation. Sorption is so far shown to be the dominant process determining the fate of TBT in the aquatic environment.

2. Objectives

The studies on butyltin compounds have been under the way for more than 20 years. There are many nice results about characteristics such as sorption and biodegradation of these compounds, especially of TBT. However, due to the complication of the behaviours of butyltin compounds, some results are under the debate. As mentioned in Chapter 1, biodegradation is so complicated process to decompose TBT to less toxic compounds that sorption is the main way to determine the fate of TBT in the aquatic environment, although biodegradation process has been reported as an effective way.

However, in the open marine environment, sorption is not a simple process because it depends on a lot of conditions such as sediment charactersitics, salinity and temperature and so on. So some theoretical assumptions are made in this study. The objectives are listed in detail as follows.

- Have a general idea of butyltin compounds, TBT, DBT and MBT and their effects on marine environment
- Know about the pollution condition of TBT, DBT and MBT in Hovedøya harbour through laboratory analysis and experiments
- Test of POM as a sorbate material for measurement
- Set up sorption evaluation with BC models in order to have an idea of the partitioning of TBT, DBT and MBT in marine system

3. Materials and methods

3.1 Characteristics of sediment

3.1.1 Description of sediment

Figure 3.1 Core sample of X1

The sample focused on in this report is from Hovedøya harbour, an island close to Oslo city with a small boat harbour and maintenance yards. The sample X1 was taken from the top 20cm of the sediment because butyltin compounds are used for recent decades and the sediment layers with butyltin compounds will not be very deep. tThe equipment for sampling is shown in Figure 3.2. The sediment shown in Figure 3.1 was the core sample in station X1. The gray top part showed the aerobic status and the dark part on the bottom showed that anaerobic status. The black and gray lines in the core sample showed the process of sedimentation. Since this sample was taken from the harbour, relatively shallow part, the sediment was soft. The deeper the sediment, the harder it will be as a result of consolidation.

3.1.2 Bulk density of sediment

Figure 3.2 Equipment for sediment sampling

The sample was stirred lightly to make it homogenous. Then, clean spoon was used to take the sediment into the container. The container with the wet sediment was weighted on the scale and then was put in the oven at 110 ^{o}C. After heating for one day the container with dry sediment was weighted again. In order to confirm that the sediment was dry enough, we put the container in the oven one day more and we weighted it after heating.

3.2 Experiment preparations

3.2.1 Composition of organotin solution

Before the sorption and extraction experiment, the composition of organotin solution and calibration of the organotin compounds have to be done.

1. Assumption and calculation

The concentration in tubes for GC should be 100 ug/l in order to get the peaks in the chromatogram and the volume of each tube was 1 ml. The assumptions for seawater spiking were made as the seawater for each spiking was 50 ml; the organotin solution for each spiking was 5 ul; the weight of POM for each sorption was 100mg; log K_{POM} of TBT was 3.25 that was the same value as of K_{POM} of PAH (Oen et al., 2006).

M_{TBT_water} = 100 ug/l*(1E-3) l = (1E-4) mg
C_{TBT_water} = (1E-4) mg / 50 ml = (2E-3) mg/l
$C_{TBT\_POM} = K_{POM} * C_{TBT\_water}$ = (1E+3.25) l/kg *(2E-3) mg/l = 3.56 mg/kg
$M_{TBT\_POM} = M_{POM} * C_{TBT\_POM}$ = 100 mg * 3.56 mg/kg = (3.56E-4) mg
$M_{TBT} = M_{TBT\_POM} + M_{TBT\_water}$ = (3.56E-4) mg + (1E-4) mg = (4.56E-4) mg
$C_{TBT\_organotin\_solution}$ = (4.56E-4) mg / 5 ul = 91.2 mg/l

Since TBT was the dominant compound in this research, the organotin solution with nine kinds of organotin compounds was mixed with the same concentration as TBT. For convience, the concentration of organotin solution was defined as 100 mg/l.

2. Solution composition

According to the assumption above, 100mg/l organotin solution should be prepared before the sorption and extraction experiment. The solution concluded MBT, DBT, TBT, MPhT(monophenyltin), MOT(monooctyltin), DOT(dioctyltin), DPhT (diphenyltin), TcHT(tricyclohexyltin), and TrPhT(triphenyltin). First, the organotin solution was prepared by nine kinds of organotin chloride compounds that are shown in Table 3.1.

Methanol was used as a solvent for the organotin solution. The weighted organotin chloride compounds were put into 10 ml methanol flasks respectively and dissolved. In

order to get the same concentration (100 mg/l) for every compound, different volume of organotins was taken into a new flask and 10ml methanol was filled.

Table 3.1 Organotin chloride compounds used for organotin solution

Compounds	Formula	Appearance	Mol weight_ organotin+ (g/mol)	Mol weight _ organotin chloride (g/mol)
TBTCl	$C_{12}H_{27}Cl_1Sn$	liquid	290	325.5
$DBTCl_2$	$C_8H_{18}Cl_2Sn$	semi-solid	233	303.8
$MBTCl_3$	$C_4H_9Cl_3Sn$	liquid	176	282.2
TPhTCl	$C_{18}H_{15}Cl_1Sn$	solid	350	385.4
$DPhTCl_2$	$C_{12}H_{10}Cl_2Sn$	solid	273	343.8
$MPhTCl_3$	$C_6H_5Cl_3Sn$	liquid	196	302.1
$MOTCl_3$	$C_8H_{17}Cl_3Sn$	liquid	232	338.3
$DOTCl_2$	$C_{16}H_{34}Cl_2Sn$	solid	345	416.0
TcHTCl	$C_{18}H_{33}ClSn$	solid	368	403.6

Compounds	Compound weighted (mg)	methanol (ml)	organotin+ concentration (mg/ml)	organotin+ added to solution (ml)
TBTCl	11.2	10	1.00	1.00
$DBTCl_2$	9.70	10	0.74	1.34
$MBTCl_3$	16.1	10	1.00	1.00
TPhTCl	23.4	10	2.13	0.47
$DPhTCl_2$	33.4	10	2.65	0.38
$MPhTCl_3$	15.4	10	1.00	1.00
$MOTCl_3$	14.6	10	1.00	1.00
$DOTCl_2$	27.7	10	2.30	0.44
TcHTCl	9.50	10	0.87	1.15

3.2.2 Calibration for the organotin compounds

Organotin solution, internal standard and injection standard were used for the calibration. In this experiment, TrPrT, TrPeT and DHpT were used as internal standard (50 ug/l) and TePrT was used as injection standard (50 ug/l). Internal standard was mostly for the calibration and injection standard is necessary to know the recovery of the organotin compounds and internal standard. Each internal standard was used for different organotin

compounds. TrPrT was the internal standard used for TBT, DBT, MBT, MPhT and MOT. TrPeT was used for DPhT and DHpT is for TPhT, DOT and TcHT.

The calibration interval was between 1 ug/l and 1000 ug/l and the detection limit was around 5 ug/l. Six tubes of organotin solution with different concentrations were prepared. They were 5 ug/l, 10 ug/l, 25 ug/l, 50 ug/l, 100 ug/l, 500 ug/l and 1000 ug/l respectively. $NaBEt_4$ was used for the derivatisation. Then 10 ul internal standard and 10 ul injection standard were added in each tube. These tubes were put to the Gas Chromatograph (GC). The flow rate was set as 1 ml/min. The temperature started as 40^{o}C and held for 2 minutes. And it increased 5 ^{o}C per minutes until it reached 220 ^{o}C and held for 6 minutes. Then, the temperature increased again by 30 ^{o}C per minute till 310 ^{o}C and held for 8 minutes. The run time was 55 minutes in all.

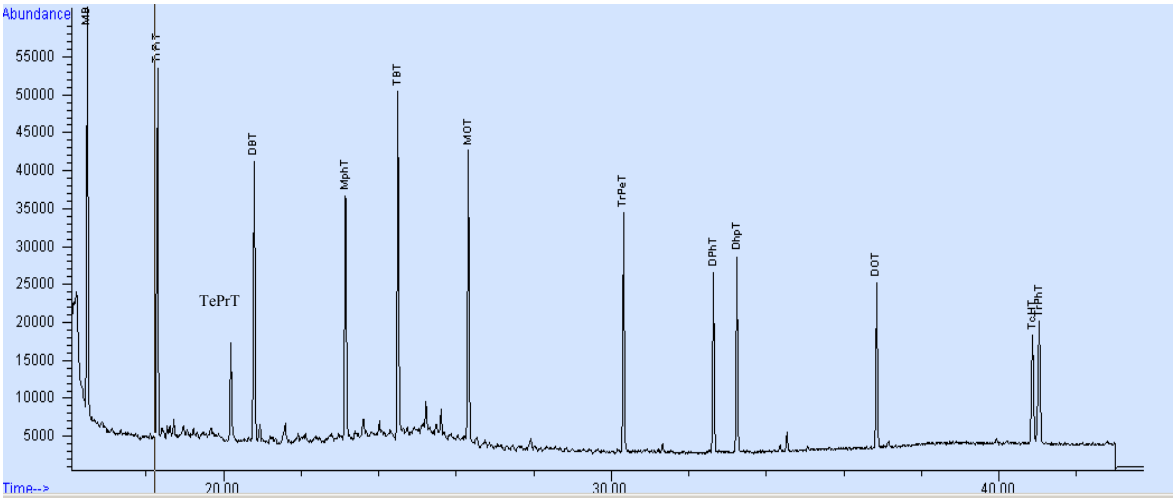


Figure 3.3 Chromatogram of organotins from GC machine

After the separation of organotin compounds, the data was transferred to the computer as chromatogram as shown in Figure 3.3. The x-axis showed the retardation time, and the y-axis showed the intensity (abundance) of the signal. For the same compounds, the higher concentration of compounds, the higher peak would show on the chromatogram.

3.3 Experiments

There were two systems for sorption experiment of organotin compounds. System 1 was for the test of POM and System 2 was for the extraction of organotin compounds.

3.3.1 System 1—spiking of artificial seawater

1. Sorption material--POM

Polyoxymethylene (POM), also known as acetal resin, polytrioxane, polyformaldehyde and paraformaldehyde, is an engineering plastic used to make gears, bushings and other mechanical parts. Its chemical formula is $–(-O-CH_2-)_n-$.

Besides the industrial use, POM can be a good sorbent for some organic matters such as PAHs and PCBs. Usually, POM is just used in the lab measurement of organic matters. Jonker and Koelmans (2001) pointed out the use of POM for PAHs sorption experiments. POM showed monophasic sorption kinetics, linear isotherms covering several orders of magnitude, and a linear relationship between distribution coefficients for POM and the octanol-water distribution coefficient. Therefore, the sorption process can be considered to be true partitioning. Application of POM for the determination of distribution coefficients for soot and sediment (POM-SPE method) resulted in highly reproducible values. Here, SPE means solid phase extraction. The method was validated by comparing values for sediment with results for the same sediment determined using the cosolvent method. This comparison resulted in an almost 1:1 relationship, proving the method's validity. And the PAHs sorption experiment with POM by Oen and co-workers (2006) showed very good results of K_{POM} as well (Table 3.5).

Moreover, Jonker and Koelmans (2001) also indicated that POM could be a good sorbent for some PCBs such as 2,2,5'-trichlorobiphenyl, 2,2,5,5'-tetrachlorobiphenyl, 3,3',4,4'-tetrachlorobiphenyl and 3,3',4,4',5-pentachlorobiphenyl. Lowry and co-workers (2005) found results quite close to those from Jonker and Koelman (2001), which shows that POM works well for PCBs sorption. K_{POM} values are shown in Table 3.5. Due to the effective sorption in lab experiment, we tried to use POM as the sorbent to determine organotin compounds in the water phase.

2. Experiment setup

This experiment aimed to know the POM-water partitioning coefficient K_{POM} which was got by spiking the artificial seawater with organotin solution. The amounts of organotins spiked in seawater are shown in Table 3.2. Four different extraction solutions were used to find out the best one for sorption.

As shown in Table 3.2 and Figure 3.4, we spiked 5ul organotin solution into 50ml seawater flasks. The flasks were shaken for 3days with weighted POM inside. POM was taken out of the flasks and put into four small flasks. 15ml extraction solutions and 10 ul internal standard were added. The flasks were shaken for another 3 days for the extraction of organotins from POM to extraction solution phase. The extraction solutions were transferred into 4 tubes (A) after complete extraction.

For the seawater, we added 10ml extraction solutions for the extraction of organotin remaining in the seawater and shook for 4 hours. Then we took the extraction solutions phase out into another 4 tubes (B). This process was repeated twice, and the shaking time was one day (Tube C) and 2 days (Tube D), respectively. This was for the complete extraction of organotin compounds in seawater.

After all the tubes were prepared, we put them to the evaporation machine until the extraction solutions phase was reduced to 5ml. When the extraction solution in Tube B, C and D was reduced, they were mixed in Tube E and the evaporation continued to 5 ml. Then, 2ml buffer ($NaCH_3COO^- + CH_3COOH$) and 0.5ml $NaBEt_4$ solution (20g/l) were added to Tube A and E for derivatisation. Since the organotin compounds in the organotin solution were organotin chloride compounds and they could not be measured by GC directly, they had to be derivatised. Derivatised extraction solutions were transferred to 8 empty tubes through pipettes with Na_2SO_4 and glass wools which were used to dry the extraction solutions phase. The eight tubes were evaporated till 1ml and transported the extraction solution to 1ml tubes for GC machine analysis with additional 10ul injection standard in each bottle.

Table 3.2 Amount of seawater spiking for K_{POM} measurement

Sample Nr.	**2.1**	**2.2**	**2.3**	**2.4**
Seawater (ml)	50	50	50	50
Organotin solution (ul)	5	5	5	5
POM (g)	0.1088	0.0958	0.0980	0.1111
Extraction solution	Heptane	Heptane&Acid	Heptane&Tropolene	Heptane&Acid &Tropolene

3.3.2 System 2—sediment extraction

Clean spoon was used to stir sample X1 lightly to confirm that it was homogenous. And then the sediment extraction of it could be done. We took three pieces of sediment to three flasks, marked as X1.1, X1.2 and X1.3. Extraction solutions were added as shown in Table 3.3. Reflux equipment was used for the sediment extraction for four hours. With the process of heating and cooling, the extraction of organotin compounds from sediments was more complete.

Table 3.3 Amounts of extraction solutions added in sediment samples

Sample Nr.	**X1.1**	**X1.2**	**X1.3**
Sediment (g)	10.57	10.36	10.63
Acetone (ml)	10	10	10
Heptane&Tropolene (ml)	50	50	50
Internal standard (ul)	40	40	40
10% HCl (ml)	10	10	10

After extraction, we took the extraction solutions (Heptane, Tropolene and Acetone) phase out into another three flasks through pipettes with Na_2SO_4 and glass wools which were used to filter the extraction solutions phase. The following processes were mostly the same as System 1. The difference was that the pipettes for drying were with additional silica gel for the filtering and drying in order to remove organic matter interfering from sediment in the extraction solutions.

In addition, to analyse the native organotin compounds in the sediment, we did the sediment spiking test to determine the organotin extraction efficiency from sediment. Sediment spiking test meant spiking the sediments with organotin solution by +50%, +100%, +150% and +200% of the nature sediment concentration of organotin compounds. The sediment concentration of TBT was used to calculate the volume of organotin solution spiked. The expected sediment concentrations of organotin compounds are shown in Table 3.4. The spiked sediments were shaken for one night and followed by the same extraction process.

Table 3.4 Amount of organotins for sediment spiking

	Compounds	X1 +50%	X1 +100%	X1 +150%	X1 +200%
Sediment (g)		11.39	12.01	10.37	10.04
	MBT	288.53	525.05	761.57	998.09
	DBT	646.60	821.62	996.64	1171.67
	MPhT	252.32	488.84	725.36	961.87
Expected sediment	TBT	686.42	921.52	1156.62	1391.72
concentration after	MOT	263.09	499.61	736.13	972.65
spiking (ug/l)	DPhT	640.70	1266.76	1892.83	2518.89
	DOT	543.05	1086.09	1629.14	2172.19
	TcHT	206.24	410.60	616.84	823.08
	TrPhT	526.21	1028.81	1531.42	2034.02
Organotin solution (ul)		12.5	25	37.5	50

Table 3.5 K_{POM} and K_{AC} values of some PAHs and PCBs

	$logK_{POM}$	$logK_{AC}$	$logK_{F,BC}$	References
PAHs				
Phen	3.25		6.3	Oen er al., 2006
Pyr	3.44		5.9	Oen er al., 2006
Bap	4.31		6.7	Oen er al., 2006
Ant	3.33		6.3	Oen er al., 2006
FluA	3.47		6.8	Oen er al., 2006
BaA	4.16		7.0	Oen er al., 2006
IcdP	4.62		>7.7	Oen er al., 2006
BghiP	4.59		7.5	Oen er al., 2006
PCBs				
2,2'-dichlorobiphenyl	3.62	8.90		CICEET, 2005
3,4-dichlorobiphenyl	4.31	8.68		CICEET, 2005
2,2,5'-trichlorobiphenyl	3.98	8.33		CICEET, 2005
3,3',4-trichlorobiphenyl	5.28	9.21		CICEET, 2005
2,2'6,6'-tetrachlorobiphenyl	4.06	8.06		CICEET, 2005
2,2,5,6'-tetrachlorobiphenyl	3.80	7.27		CICEET, 2005
2,2,5,5'-tetrachlorobiphenyl	4.18	7.71		CICEET, 2005
2,3,5,5'-tetrachlorobiphenyl	5.19	8.97		CICEET, 2005
3,3',4,4'-tetrachlorobiphenyl	5.22	9.07		CICEET, 2005

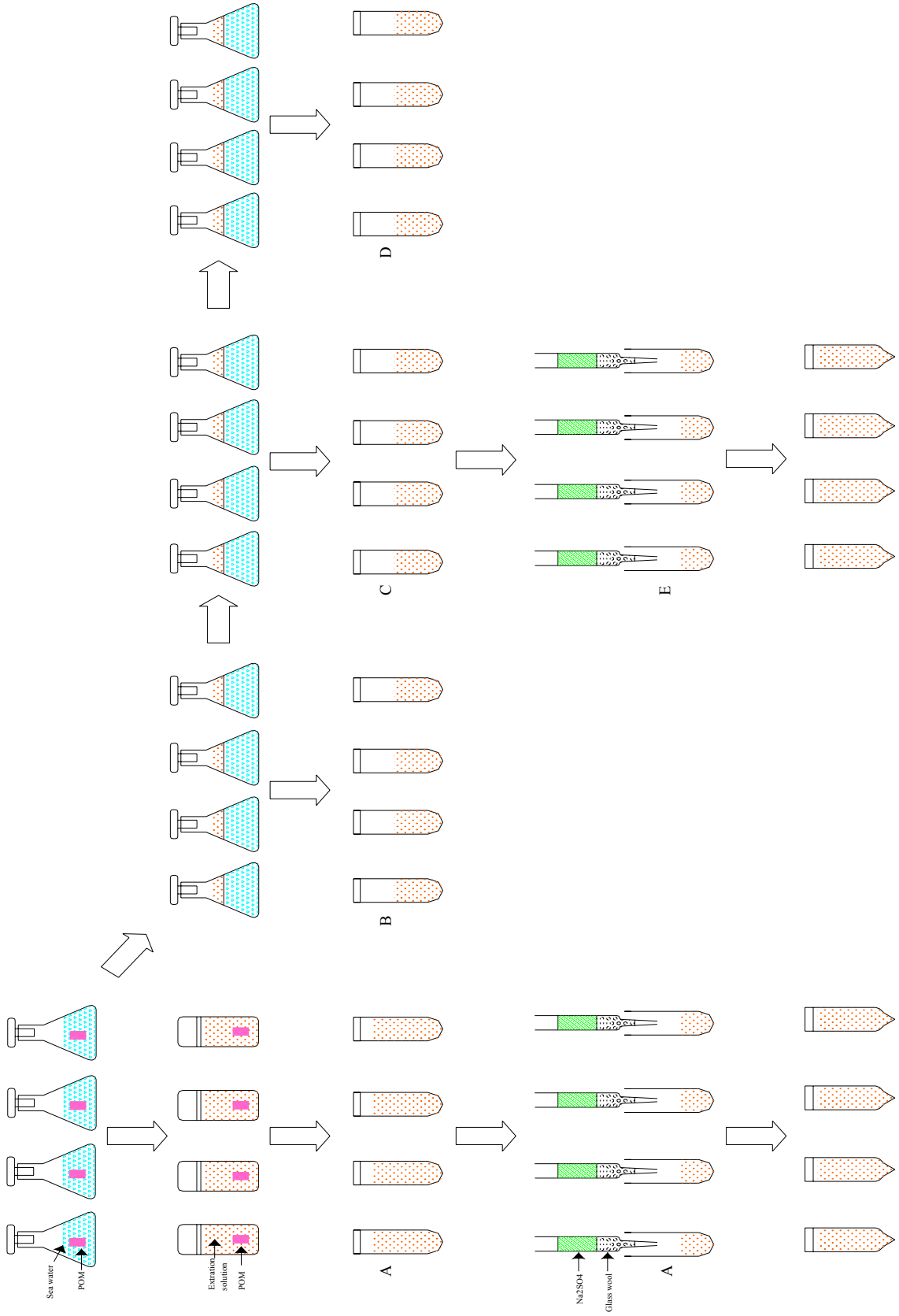


Figure 3.4 Experiment process for System 1

4. Results and discussion

4.1 Sediment and seawater characteristics

The sediment of X1 and artificial seawater characteristics are shown in Table 4.1. The speciation of TBT in seawater is indicated in Figure 1.9. The black spots indicate the fraction of TBT^+, TBTCl and TBTOH at pH 7.76. There is 91.8% TBTOH, 5.4% TBTCl and 2.8% TBT^+, which is close to Arnold and co-workers (1997) results which were TBTOH (93%), TBTCl (2-3%) and TBT^+ (4-5%). This speciation shows how TBT exists in the marine environment.

Table 4.1. Characteristics of sediment and seawater in Hovedøya harbour

	Concentration of NaCl (g/l)	**Moleweight of NaCl (g/mol)**	**pH**	**Conductivity (s/m)**	**psu**	**Bulk density %**
Artificial Seawater	29.7	58.5*	7.76	4.69	38.7	
Sediment						41.8

psu (practical salinity units)

Values with * were got by calculation.

4.2 Sorption experiments

4.2.1 Calibration of organotin compounds

The calibration results for TBT, DBT and MBT are shown in Figure 4.1. X-axis showed the ration of organotin concentration to internal standard concentration and y-axis showed the ratio of the abundance of organotin to the abundance of internal standard. As the concentration and the abundance of internal standard are almost constant, the concentrations can be derived from the calibration line. Figure 4.1 showed a quite good calibration since the results for TBT, DBT and MBT are close to the trend regression line.

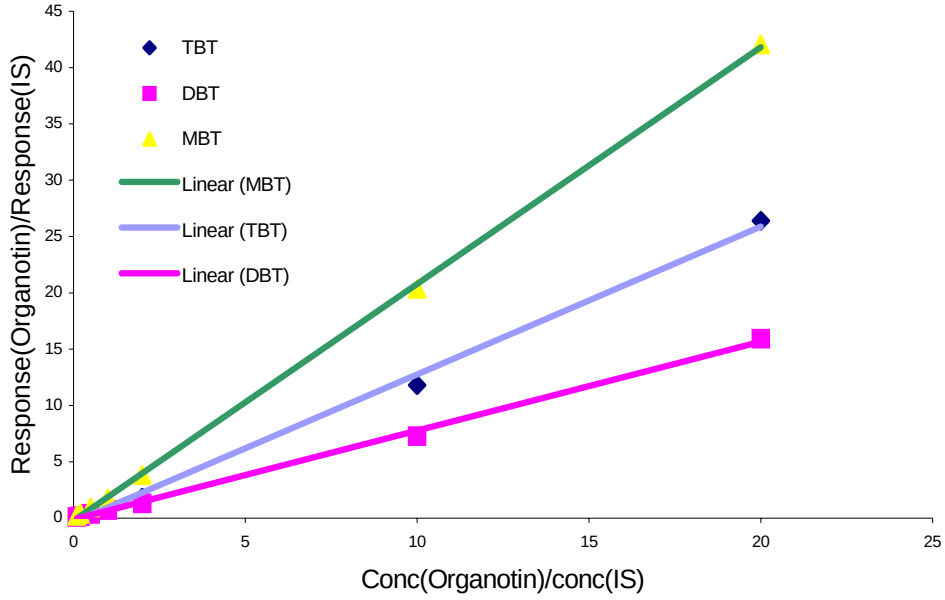
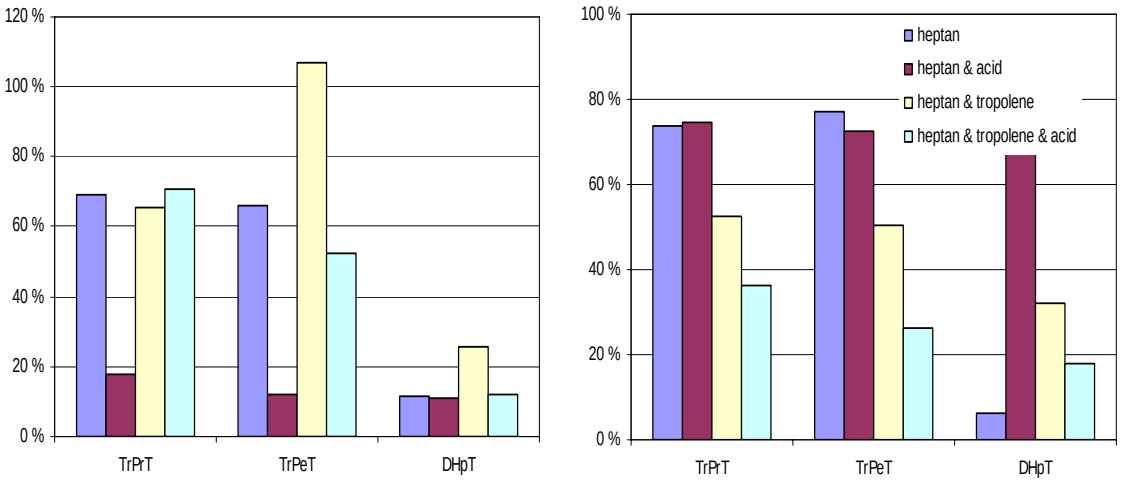


Figure 4.1 Calibration for TBT, DBT and MBT

4.2.2 System 1—spiking of artificial seawater



(a) (b)

Figure 4.2 Recovery of internal standard from (a) POM and (b) seawater

DHpT seems not a good internal standard due to the low recovery rate for almost all extraction solutions (Figure 4.2). Recoveries with heptane&acid are quite low from POM although it worked well with seawater, so this extraction solution is not stable and suitable. And recoveries with heptane&tropolene&acid are relatively low compared to the other two extraction solutions in most cases. Then heptane and heptane&tropolene are the two most proper extraction solutions in this experiment. In Figure 4.2 (a), the recovery

rate of TrPeT is more than 100%, probably because the contamination of POM in the lab work which was hard to prevent.

Figure 4.3 shows the recovery of seawater spiking with organotin solution both from POM and seawater. Obviously, heptane is not a good extraction solution due to its instability. For MPhT, TrPhT, DPhT and DBT, the values are even missing and for MOT and MBT the values are extremely low. There are not any values for TcHT and TrPhT on in Figure 4.3 because the recoveries of these two are too high. They are 1262% and 2337%, respectively. From the recoveries with the other three extraction solutions, the extremely high amounts of TcHT and TrPhT in heptane phase are not due to the contamination of artificial seawater. Although there is the same problem for heptane&acid that the DOT and TrPhT recovery amounts are high, it seems that extraction with heptane&acid for TcHT and TrPhT is much better than with heptane. Heptane&tropolene and heptane&tropolene&acid show a much better results for this extraction. There are some organotin compounds whose recoveries are more than 100% probably because the decrease in internal standard concentration, which will lead to the over reflection of relative organotin compounds. The most unsatisfactory values are for DOT and TrPhT from Figure 4.3. The internal standard used for these two compounds were DPhT which shows quite unstable results in Figure 4.2. Therefore the over measurement of DOT and TrPhT is more likely due to the internal standard used.

The fractions of organotin compounds in POM, seawater and lost amount are shown in Figure 4.4 for four kinds of extraction solutions. Heptane is not a good choice due to high lost amount for most compounds. Heptane&acid is better than heptane, but the extraction from POM phase is not that good. Compare the results of heptane&tropolene and heptane&tropolene&acid, the former shows a less lost amount and more amounts in POM phase. The fractions with negative values mean that the organotin compounds extracted from the seawater are more than those spiked in, which is indicated clearly in Figure 4.3. Those recovery amounts more than 100% in Figure 4.3 show negative values in Figure 4.4.

Consequently, considering results of internal standard recoveries and seawater and POM recoveries, heptane&tropolene seems the best extraction solution for the experiment.

The results from System 2 indicate extremely high concentrations of TBT and DBT in the sediment compare to other organotin compounds, and MBT concentration is higher than the other six although it is much lower than TBT and DBT concentrations (Figure 4.5). In addition, as mentioned in Chapter 1, TBT is the most toxic compound among organotin compounds and it can be broken down to DBT and MBT by degradation. Therefore, I will pay attention to these three compounds in the following discussion.

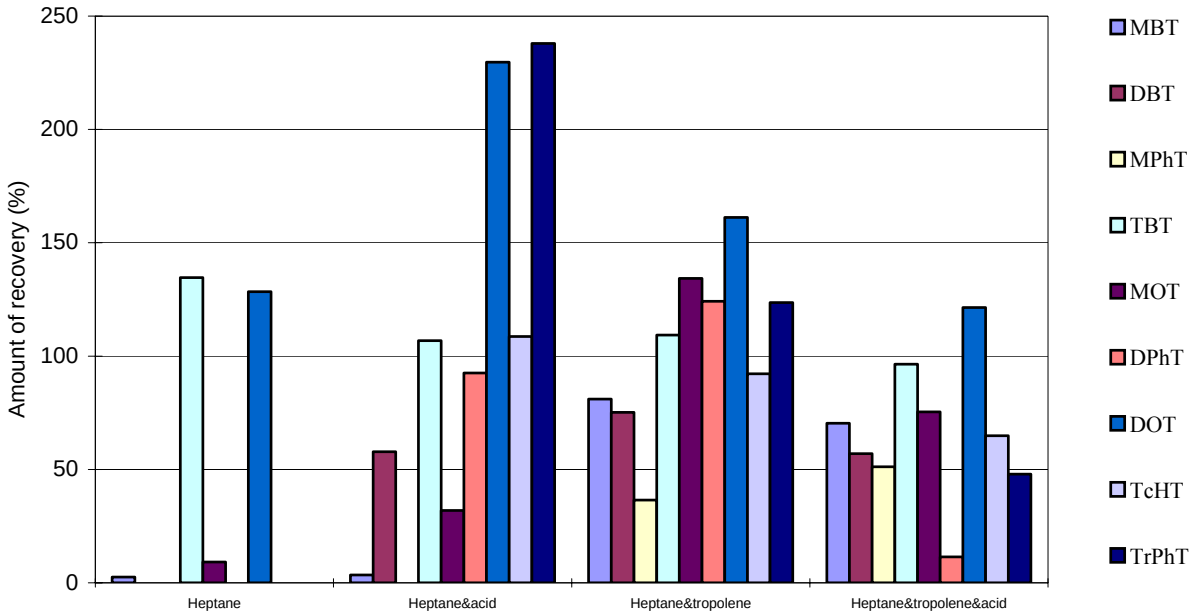
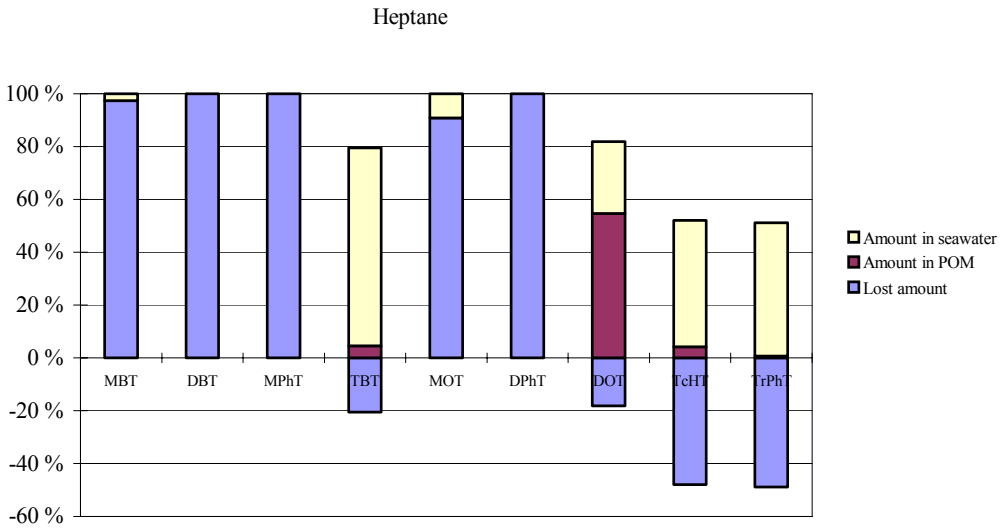


Figure 4.3 Recovery of organotin compounds from seawater spiking



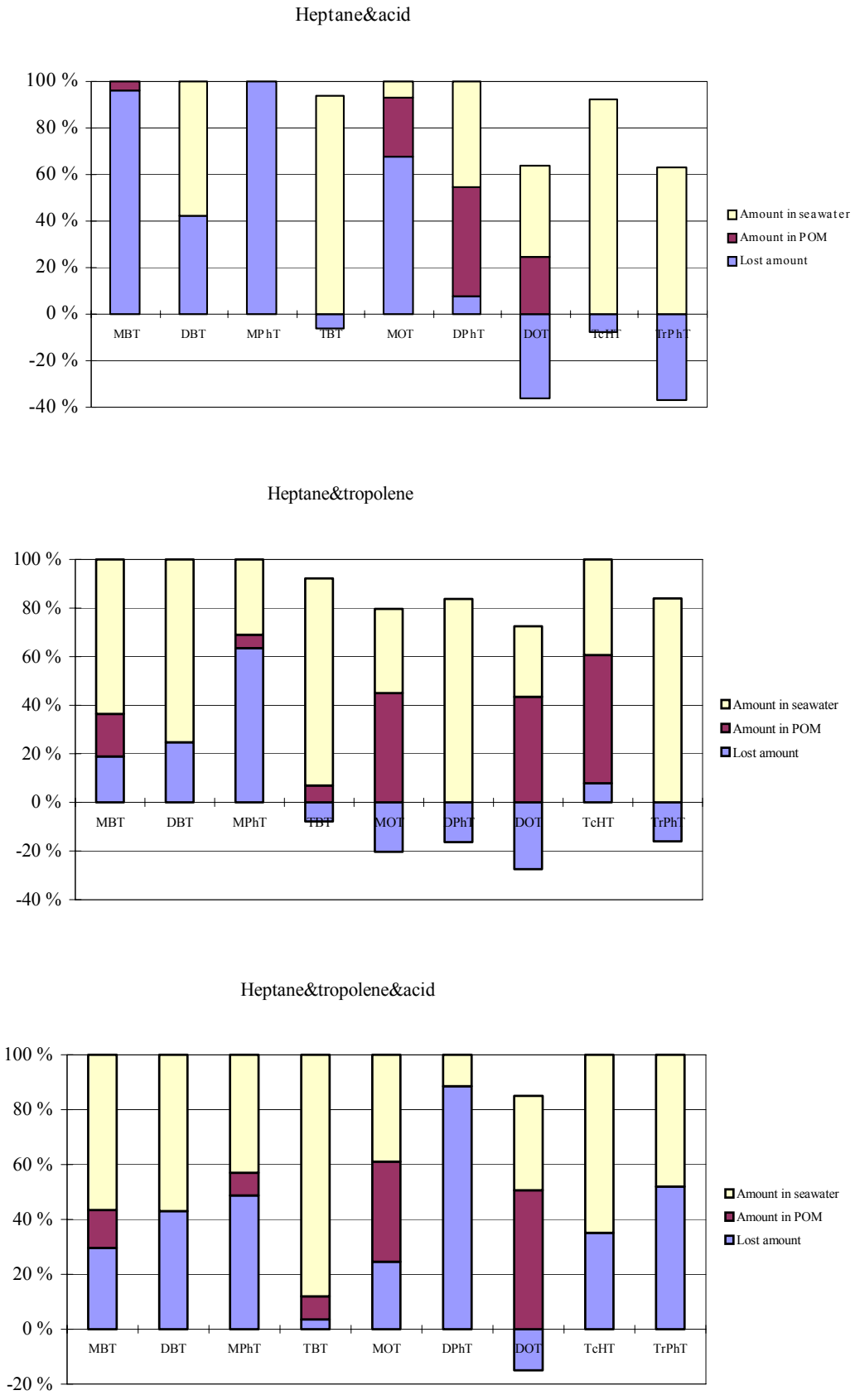


Figure 4.4 Amount of organotin compounds in POM, seawater and lost amount

The K_{POM} results from the experiment are small for most organotin compounds (Table 4.2), comparing with K_{POM} values for some PAHs and PCBs as shown in Table 3.5. DBT was no found in the POM phase with all kind of extraction solutions. The results of K_{POM} in this measurement emphasize that POM is likely not a good material for the sorption measurement of TBT, DBT and MBT in the water phase. But for other organotin such as DOT, POM acts as a good sorbate material.

Table 4.2 TBT, DBT and MBT distribution in water column and POM

	2.1 POM	**2.1 seawater**	**2.2 POM**	**2.2 seawater**	**2.3 POM**	**2.3 seawater**	**2.4 POM**	**2.4 seawater**
Concentration--POM&water	(ug/g dw)	(ug/ml)	(ug/g dw)	(ug/ml)	(ug/g dw)	(ug/ml)	(ug/g dw)	(ug/ml)
MBT	nd	0.26	180.4	nd	894.1	6.3	622.3	5.7
DBT	nd	nd	nd	5.8	nd	7.5	nd	5.7
TBT	353.5	12.7	nd	10.7	420.6	10.1	377.5	8.8
K_{POM} value	2.1		2.2		2.3		2.4	
MBT	nd		No value		141.0		110.1	
DBT	nd		nd		nd		nd	
TBT	27.9		nd		41.7		42.9	

4.2.3 System 2 —sediment situation of organotin compounds

1. Organotin compounds in the sediment

The sediment pollution condition of organotin compounds is revealed in Figure 4.5. The concentrations are the average values of X1.1, X1.2, and X1.3. Obviously, DBT, TBT and MBT are the three most abundant organotin compounds in the sample.

In the sediment, DBT concentration is higher than TBT's, which indicates a good condition of biodegradation or other degradations processes in the sediment in Hovedøya harbour. DBT and MBT can also come from the leaking of PVC products as mentioned in Chapter 1; however this is not as dominant as biodegradation. The test results on *C. vulgaris* from Tsang et al. (1999) indicated the important role of biodegradation in the removal of TBT (Figure 1.10).

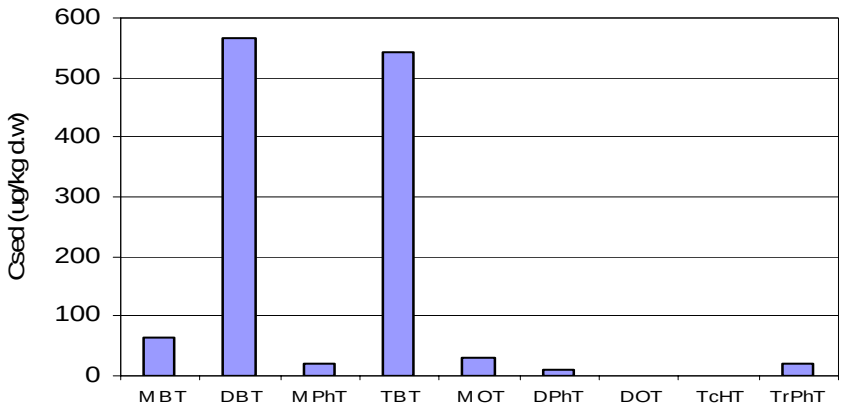


Figure 4.5 Concentrations of organotins in sediment

Comparing X1 results with NGI report (2007) results in Table 1.1, X1 shows higher concentration than Station 2, 3 and 4 for all the TBT, DBT and MBT, whereas Station 1 shows higher TBT concentration. TBT concentration in Station 1 is extremely high maybe because it is in a closer area, which prevents contaminants from releasing out. However, NGI report (2007) does not show as good as degradation condition as X1.

The measured and expected values of sediment spiking by +50%, +100%, +150%, +200% of the concentration of sediment shows fine results for TBT and DBT as the slopes of trend regression lines are close to 1 (Figure 4.6). This means that the extraction of these two organotins from sediment worked well in the experiment. But for MBT, the measured value is much lower than the expected value, probably because MBT was not derivatised enough due to its structure. And this probably is why the sediment concentration of MBT is much lower than TBT and DBT. Underivatised compounds could not be measured by GC.

2. Solid-water partition

The butyltin compounds measured from the extraction experiment were from both the solid phase and the water phase. With bulk density of sediment, K_d values of butyltin compounds, solid-water partitioning can be calculated. The results are listed in Figure 4.7. K_d values are calculated by Eq. (4) and (5). K_{ow} values are listed in Table 1.2.

TBT seems extremely hydrophobic since 99.5% TBT stays in the solid phase (Figure 4.7). MBT, however, is on the opposite. 96.5% MBT is dissolved or suspending in the water

phase. DBT shows more hydrophilic as there is 67.8% DBT in the water phase. Due to the characteristics of three butyltin compounds, TBT is dominant in the solid phase and DBT is dominant in the water phase (Figure 4.8 a&b). MBT concentration in the water phase in lower than that of DBT's because measured sediment concentration of MBT is quite low, although MBT is more hydrophilic.

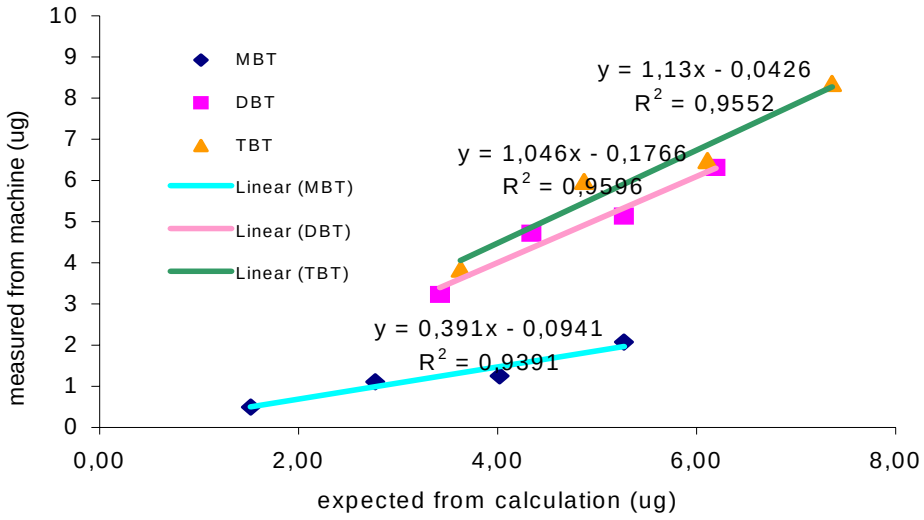


Figure 4.6 Expected and measured values of TBT, DBT and MBT

Consequently, the sediment analysis shows a good condition of degradation of TBT to DBT. But the result of MBT is not that satisfactory, probably due to derivatisation problem in the experiment. There is mainly DBT in the water because not only DBT is more hydrophilic, but also water phase is a more aerobic situation than solid phase to occur biodegradation.

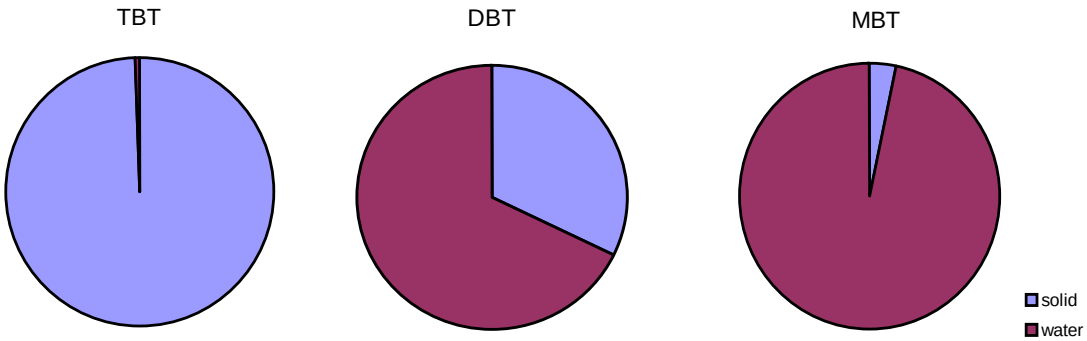
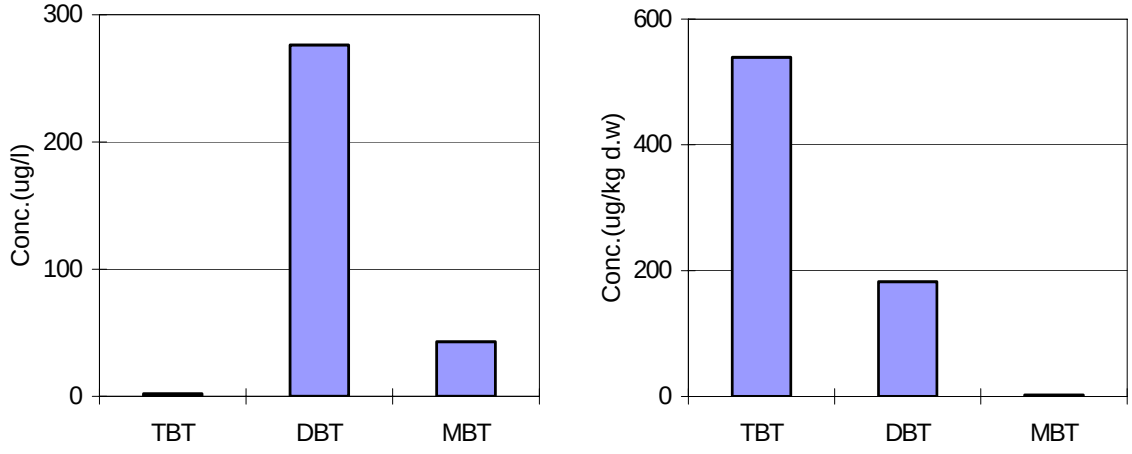


Figure 4.7 Fraction of TBT, DBT and MBT in the solid phase and water phase



(a) (b)

Figure 4.8 Concentration of TBT, DBT and MBT in (a)water phase and (b) solid phase

5. Sorption and bioaccumulation Evaluation

Due to the importance of black carbon (BC) sorption of hydrophobic compounds, it will be considered in the models for butyltin compounds in this chapter. POM will be considered as a sorbent in the system as well. Sorption evaluation and BSAF calculation will be done with three systems. Assume that there is no butyltin compounds in the artificial seawater and all the compounds measured in the seawater are released from the contaminated sediment from X1. Organisms studied on are staying in the sediment or in the water.

5.1 System A—Sediment and artificial seawater

5.1.1 Sorption evaluation

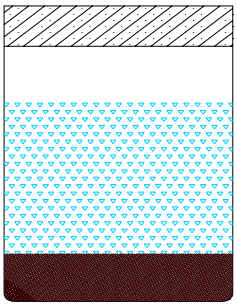


Figure 5.1 System with sediment and artificial seawater

Assume that there is 10 g contaminated sediment and 50 ml artificial seawater in this system (Figure 5.1). The brown area indicates sediment and the blue area means seawater.

The measured masses of TBT, DBT and MBT in the sediment were listed in Table 5.1 (a). There is 0.37% BC in the sediment that will be the sorbent for butyltin compounds in this system if BC is considered. The sediment concentration can be calculated by following formula.

$$Cs = f_{oc}K_{oc}C_w + f_{bc}K_{F,BC}C_w^{nBC} = C_{BC}+C_{OC} \quad (7)$$

Where f_{bc} is the fraction of BC; f_{oc} is the non-BC organic carbon present in the sediment sample; $K_{F,BC}$ is the Freundlich BC-water distribution ratio for BC and n_{BC} is the BC Freundlich exponent; C_{BC} is the concentration in BC; C_{OC} is the concentration in organic carbon (OC); C_w is the pore water concentration. As $\log K_{ow}$ value of TBT is close to that of Phenanthrene, I choose the same $logK_{F,BC}$ and n_{BC} values as phenanthrene's. They are 6.3 for $logK_{F,BC}$ and 0.61 for n_{BC} (Oen et al., 2006). The partitioning of TBT in the system can be described as follows.

$$M_{TBT} = M_{TBT\_BC} + M_{TBT\_water} + M_{TBT\_OC}$$
$$= M_{sed} * f_{bc}K_{F,BC}C_w^{nBC} + V_w * C_w + M_{sed} * f_{oc}K_{oc}C_w \quad (8)$$

The calculation results are as follows.

C_w = 0.0137 ug/l M_{TBT_water} = 6.85E-4 ug

C_{OC} = 3.15 ug/kg M_{TBT_OC} = 0.032 ug

C_{BC} = 539.0 ug/kg M_{TBT_BC} = 5.39 ug

M_{TBT_BC}: 99.4%; M_{TBT_OC}: 0.6%

In the partition calculation of DBT and MBT, the n_{BC} values are chosen the same as that of TBT, and log$K_{F,BC}$ values are listed in Table 5.1 (a), which are assumed as the same reduction of magnitude of logK_{oc} since no literature values are available.

It has to be noted that the water concentrations listed in Table 5.1 (b) are for System A with 50 ml seawater. They are calculated by $M_{TBT} = M_{TBT\_sediment} + M_{TBT\_water}$ and they are different from the porewater concentration calculated in Chapter 4. Comparing with the TBT water concentration without considering of BC (table 5.1 b), water concentration in System A is much lower and even can be ignored. It is clear that BC has an effect on the sorption of butyltin compounds to the sediment. The reduction of water concentration of TBT is especially significant because TBT is more hydrophobic than DBT and MBT as Figure 5.2 indicates

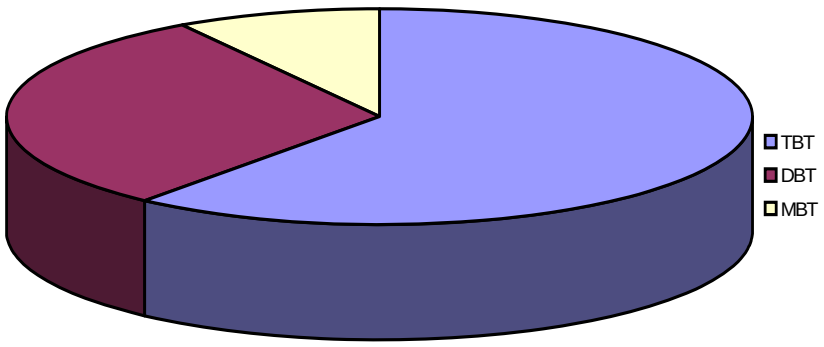


Figure 5.2 Reduction rate of water concentration with considering of BC

5.1.2 BSAF calculation

1. Bioaccumulation estimation without considering of BC

If BC is not considered in system A, after shaking bottle shown in Figure 5.1, the butyltin compounds will release from the sediment to the water. The water concentration and sediment concentration will be stable when the system reaches the equilibrium (Table 5.1 b).

As mentioned in chapter 1.4.2, TBT has shown a strong tendency of bioaccumulation. With BSAF values and sediment concentration, the tissue concentrations can be estimated. The BSAF and lipid % values of some organisms are shown in Table 5.1 (a). Assuming that BSAF values will not be changed with the conditions, the tissue concentrations of TBT, DBT and MBT in Hovedøya harbour can be evaluated by Eq. (3). The results are listed in Table 5.1 (b).

Combining the results in Table 5.1 (b) with values in Table 1.4, TBT concentration in water seriously threatens four organisms listed in Table 1.4, because TBT water concentration exceeds the LC_{50} values for water concentration of those organisms. But TBT concentration in the sediment is lower than LC_{50} values for sediment concentration for all the organisms in the table. But this does not mean that there is no threat to the organisms since EC_{10}/EC_{20} is widely used for risk assessment as referred to in Chapter 1.4.2.

The tissue concentrations reveal that *Potamocorbula amurensis* (Molluscs) are the organisms most likely to accumulate TBT in their bodies, which conforms to the conclusion in Chapter 1.4.2. Molluscs releases TBT very slowly from its body, leading to the high tissue concentration. Since the value for this organism is dry weight, it will go down when measured as wet weight. The interesting thing is that the tissue concentration of DBT in *Potamocorbula amurensis* is still high. Among the organisms listed in Table 5.1, *Echinocardium cordatum* seems the best organism to break down TBT or release TBT.

Table 1.5 implies a TBT research on *Nucella lapillus* in Oslo fjord. The tissue concentration in this organism is 32.9 ug/kg d.w. Refering to BCF value for *Nucella lapillus* in Table 1.6 and assuming that BCF value will not be changed with conditions,

water concentration signed as C_{water_obs} can be calculated by Eq. (2). The result of C_{water_obs} is 0.0011345 ug/l. Then K_d value signed as K_{d_obs} can be got by Eq. (6) as sediment concentration in the system is 222 ug/kg d.w. $\log K_{d\_obs}$ is equal to 5.3 which is much higher than theoretical K_d value calculated from K_{ow}. The existence of BC could be that reason for underestimation of K_d value because generally OC content is regarded as TOC content since the BC content is a small portion in TOC. This is quite normal for the field research. Oen and co-workers (2006) showed almost the same problem in their research on PAHs. Theoretical K_d value was 772, whereas log K_{d_obs} value is 5.6 for phenanehrene. It seems that BC shows quite good sorption ability to hydrophobic compounds and plays an important role on the sorption to sediment.

The analysis of water concentrations, sediment concentration and tissue concentrations of butyltin compounds in the systems just depends on the theoretical values. The observed field values will probably be quite different. The analysis aims to have a general idea of how these three compounds distribute in the sediment, water and organisms.

2. BSAF model with considering of BC

Since BC plays a significant role in the sorption of butyltin compounds to the sediment, it is necessary to set up a BC-inclusive BSAF model. Cornelissen and Gustafsson (2005) included BC in the BSAF.

$$BSAF_{BC\text{-}model} = K_{lipid}/[(1-f_{BC}/f_{TOC})*K_{OC}+f_{BC}/f_{TOC}*K_{F,BC}*C_w^{\,nBC-1}] \qquad (9)$$

$$K_{lipid} = C_{tissue} / (C_w * f_{lip}) \qquad (10)$$

Where K_{lipid} is lipid-water partition coefficient (l/kg). In the calculation of K_{lipid}, I assume that tissue concentrations will not change. Actually, due to the extremely low weight of organisms, the masses of TBT, DBT and MBT in their bodies are very small portions in the calculations by Eq. (8). So it is hard to use Eq (8) to estimate the tissue concentrations of any compounds among these three ones.

The measured values and references data in Table 5.1 (a) and calculated results in Table 5.1 (b) indicate that in the presence of BC, there is much less TBT in water phase. BSAF values show reduction for all the organisms. The reduction can even reach a factor of more than 200 for some organisms at the presence of BC.

Table 5.1 Measured and modelled values of TBT, DBT and MBT

(a)

	Organism species	Lipid %	TOC %	BC/TOC	Total mass (ug)	BSAF	Kd	$logK_{F,BC}$	Reference
TBT	Armandia brevis (Polychaete)	5.6	4.78	0.076	2.27	1.2	250	6.3	Meador and Rice 2001
	Buccinum undatum (Common whelk)	1.8	4.78	0.076	2.27	0.6	250	6.3	Hallers-Tjabbes et al. 2003
	Echinocardium cordatum	0.29	4.78	0.076	2.27	0.12	250	6.3	Stronkhorst et al. 1999
	Eohaustorius washingtonianus (Amphipod)	6.6 *	4.78	0.076	2.27	4.6	250	6.3	Meador et al. 1997
	Potamocorbula amurensis (Molluscs)	26.7 *	4.78	0.076	2.27	1.93	250	6.3	Pereira et al. 1999
	Rhepoxynius abronius (amphipod)	7.7 *	4.78	0.076	2.27	0.41	250	6.3	Meador et al. 1997
DBT	Buccinum undatum	1.8	4.78	0.076	2.37	1	0.66	3.7	Hallers-Tjabbes et al. 2003
	Potamocorbula amurensis	26.7	4.78	0.076	2.37	0.36	0.66	3.7	Pereira et al. 1999
MBT	Buccinum undatum	1.8	4.78	0.076	0.26	0.41	0.05	2.6	Hallers-Tjabbes et al. 2003

Measured or reference data are in Table (a) and calculated data are in Table (b).
BSAF and Lipid% values are from References. BSAF values refer to the sediment concentrations in references closest to that in Oslo harbour. Total mass data are measured from Sample X1.
The C_{water} and C_{tissue} values are calculated by $M_{TBT} = M_{TBT\_water} + M_{TBT\_sediment}$ and Eq (3), respectively.
Those with * are dry weight of tissues.

(b)

	Organism species	K_{lipid}	Ctissue (ng/g)	Cwater (µg/l)	Csediment (ng/g d.w)	Cwater_BC (ug/l)	BSAF_BC
TBT	Armandia brevis	6146.32	306.33	0.89	222	0.0045	0.0049
	Buccinum undatum	3073.16	49.23	0.89	222	0.0045	0.0025
	Echinocardium cordatum	614.63	1.59	0.89	222	0.0045	0.0005
	Eohaustorius washingtonianus	23560.90*	1383.97*	0.89	222	0.0045	0.0188
	Potamocorbula amurensis	9885.33*	2349.05*	0.89	222	0.0045	0.0079
	Rhepoxynius abronius	2099.99*	143.91*	0.89	222	0.0045	0.0017
DBT	Buccinum undatum	13.55	10.21	41.9	27.6	21	0.104
	Potamocorbula amurensis	4.88	54.53	41.9	27.6	21	0.0376
MBT	Buccinum undatum	0.43	0.04	5.15	0.26	4.4	0.0235

5.2 System B—Sediment, artificial seawater and POM

5.2.1 Sorption evaluation

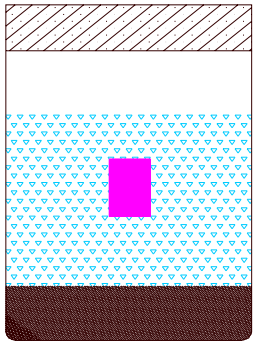


Figure 5.3 System with sediment and artificial seawater and POM

The same assumption is made for the sediment sample and seawater. And assume that there is 100 mg POM used in this system, which is almost the same weight of POM in seawater spiking experiment. In Figure 5.3, the pink area indicates POM. The calculation formula is $M_{TBT} = M_{TBT\_BC} + M_{TBT\_water} + M_{TBT\_OC} + M_{TBT\_POM}$. I chose the highest K_{POM} value for TBT from Table 4.2.

$M_{TBT\_POM} = M_{POM} * K_{POM}C_w = (1\text{-}4E)*43*C_w$. It is a very small fraction compared with the other three. And the calculation results point out that M_{TBT_POM} can be ignored as M_{TBT_water}. Therefore, fractions of TBT in BC and OC are the same as those in System A. The low TBT in POM is because of the low K_{POM} value. POM did not work on DBT at all in the experiment. But using following formula, water concentration of MBT at the presence of POM can be calculated.

$$\boldsymbol{M_{TBT} = M_{TBT\_BC} + M_{TBT\_water} + M_{TBT\_OC} + M_{TBT\_POM}}$$

$$\boldsymbol{= M_{sed} * f_{bc}K_{F,BC}C_w^{nBC} + V_w * C_w + M_{sed} * f_{oc}K_{oc}C_w + M_{POM} * K_{POM}C_w} \qquad \textbf{(11)}$$

The calculation results are as follows.

$C_w = 3.54$ug/l

M_{TBT_BC}: 12%; M_{TBT_water}: 68%; M_{TBT_OC}: 0.7%; M_{TBT_POM}: 19.3%

The results show a better sorption to MBT comparing with the sorption to TBT and DBT. But the most partitioning of MBT is still in the water phase, which indicates POM not a good measurement material for MBT as well.

6.2.2 BSAF calculation

BSAF value with POM in this system can be calculated by Eq. (12).

$$\boldsymbol{BSAF_{POM} = K_{lipid}*C_W* f_{OC}/C_{sed}} \qquad \textbf{(12)}$$

Where TOC is regarded as OC.

Due to the low POM concentration, the water concentrations of TBT and DBT almost do not change. BSAF values with POM for these two compounds will be the same as those in System A. The calculated BSAF value with POM for MBT is 0.0034 for *Buccinum undatum*. Comparing with the BSAF value without POM and BC in Table 5.1 (a) and with just BC in Table 5.1(b), the presence of POM effects the BSAF much due to the better sorption of MBT than BC. However POM is just the measurement material for organic matters.

5.3 System C—Sediment, artificial seawater and additional BC

5.3.1 Sorption evaluation

In this system, BC is added as a sorbent due to its ideal sorption ability as shown in the calculation in System A. The assumption for sediment and seawater is the same as that for System A and B. I add +2%, +10%, +20% BC to the system to find the relationship between water concentration and sediment concentration. K_{lipid} values are regarded as the same as K_{ow} values for the calculation, so this system aims to give a general view of how BC works on TBT, DBT and MBT partitioning. In Figure 5.4, the black area between seawater and sediment indicates black carbon.

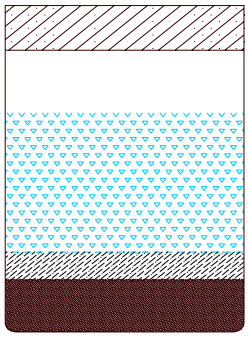
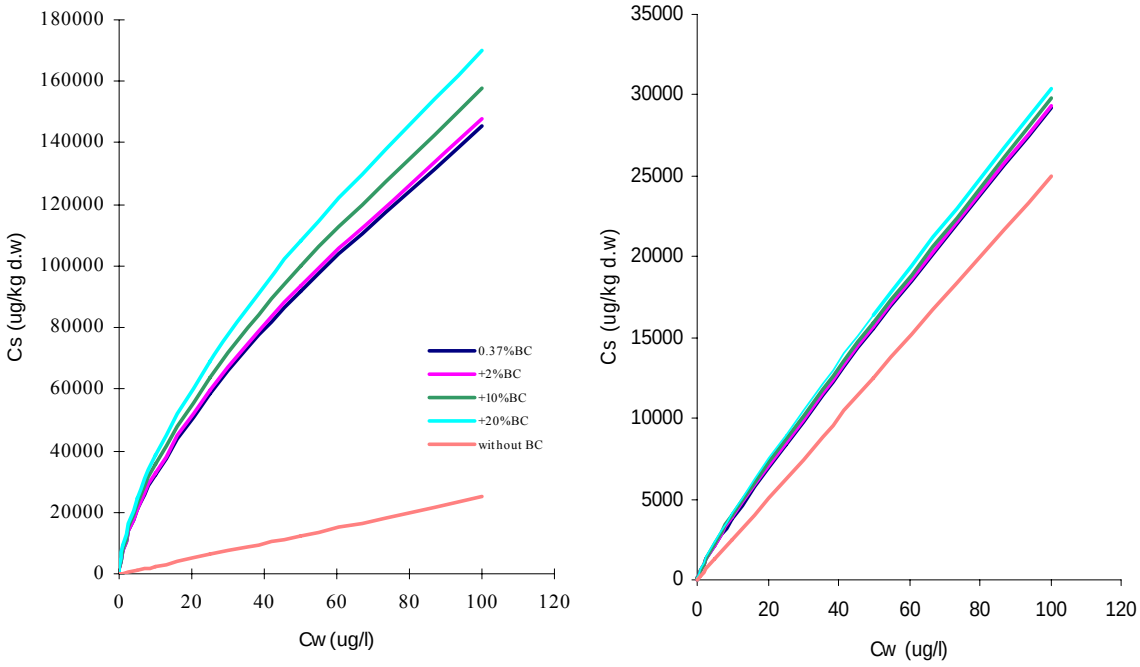


Figure 5.4 System with sediment and artificial seawater and additional BC

It is obvious that sediment concentrations increase with the increase amount of added BC (Figure 5.5 a). The model in System A has shown the importance of BC in the sorption of TBT, DBT and MBT. Therefore, if additional BC is added to the sediment, there will be more sorption to the sediment and less release to the water phase. Then the threat to the aquatic life will be reduced.

In Figure 5.5 (a), the relationship between sediment concentration and water concentration is linear if there is no BC in the system. And the ratio of sediment concentration to water concentration is K_d. The sorption to the sediment without BC is limited comparing with sorption with BC. Due to $f_{bc}K_{F,BC}C_w^{nBC}$ partition in Eq. (7), the relationship between sediment concentration and water concentration will be nonlinear. The curve with 0.37% BC is for the sediment of sample X1. The sediment concentration

does not change obviously when +2% BC is added. However, when there is more BC added in the system, the increase of the sediment concentration will be apparent.



(a) (b)

Figure 5.5 Modelled sediment concentration as a function of water concentration for TBT at (a) log $K_{F, BC}$ = 6.3, (b) log $K_{F, BC}$ = 5.0

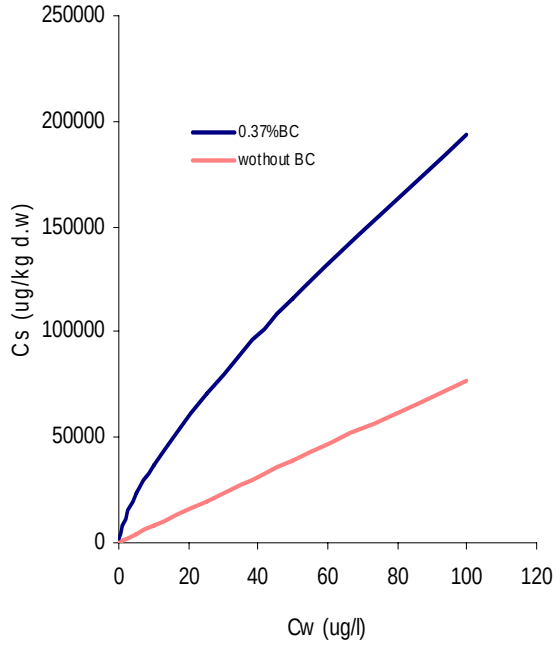


Figure 5.6 Modelled sediment concentration as a function of water concentration for phenanthrene

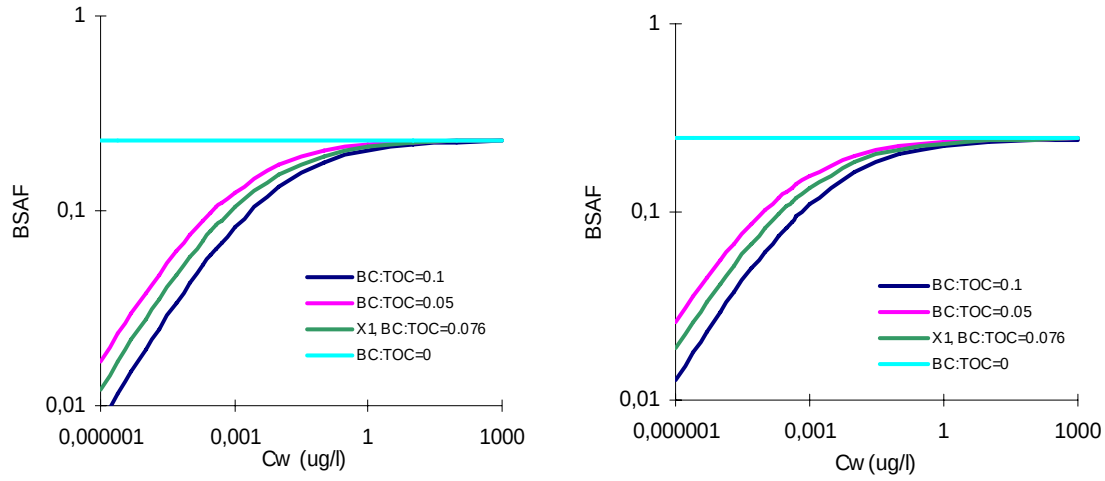
Figure 5.5 (b) is modelled with log $K_{F, BC}$ = 5.0. It implies a much less sediment concentration at the same water concentration. The sorption with BC and without BC in Figure 5.5 (b) is not a difference as huge as that in (a). And with added BC, sorption to the sediment increases more slowly in (b). Figure 5.5 (a) shows an extremely high increasing of sorption to sediment with considering of BC, whereas, (b) shows a quite low tendency. The modelled result implies that log $K_{F, BC}$ value affects the BC sorption very much and it has to be chosen carefully.

As $K_{F,\ BC}$ value for TBT is the same as that for phenanthrene, I made the same C_{water}-$C_{sediment}$ model for phenanthrene (Figure 5.6), using $\log K_{F,\ BC}$ and K_d value from Oen and co-worker (2006) results. Theoretical K_d value is equal to 772 l/kg. The modelled outcome indicates a relatively good result for BC sorption.

5.3.2 BSAF calculation

Figure 5.7 (b) shows the BSAF values with the changing of water concentrations for TBT. BSAF values depend on water concentration very much. In this model, water concentration starts at 1 pg/l and BSAF value increases quickly at the beginning and slows down when the water concentration goes up. Cornelissen and Gustafsson (2005) pointed out that over 100 ng/l, BC's importance to overall PAH sorption diminishes to <20%. This implies that the BC effect of reduced bioavailability and, thus, reduced ecotoxicological risks is least pronounced for the most highly contaminated situation. Consequently, the effective use of BC is the sorption to slightly contaminated sediment. For sediment from Hovedøya harbour whose water concentration is 0.0137 ug/l, the effect of additional BC on reduced sorption and bioavailablity will not be as evident as that at lower water concentration. Figure 5.9 indicates the BSAF as a function of BC:TOC for TBT at water concentration of 0.1 ng/l and 10 ug/l, respectively. BSAF reducing rates decrease with the increase of water concentration. The figure emphasizes and proves the conclusion that BC shows more effective sorption to low concentration in the water. Actually, water phase could be regarded as a channel between sediment and organisms. When there is little TBT in the water, the relationship between the sediment and organims will be more important and considerable. And with the increase of water concentration, this relationship will go down. As BSAF is related to tissue concentration and sediment concentration, when the relationship between these two fractions reduces, the reflection of BSAF values will become less and less.

Moreover, BC content has a significant influence on BSAF values as indicates in Figure 5.7 (b). If there is no BC, BSAF value will be a constant as it is just related to tissue concentration and sediment concentration, whereas, the BSAF values will decrease with the increase of BC content. At the same water concentration, BSAF value with more BC is lower than that with less BC because there is more TBT in the sediment when the BC content is high.



(a) (b)

Figure 5.7 Modelled BSAF as a function of water concentration for (a) DBT, (b) TBT

Figure 5.7 (a) models the BSAF as a function of water concentration for DBT. Comparing (a) and (b), the outcomes are almost the same due to the $\log K_{F,\,BC}$ assumed. Since $\log K_{F,\,BC}$ values for DBT and MBT are chosen as the same reduction magnitude of log K_{oc} among TBT, DBT and MBT, the reduced magnitudes will be cancelled each other. As the water concentration and BC content are the same, the DBT and TBT graphs will not be different obviously. Therefore, MBT graph will be the similar one.

If BC:TOC value is zero, BSAF will be equal to K_{lipid}/K_{oc} refer to Eq. (9). That is K_{ow}/K_{oc} as the assumption in this system. So the BSAF values at the beginning for TBT, DBT and MBT are close to each other (Figure 5.8). However, with an increasing amount of BC added, the BSAF values go down for the three compounds.

It has to be noted that the BC:TOC values are used to calculate water concentrations. They form the basis to calculate BSAF values. BSAF value of TBT goes down faster than the other two compounds because TBT is much more hydrophobic. DBT curve and MBT curve are relatively close each other because the K_{ow} values are close. DBT and MBT show more hydrophilic, which indicates that these two compounds will be more difficult to be absorbed by BC since considerable amount is dissolved in the water, especially for MBT.

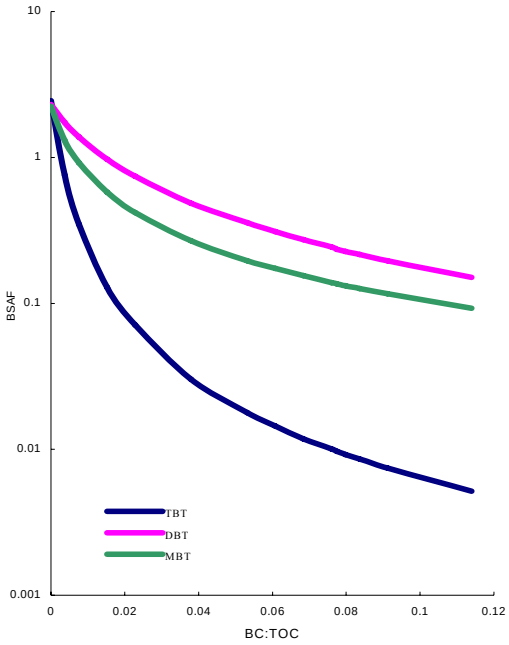


Figure 5.8 Modelled BSAF as a function of BC:TOC for TBT, DBT and MBT

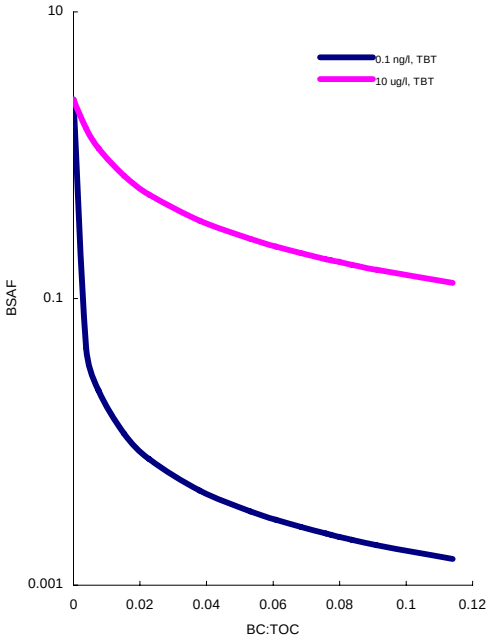


Figure 5.9 Modelled BSAF as a function of BC:TOC for TBT at water concentration 0.1 ng/l and 10 ug/l

Consequently, the models in this study imply that BC works well for the sorption of TBT, whereas not ideal for DBT and MBT. And the water concentration of TBT in Hovedøya harbour shows a disadvantageous situation for effective BC sorption.

6. Conclusion

TBT is widely used in antifouling paints on boats and is considered as the most toxic compound among the butyltin compounds. Although it has been banned to be used on ships longer than 25m, and there are some alternative paints used instead of TBT paints, TBT that has released to and been in the environment is still a huge threat to the ecosystem due to its high toxicity.

There are a lot of studies on TBT, DBT and MBT, about toxicity, characteristics, partition in the aquatic condition and so on. Based on their results and conclusion, we did the experiment to know about the pollution situation with these three compounds in Hovedøya harbour, which is the closest harbour to Oslo city. TBT is definitely the compound most focussed on because it not only showed highest sediment concentration, but also represents the highest threat to aquatic life. The measured sediment concentration showed abundant values for TBT and DBT, which indicated a good degradation condition in the harbour. The solid-water partition implies that the solubility is MBT>DBT>TBT, which can be explained by K_{ow} values as well, so TBT would like to combine with the sediment most.

Beside sediment extraction experiment, artificial seawater spiking was done as well. Four kinds of extraction solutions were used, whereas, only heptane&tropolene showed relatively good extraction results. POM was used as a measurement material in this experiment. Unfortunately, POM experiment showed an unsatisfied sorption result due to the quite low K_{POM} value. Therefore, POM is not an ideal sorption material for all the butyltin compounds. In chapter 5, POM was considered as a sorbent in system B, but the modelled outcome showed that there was almost no difference between with and without POM except for MBT. However it can be concluded from the experiment that POM is not an ideal material for the measurement of TBT, DBT and MBT.

As BC shows good sorption ability to hydrophobic compounds, it was considered in the sorption models in Chapter 5. Although it is only a small portion of TOC, it was evident that the sorption results with and without BC are extremely different. However, BC was not effective in all kind of situations. At high water concentration conditions, sorption with BC went down relatively. The water concentration in Hovedøya harbour is not a

good condition for BC sorption because it is not low enough. But BC still works on the sorption of TBT, DBT and MBT if additional BC is added to the sediment.

With the known BSAF or BCF values, tissue concentrations of some organisms were estimated. The evaluated outcomes in the assumed system showed an acceptable condition of TBT concentration in the sediment for organisms, but not in the water comparing with LC_{50} values in Table 1.4. The underestimation of K_d value could be the reason of high tissue concentration, and it is reasonable and possible that the observed K_d value is higher than the theoretical value because of the presence of BC.

7. Future researches

The experiment in this research just focused on the sorption of organotin compounds with POM and the results were unsatisfactory. But from the models in chapter 5, BC could be a good sorbent for organotin compounds, especially for TBT. Unfortunately, there are very few literatures about BC sorption for TBT, which means that this field of research should be given priority.

Activated carbon (AC) can be a good sorbent as well whose Freundlich BC-water distribution ratio ($K_{F,AC}$) values for PCBs are listed in Table 3.5. $K_{F,AC}$ values for PCBs are higher than $K_{F,BC}$ values for PAHs, probably because of the characteristics of PAHs and PCBs or the better sorption ability of AC. There are a couple of studies on AC sorption for TBT. Prasad and Schafran (2006) claimed that TBT has a high affinity for granular activated carbon (GAC) based on their preliminary test for the full-scale treatment, especially for dissolved TBT. And their full-scale treatment reduced TBT concentration from 1,000,000 ng/L to 50 ng/L successfully in three years. Its application in the marine tank is also under the way although it is still under the debate.

Beside sorption, biodegradation is a widely known way to break down TBT to DBT and MBT. But this process is much more complicated and harder to control. There are a lot of literatures about biodegradation of TBT and some were mentioned in chapter 1. Although some conclusions are under the debate, no doubt that it is an effective way to reduce the toxicity of TBT. Further researches in this field will be meaningful for the ecosystem.

However, the most important thing is to prevent the source of TBT. Besides the ban on TBT paints, some new paints with less toxic materials should be used instead of TBT paints. This will result in an improvement of marine environment on the long-term.

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Appendix I. Oslo and Paris Commission biological effects assessment criteria for imposex in *N. lapillus*, based on VDSI (OSPAR, 2004)

Assessment class	VDSI	Effects and impacts
A	VDSI = <0.3	The level of imposex in the more sensitive gastropod species is close to zero (0 - ~30% of females have imposex) indicating exposure to TBT concentrations close to zero, which is the objective in the OSPAR strategy of hazardous substances.
B	VDSI = 0.3 - <2.0	The level of imposex in the more sensitive gastropod species (~30 - ~100 % of the females have imposex) indicates exposure to TBT concentrations below the EAC derived for TBT. E.g. adverse effects in the more sensitive taxa of the ecosystem caused by long-term exposure to TBT are predicted to be unlikely to occur.
C	VDSI = 2.0 - <4.0	The level of imposex in the more sensitive gastropod species indicates exposure to TBT concentrations higher than the Environmental Assessment Criteria (EAC) derived for TBT. e.g. there is a risk of adverse effects, such as reduced growth and recruitment, in the more sensitive taxa of the ecosystem caused by long-term exposure to TBT.
D	VDSI = 4.0 - 5.0	The reproductive capacity in the populations of the more sensitive gastropod species, such as *N. lapillus*, is affected as a result of the presence of sterile females, but some reproductively capable females remain. e.g. there is evidence of adverse effects, which can be directly associated with the exposure to TBT.
E	VDSI = > 5.0	Populations of the more sensitive gastropod species, such as *N. lapillus*, are unable to reproduce. The majority, if not all females within the population have been sterilized.
F	VDSI = -	The populations of the more sensitive gastropod species, such as *N. lapillus* and *Ocinebrina aciculata*, are absent/expired.

Appendix II. Butyltin solid-water partition in the sediment

Compound	Solid (ug/kg d.w)	Porewater (ug/l)	Sediment (ug/kg d.w)
TBT	539	2.16	542
DBT	182	276	567
MBT	2.15	43	62

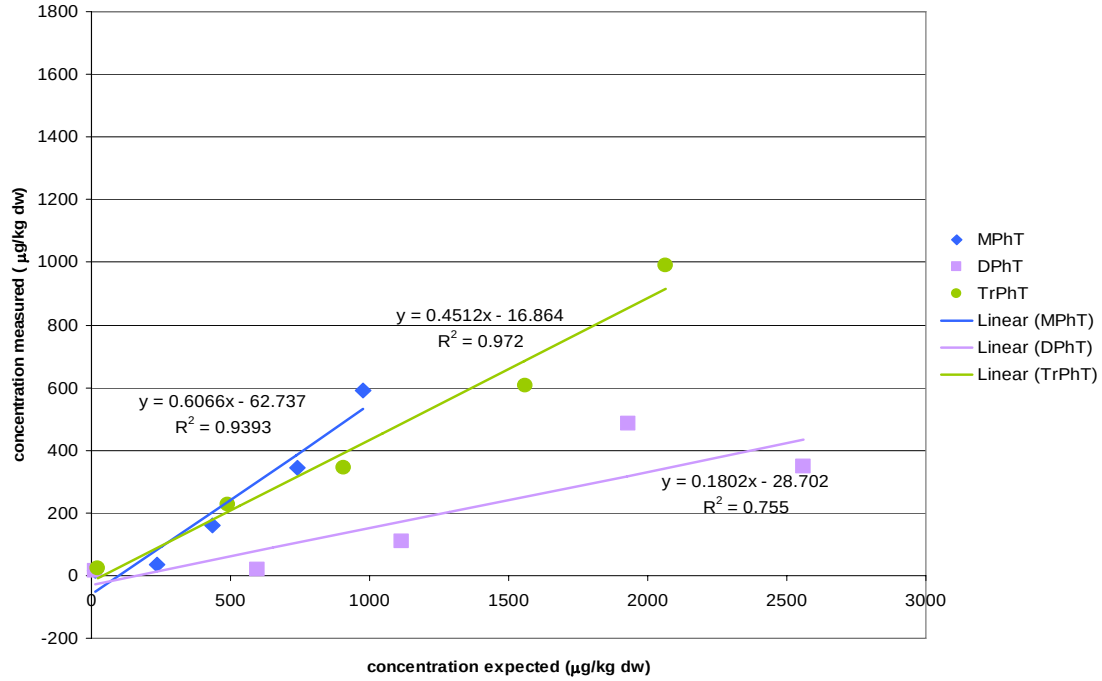
Appendix III. Butyltin fraction in model of System A

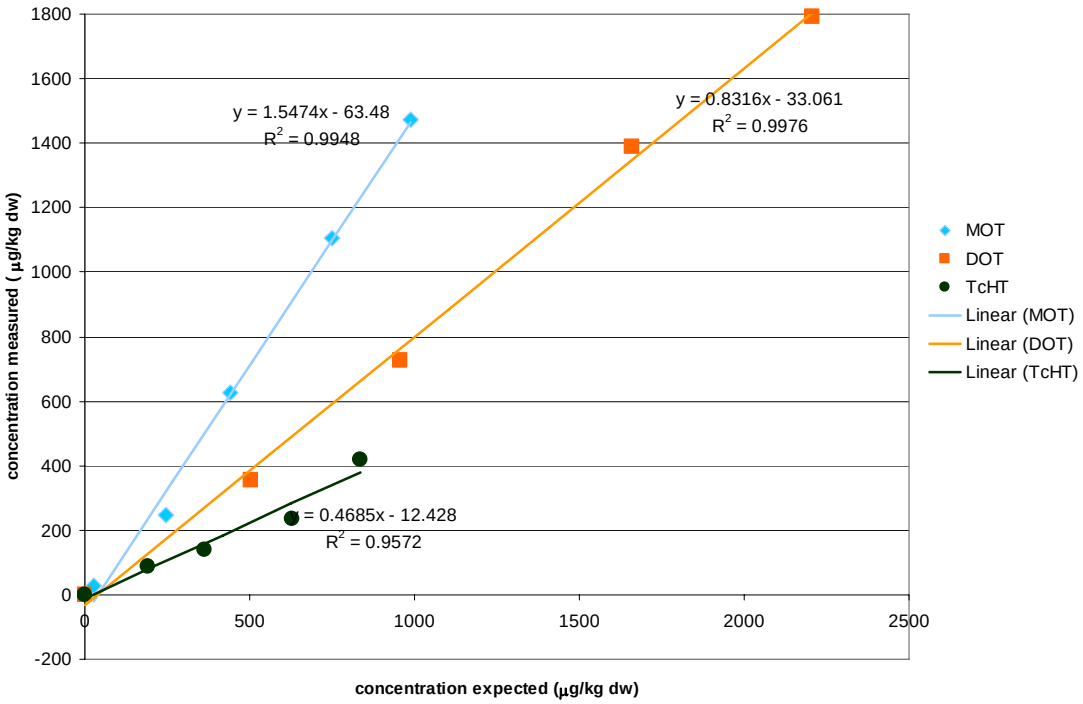
Compound	OC %	BC %	Water %
TBT	0.6	99.4	0
DBT	5.5	50	44.5
MBT	0.8	15	84.2

Appendix IV. Sediment concentration of organotin compounds from sediment extraction

	X1 1	X1 2	X1 3
Extraktkonzentrationen [pg/uL]			
MBT	71.80	69.68	64.70
DBT	653.05	630.79	585.36
MPhT	22.25	23.15	17.23
TBT	628.57	599.37	560.98
MOT	36.59	36.03	32.71
DPhT	19.20	19.47	N.D.
DOT	N.D.	N.D.	N.D.
TcHT	N.D.	N.D.	N.D.
TrPhT	36.70	N.D.	25.69
Konzentrationen [ug/kg dw]			
MBT	54.34	53.81	48.69
DBT	494.27	487.10	440.53
MPhT	16.84	17.88	12.97
TBT	475.74	462.83	422.19
MOT	27.69	27.82	24.62
DPhT	14.53	15.03	nd
DOT	nd	nd	nd
TcHT	nd	nd	nd
TrPhT	27.78	nd	19.33

Appendix V. Expected and measured values of other six organotin compounds from sediment spiking





Appendix VI. Concentration of organotin compounds in sediment spiking

+50%			+100%			+150%			+200%		
X1 1	X1 2	X1 3	X1 1	X1 2	X1 3	X1 1	X1 2	X1 3	X1 1	X1 2	X1 3
Extra organotin to add (ul)											
1.44	1.39	1.29	2.87	2.79	2.59	4.31	4.18	3.88	5.74	5.57	5.18
13.06	12.62	11.71	26.12	25.23	23.41	39.18	37.85	35.12	52.24	50.46	46.83
0.44500	0.46	0.34	0.89	0.93	0.69	1.34	1.39	1.03	1.78	1.85	1.38
12.57	11.99	11.22	25.14	23.97	22.44	37.71	35.96	33.66	50.29	47.95	44.88
0.73	0.72	0.65	1.46	1.44	1.31	2.20	2.16	1.96	2.93	2.88	2.62
0.38	0.39	N.D.	0.77	0.78	N.D.	1.15	1.17	N.D.	1.54	1.56	N.D.
N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
0.73	N.D.	0.51	1.47	N.D.	1.03	2.20	N.D.	1.54	2.94	N.D.	2.06
Extra organotin to add (ug/kg dw)											
32.48	32.16	29.10	64.96	64.32	58.20	97.43	96.47	87.30	129.91	128.63	116.41
295.40	291.12	263.29	590.80	582.23	526.58	886.21	873.35	789.87	1181.61	1164.47	1053.15
10.06	10.68	7.75	20.13	21.37	15.50	30.19	32.05	23.25	40.26	42.74	31.00
284.33	276.62	252.32	568.66	553.23	504.65	852.99	829.85	756.97	1137.32	1106.46	1009.29
16.55	16.63	14.71	33.10	33.26	29.43	49.65	49.88	44.14	66.20	66.51	58.85
8.68	8.99	nd	17.37	17.97	nd	26.05	26.96	nd	34.74	35.94	nd
nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
16.60	nd	11.56	33.20	nd	23.11	49.80	nd	34.67	66.40	nd	46.22

Appendix VII. Recovery calculation for organotin compounds from seawater spiking

	Heptane	Heptane&acid	Heptane&tropolene	Heptane&tropolene&acid
Amount of organotins from both POM and seawater				
MBT	12.97	17.31	405.43	351.95
DBT	N.D.	289.1	376.12	285.06
MPhT	N.D.	N.D.	182.73	256.09
TBT	673.33	533.98	546.41	482.24
MOT	45.82	159.72	671.36	377.09
DPhT	N.D.	463	621.01	57.33
DOT	642.11	1148.37	805.75	607.01
TcHT	6308.69	543.38	460.9	324.45
TrPhT	11686.14	1189.79	617.92	239.91
Recovery of organotins from both POM and seawater				
MBT	2.594	3.462	81.086	70.39
DBT	nd	57.82	75.224	57.012
MPhT	nd	nd	36.546	51.218
TBT	134.666	106.796	109.282	96.448
MOT	9.164	31.944	134.272	75.418
DPhT	nd	92.6	124.202	11.466
DOT	128.422	229.674	161.15	121.402
TcHT	1261.738	108.676	92.18	64.89
TrPhT	2337.228	237.958	123.584	47.982
Amount of organotin lost				
MBT	487.03	482.69	94.57	148.05
DBT	500	210.9	123.88	214.94
MPhT	500	500	317.27	243.91
TBT	-173.33	-33.98	-46.41	17.76
MOT	454.18	340.28	-171.36	122.91
DPhT	500	37	-121.01	442.67
DOT	-142.11	-648.37	-305.75	-107.01
TcHT	-5808.69	-43.38	39.1	175.55
TrPhT	-11186.14	-689.79	-117.92	260.09

	Heptane		Heptane&acid		Heptane&tropolene		Heptane&tropolene&acid	
	POM	water	POM	water	POM	water	POM	water
MBT	N.D.	12.97	17.31	N.D.	87.76	317.67	69.24	282.71
DBT	N.D.	N.D.	N.D.	289.1	N.D.	376.12	N.D.	285.06
MPhT	N.D.	N.D.	N.D.	N.D.	27.44	155.29	41.15	214.94
TBT	38.52	634.81	N.D.	533.98	41.28	505.13	42	440.24
MOT	N.D.	45.82	123.34	36.38	379.19	292.17	182.04	195.05
DPhT	N.D.	N.D.	235.72	227.28	N.D.	621.01	N.D.	57.33
DOT	428.11	214	440.33	708.04	482.61	323.14	361.8	245.21
TcHT	510.69	5798	N.D.	543.38	264.22	196.68	N.D.	324.45
TrPhT	137.33	11548.81	N.D.	1189.79	N.D.	617.92	N.D.	239.91

Appendix VIII. Calibatation of organotin compounds

		MBT	DBT	MphT	TBT	MOT	DPhT	DOT	TcHT	TrPhT
Area(organotin)/Area(IS)	5 ug/l	0.189927	0.080455	0.123531	0.142919	0.137382	0.142864	0.113291	0.131626	0.30043
	10 ug/l	0.37446	0.150456	0.248501	0.231275	0.240255	0.261397	0.226284	0.205238	0.560158
	25 ug/l	0.934049	0.360842	0.578329	0.500558	0.559995	0.569225	0.529527	0.474291	1.264168
	50 ug/l	1.719266	0.71201	1.049609	0.94592	1.171056	1.125508	0.973924	0.855096	2.452535
	100 ug/l	3.813026	1.300471	1.876302	1.820707	2.204843	2.473385	1.857912	1.748306	4.877071
	500 ug/l	20.34861	7.271539	12.09875	11.80642	15.23364	13.10946	10.94711	9.350875	30.42407
	1000 ug/l	42.05257	15.92621	25.98826	26.39422	35.21033	30.98019	24.60832	19.2848	73.05696
Conc(organotin)/Conc(IS)	5 ug/l	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
	10 ug/l	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
	25 ug/l	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
	50 ug/l	1	1	1	1	1	1	1	1	1
	100 ug/l	2	2	2	2	2	2	2	2	2
	500 ug/l	10	10	10	10	10	10	10	10	10
	1000 ug/l	20	20	20	20	20	20	20	20	20

Appendix IX. BC-inclusive model values for System C

	BC%	0	0.0185	0.037	0.074	0.111	0.185	0.259	0.296	0.333	0.37	0.377	0.3885	0.407	0.444	0.555
	Cw	1.15	0.34	0.158	0.057	0.033	0.013	0.0079	0.006	0.0052	0.0045	0.004	0.0041	0.0038	0.0033	0.0023
TBT	BC/TOC	0	0.0038	0.0076	0.0152	0.023	0.038	0.0532	0.061	0.0684	0.076	0.077	0.0798	0.0836	0.0912	0.114
	BSAF_BC	2.455	0.755	0.347	0.129	0.07	0.03	0.018	0.014	0.012	0.01	0.01	0.009	0.009	0.007	0.005
	Cw	42.2	41	39	36.2	34	29	26	24	22.5	21	20	19.5	19	18	15.5
DBT	BC/TOC	0	0.0038	0.0076	0.0152	0.023	0.038	0.0532	0.061	0.0684	0.076	0.077	0.0798	0.0836	0.0912	0.114
	BSAF_BC	2.305	1.7381	1.3843	0.9729	0.742	0.487	0.3572	0.31	0.2738	0.2435	0.235	0.2271	0.2158	0.1955	0.1507
	Cw	5.14	5.1	5.05	4.99	4.89	4.76	4.6	4.58	4.5	4.4	4.39	4.38	4.37	4.37	4.19
MBT	BC/TOC	0	0.0038	0.0076	0.0152	0.023	0.038	0.0532	0.061	0.0684	0.076	0.077	0.0798	0.0836	0.0912	0.114
	BSAF_BC	2.243	1.3075	0.9207	0.5772	0.418	0.269	0.1963	0.173	0.1545	0.1388	0.136	0.1324	0.1266	0.1166	0.0928