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analysis and fate studies

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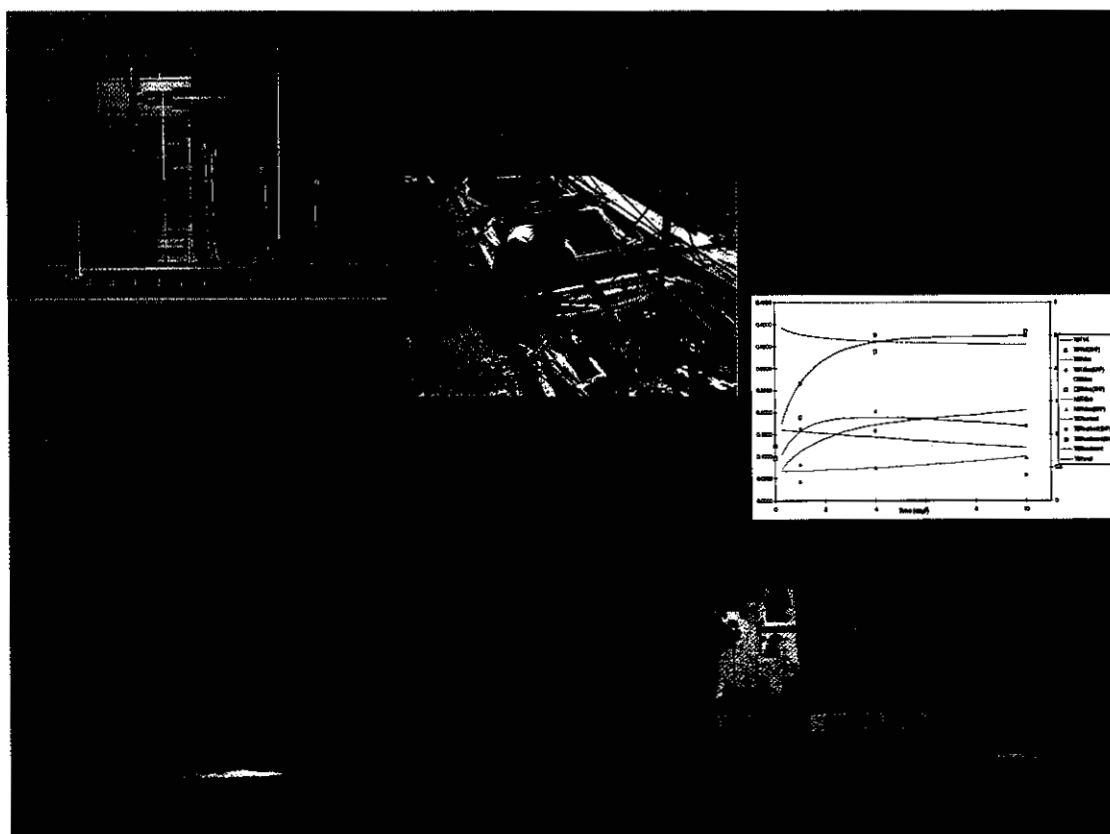
PhD Thesis

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Organotin compounds in the Danish marine environment: analysis & fate studies

PhD thesis
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Table of Contents

1   Preface and general introduction

The most significant environmental chemicals have usually been identified as a result of their ecological damage to non-target organisms, rather than by routine laboratory testing. Tributyltin (TBT), through its widespread effects, particularly on molluscs, must rank among the most significant of all.

W.J. Langston 1996

The PhD thesis is based on 5 years of research at the Dept. of Marine Ecology and Microbiology, National Environmental research Institute (NERI) in co-operation with Roskilde University. The study has partly been financed by NERI, The Danish EPA, the Nordic Council of Ministers, and the EU MAST(project . The PhD title is "Organotin compounds in the marine environment: analysis, fate experiments and modelling". The Supervisors at University of Roskilde was Prof. Ole Andersen. Supervisor at NERI was senior researcher Dr. Britta Pedersen.

The thesis is part of on going research activities at NERI on antifouling agents used on ships and their impact on marine ecosystems. The antifouling research at NERI has taken part for a decade, more or less intensive and is currently employing approximately 4 staff full time (2 researchers). The strong NERI involvement in antifouling research is based on the hypothesis, that the Danish marine environment is likely to be one of the most antifouling polluted areas, due the dense commercial shipping traffic and the narrow and shallow waterways. The hypothesis is supported by recent reports from the antifouling group, organotin measurements in the marine environment could be linked to widespread effects from TBT. For a number of years, the use organotin compounds in the marine environment has been debated by environmental researchers, non-governmental organisations and regulatory authorities. Recent national regulation in 1991, where TBT was banned for use on boats < 25 m, followed an international legislation. These measures were expected to reduce the TBT use to a tolerable level. However, only little information was available about the extent of TBT contamination and its effects on a national scale. The knowledge on how to follow the fate of organotins in the Danish marine environment was not in place and therefore a project was initiated by NERI and the Danish EPA.

The thesis is divided in three parts:
(1) Introduction to the thesis
(2) Technical annex – modelling of triorganotin (TBT and TPhT) in marine enclosures
(3) Papers produced for this thesis (5 papers)

The introduction part is linking the five papers together. In the technical annex, there is a more detailed description of TBT and TPhT fate modelling. A major link between the papers is the demonstration of the versatility of the developed analytical methodology to speciate organotins in different matrices. In addition, the papers illustrate the ongoing process of trying to get a better understanding of how anthropogenic substances are distributed in the environment. The work is focusing on the shallow and densely utilised Danish estuarine coastal marine environment and the adjacent Swedish West Coast. In addition, these seawaters are highly influenced by nutrient loading from human effluents originating from agricultural, industrial and household sources.

In paper I the development of a cost-effective method is described. The work was done in order to enable the measurements of organotin compounds at ultra trace levels in aqueous, sedimentary and biota phases. The method is based on GC techniques combined with pulsed flame photometer detection (PFPD). This is a novel detector type, which is here shown to be effective both regarding to sensitivity and selectivity for determination of organotin compounds.

Paper II describes an experiment where the capability and versatility of the new method is demonstrated when applied to mesocosm experiments at environmentally realistic contamination levels. The paper determines organotin desorption rates for newly contaminated sediments. Such rates are important in risks assessments for the environment e.g. when contaminated harbour dredge spoils are to be deposited in more pristine environments. The possibility to estimate the release of contaminants from sediments is important, as sediments are known to act as sinks for contaminants and thus during dredging can become sources for such contaminants.

In paper III the method is applied to environmental measurements are made in relation to sources. The main conclusion of paper III is that even if sediment is a sink for contaminants, substances as TBT are still bioavailable for living organisms, which can bioaccumulate TBT to much higher levels from sediments than from aqueous phases.

In paper IV, the vertical distribution of TBT and degradation products measured in sediment cores, suggests that TBT is not easily degradable in Swedish and Danish marine sediments, with half live in the order of decades. Nevertheless, trends from the sediment indicate that the TBT pollution has peaked a few years ago.

Paper V is a presentation of TBT pollution in the Arctic area off the West Coast of Greenland. This is a demonstration of the sensitivity of the analytical method, but also of the widespread contamination of organotins in the environment.

Papers submitted for the thesis. Manuscripts can be seen in Appendices.

PAPER I
Jacobsen, J.A., Stuer-Lauridsen, F. and Pritzl, G. (1997): Organotin Speciation in Environmental Samples by Capillary Gas Chromatography and Pulsed Flame Photometric Detection (PFPD) Appl. Organometallic Chem., 11, pp 737-741.

PAPER II
Jacobsen J.A. and Stuer-Lauridsen, F. Sorption and desorption rates of tri-*n*-butyltin (TBT) and triphenyltin (TPhT) in marine enclosure experiments (Submitted to *Environmental Toxicology and Chemistry*)

PAPER III
Jacobsen, J.A., Strand, J., Pedersen, B & Granmo, Å (Subm. 2000) Organotin compounds in Biota in the Shipping Strait between Sweden and Denmark (Øresund) (Submitted to:*Chemosphere*)

PAPER IV
Jacobsen J.A., and Strand, J.(Subm. 2000) Depositional Profiles of Butyltin Residues in Marine Sediments from the Sound Between Sweden and Denmark, (Submitted to *Environmental Technology*)

PAPER V
Jacobsen, J. A. and Asmund, G.(2000) TBT in marine sediments and blue mussels (*Mytilus edulis*) from Central-West Greenland *Science of the Total Environment*, 245, 131-136.

Acknowledgements

2 Summary

The environmental chemistry of antifouling compounds in the marine environment is of special concern to the ecosystems in the Danish waters, due to the high shipping intensity and the shallow waters. This study is focussed on the regional distribution of one of most toxic substances deliberately released to the marine environment.

Selective and sensitive determination methods are necessary for organotin compounds in various matrices in order to study the fate and effects in the marine environment. The target limit of detections better than 1 ng/L in seawater and 1 µg/kg in sediment and biota were achieved.

A novel detectortype (pulsed flame photometric detector, PFPD) for gas chromatography was implemented and used as the main analytical instrument for this work. The major features are the long-term stability and the sensitivity and selectivity for tin.

Spiking experiments of TBT and TPhT in marine mesocosms show that the most important short-term fate was related to sorption and sedimentation processes. Release rates of both TBT and TPhT form polluted sediments were determined.

TBT and degradation products are widespread in the Danish marine environment. Studies from a shipping lane show that concentrations depend on distance to hot spots and to a lesser extent shipping lanes. The same study shows TBT in sediments are seemingly bio-available to sediment feeding organisms.

Sediment cores from the same region show historical trends of TBT. Estimated degradation half-lives is comparable to the slowest rates found elsewhere (more than 10 years). Nevertheless, indications of decreasing TBT concentrations in the top sediment layers could be reported.

Measurements of detectable concentrations of TBT in blue mussels from the Greenland marine environment show that TBT is widely distributed even in this remote region. TBT in sediments from the same region indicate that degradation is very slow.

3 Dansk sammendrag

En analysemetode til måling af TBT på ultra sporstofniveau i samtlige matricer er nødvendig hvis relevante studier af stoffets forekomst skæbne og effekter skal kunne gennemføres. TBT er giftigt i niveauer der i mange år ikke har været muligt at måle. Et af formålene med dette projekt var derfor at udvikle en målemetode, der kunne kvantificere og identificere ikke blot TBT, men også TPhT og disses nedbrydningsprodukter i koncentrationer under 1 ng/L og alternativt under 1 µg/kg sediment eller biologisk materiale. Hermed var det også muligt at undersøge hvordan TBT og TPhT fordeler sig i miljøet og om det nedbrydes og hvordan det genfrigives fra forurenede sedimenter.

Den nyligt udviklede pulserende flammefotometriske detektor til gaskromatografi viste sig at være et væsentligt værktøj i processsen. Den viste sig at være en både en følsom og ideel detektortype til tinorganiske forbindelser i miljøprøver.

TBT og TPhT spredningen i et nær naturligt system, marine mesocosmer på 6000 liter indikerer at de vigtigste fjernelsesprocesser for TBT og TPhT i miljøet er sorption og sedimentation.

TBT og nedrbydningsprodukter findes udbredt i de danske farvande i alt undersøgt biologisk materiale, i sedimenter fra åbne farvande. Der er en tilsyneladende afhængighed af kilden, såsom skibstrafik og havneområder.

Sedimentkerner fra Øresund viser, at TBT enten nedbrydes meget langsomt eller på udvalgte steder, stort set ikke. En enkelt kerne viser TBT historikken over de seneste 30 år , og tilsyneladende er der en faldende TBT koncentration i de øverste sedimenter.

I muslingeprøver fra området omkring Nuuk, Grønland er der fundet TBT i mængder der kan vække bekymring. Sedimentmålinger viser at TBT stort set ikke nedbrydes i det Grønlandske miljø.

4 Introduction and scope of this thesis

Organotin (OT) compounds comprise of a group of very important industrially used group of compounds. They are frequently used as stabilising or process related additives in PVC plastics, polystyrene, polymers and silicone products. Another frequent use of this group of compounds is as active ingredients in wood protecting paints and disinfectants in general (CAS 1998).

Environmental concern has been for the pest controlling applications –the so-called booster biocides. Of special concern in the marine environment is the continuous use of tributyltin (TBT) and triphenyltin (TPhT) as the active compounds in antifouling paints on ships, where TBT is probably the most toxic compound deliberately used in the marine environment.

Effects
The first severe effects from TBT use as antifouling agent on boats was discovered by the group of Dr. Alzieu at University of Bordeaux. The oyster production almost stopped for a period of years because of elevated TBT concentrations in Arcachon Bay, which caused the development of oyster shell anomalies and low growth rates. (Alzieu *et al.*, 1982; Alzieu *et al.*, 1986). In 1982 France was also the first country to ban TBT to be used on boats below 25 meters in length.

Almost simultaneously, effects on marine snails from TBT in seawater were discovered. At TBT concentrations below one ng/L, 50 % of a marine snail population (dogwhelk, *Nucella lapillus*) developed a physical deformation of the genitalia later named, imposex (Gibbs & Bryan, 1986). This group at Plymouth Marine Laboratory, UK, associated the sexual malfunction and masculinisation of the dogwhelk, with low ng/L concentrations of TBT found in seawater. The worldwide use of TBT is matched by the widespread finding of similar effects throughout the marine environment, even in remote areas (Langston 1996). These effects from TBT in the marine environment underlines the importance of gathering all available data on the behaviour and fate of organotin compounds

Early concentration measurments
Measurements of TBT started to develop after the severe effects were discovered. However, the task was very challenging and very costly, due to the low concentrations at which TBT had to be measured. Methods are described and discussed in the analytical development (Chapter 6).

The concentration of TBT was often measured as total organic extractable tin and not specifically as the TBT species. This could lead to erratic results due to the widely use of other organotin compounds than TBT for e.g. laboratory equipment or sampling devices (Sadiki *et al.*, 1996).

The very first measurements were from the Arcachon bay in France, where organotin concentration levels in the late 70ies and early 80ies reached µg/L range. In addition, in the United Kingdom early measurements of organotin concentration levels were in the low µg/L range.

4.1 Scope of the thesis

The alarming results because of the presence of TBT in the marine environment found in several other countries stresses the importance to investigate the situation in Danish waters. Only little information was available at the time, when the partial ban was effectuated. The Danish marine environment was expected to be highly TBT polluted, because of high shipping intensities coupled with the rather shallow Danish waters.
Organotin compounds continue to represent a risk to the marine environment even after the partial ban, due to their toxicity, slow degradation rate and high bioaccumulation potential. The Danish marine environment was expected to be highly TBT polluted, because of high shipping intensities continuously distributes TBT into these shallow waters.

The Objectives of the work behind the thesis was therefore:
- To develop analytical procedures for detection of organotins on the recently developed GC-PFPD.
- To apply the method on primarily environmental materials (water, biota and sediment) at environmentally relevant concentrations.
- To develop a predictive (descriptive) model for the simplified marine environment based on mesocosm experiments.
- To support the work on TBT (and TPhT) effect measurements

5 Properties of organotin compounds

Organotins (OT) were first synthesised in the 19th century, but their industrial production increased simultaneously to the boom in plastic products after World War II. Findings showed that dioctyl and dibutyltin added as PVC stabilisers in these products aided against decay especially from heat and light. This is connected to the strong affinity of tin for donor atoms, such as oxygen and sulphur. Another important property is the physiological reactions of triorganotins (TOT) used as pesticides, disinfectants or fungicides, which were marketed in the 1950ies. The triorganotins as tributyltin (TBT) and triphenyltin (TPhT) were considered common sense, due to the low mammalian toxicity. Antifouling paints containing TBT were marketed first in the 1960ies (Omae 1989; Stäb 1995).

5.1 Compound Structures

Organotin compounds are tetra or divalent tin with one or more covalent bonded organic group. They form chemically stable compounds with aliphatic as well as aromatic groups.
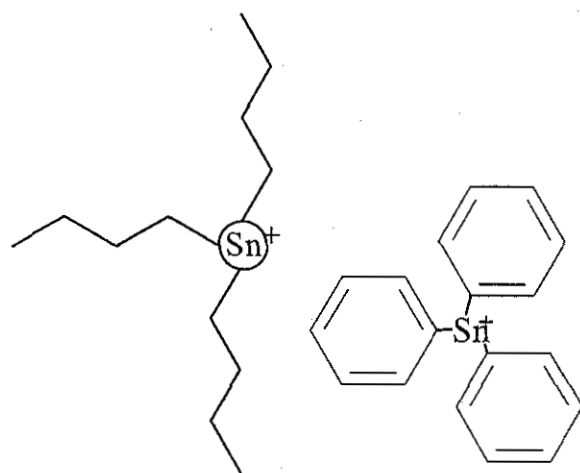
*Fig.5.1 Tri-*n-*butyltin (TBT) and triphenyltin (TPhT) as cations.*

In aqueous phase, the triorganotins are in equilibrium with anions as Cl⁻ and OH⁻, depending on ioncomposition and pH.

5.2 Environmental behaviour of organotins

Table 5.1 summarises selected basic properties of the chloride derivatives of TBT and TPhT, which are the standards used here.

Table **5.1** Selected chemical properties of TBTCl and TPhTCl,

	TBTCl	TPhTCl	Ref.
CAS No.	[1461-22-9]	[76-87-9]	
Formula	$(C_4H_9)_3SnCl$	$(C_6H_5)_3SnOH$	
Phase (20° C, 1 atm.)	liquid	solid	1
Mole weight	325 g/mole	385.46 g/mole	1
Melting point	-16 °C	106	1
Boiling point	140 °C (13 mbar)	>350 °C	1
Vapour pressure (20 °C)	-	$< 10^{-3}Pa$	1
pKa	6.25	5.20	2
Density (20 °C)	1.2 kg/L	1.41 kg/L	1
Aqueous solubility (20 °C)	75.8 mg/L	5 mg/L	1
Organic solvent solubility	good	good	1

[1]Miljøstyrelsen 1993, [2]Arnold *et al.* 1997

TBT and TPhT are mainly speciated as hydroxides at water condition found in the Danish waters. The general environmental relevant inherent properties of TBT and TPhT, as summarised in table 5.2, are information found in the literature. Sorption of organotin compounds onto particles, which is mostly followed by sedimentation (Weidenhaupt 1995, Stewart and Thompson 1997). These processes could scavenge most of the organotin compounds to the sediment. According to the literature, the aqueous degradation rates are faster than those found in the aerobic sediment and again faster than the anaerobic sediment (Stewart and de Mora 1990) Sediments are consequently important sinks for organotin compounds. TBT in sediments can accumulate in benthic organisms (See Paper III). Remobilization of organotin compounds can occur (Unger *et al.* 1987), e.g. due to disturbance of the sediments. This can again have possible toxicological implications for the marine environment.

Table **5.2**Environmental behaviour of TBT and TPhT:

Property	TBT	TPhT	Ref.
Kd (L/kg)	$(0.34 - 64) \times 10^3$	$(21-114) \times 10^3$	2
$logK_{OW}$	2.3-4.4	2.02-4.08	2
	4.1[1]	3.53[1]	3
log BCF	0.41-3.2	0.08-4.1	2
Degradation in sea-water (half lives)	4 – 26 days		4
Mediteranean deep seawater (no light)	> years		5
Degradation in sediments (half lives)	0.9-5.2 years		4

[1]Values for the triorganotin hydroxide species, [2]Fent 1996, [3]Arnold *et al.* 1997, [4]de Mora 1996. [5]Michel & Averty, 1999

5.3 Organotin sources to the environment

The primary source of organotin compounds to the marine environment is the use of trialkyltin based antifouling paints (TBT and TPhT). Di- and mono-organotins occur as a result of the degradation of these and the use of di- and monoalkylated (butyl, cyclohexyl and octyl) compounds as stabilisers in PVC and as catalysts in polymer production (Lawson 1986). The worldwide annual production of organotin (OT) compounds from 1940 to 1986 is shown in fig 5.1
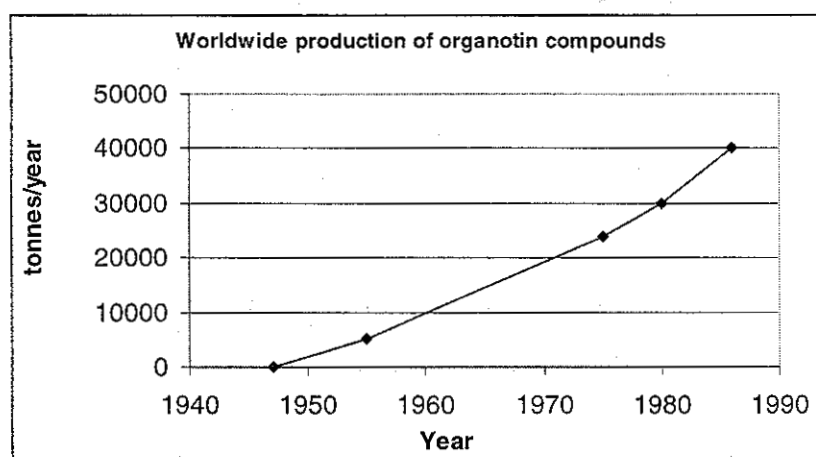
Fig. 5.2 Annual production of OT compounds (Stäb 1995).

The worldwide production of TBT was estimated by WHO to bearound 2-3000 tonnes per year (WHO report 1990) and later by Davies *et al.* in 1998 to around 1200 tonnes yr^{-1}(as TBT).

Table 5.3 Organotin utilisation in Denmark

Substance	Selected uses[1]	Estimated Danish consumption 1994[2] (tonnes per year)
Tri-organotin (primarily TBT and TPhT)	accelerator in polystyrene, anti-fouling agent, anti-tumor test substance, catalyst and accelerators in polymers and epoxy resins, disinfecting agent, insecticide, acrylic glass, molluscicide, spray-pyrolysis, wood preservatives, fungicide	30-36
Di-organotin (Primarily DBT, and dioctyltin)	PVC stabiliser, acrylic glass additive, co-polymer in rubber, heat and electro-conductive coatings, cross linking, , stabilisation in polymers	66-100
Mono organotin (Primarily MBT	glass coating[3], cross linking, stabilisation in polymers	0.5-0.8
Total consumption as tin (Sn)		22-32[4]

[1](Chemical Abstract Services Index 1995), [2]Danish EPA WR No. 7 1997, [3]End product tinoxide (non- organic), [4]calculated as Sn to facilitate comparison between products.

*PVC is accounting for 60 %
of the Danish OT
consumption*

In Table 5.3 the national mass balance of OT products are outlined in selected products and consumed amounts. Di- and mono-organotins (butyl- and octyltins) are used primarily as stabilisers in PVC and catalysts in the production of polyurethane and silicone. The triorganotin compounds are used almost exclusively in wood preservation and in the production of antifouling paints.

According to the a recent report (Danish EPA 1997), the important inputs of OT to the aquatic environment are from antifouling paints and municipal wastewater treatment plants (WWTP).

In WWTP, effluents of TBT, DBT and MBT were detected in concentrations from below limit of detection (<1 ng/L) to 40 ng/L (as Sn). The dominant OT species found is dibutyltin (Jacobsen 1999, unpublished results). This is confirmed by findings in WWTP sludge where mono-, di- and tributyltin as well as dioctyltin has been detected (Pritzl, pers. comm.). These amounts were estimated to be 0.6 to 12 tonnes yr^{-1} (as Sn). The yearly input of TBT from antifouling paints into the marine environment has been estimated to be between 0.2 and 1.4 tonnes yr^{-1} (as Sn) (Danish EPA 1997). A total estimate of organotin input to the aquatic environment (not solely marine) was between 4 and 17 tonnes per year (as Sn) (Danish EPA 1997).

5.4 TBT legislation

In Denmark the legislation on TBT, followed the implementation of EU directives in 1991, TBT was banned to be sold or used in antifouling paints for boats < 25 m length, fishing nets, marine constructions and buoys. Prior to this regulation, France had already banned TBT use on boats < 25 meters in 1982 and UK issued a similar ban in 1987. This regulation is now implemented in many countries.

Because of the partial ban in 1991, TBT has mainly been used for merchant ships and for wood preserving paints in the Danish region. The concentrations of OT compounds in the Danish waters are influenced by the busy shipping traffic of ships and ferries. Large displacement ships are constructed in Denmark, but after finishing most of them leave never to return (Kjær pers. comm.). The sources in the water column are therefore recent contamination and especially in marinas desorption from the polluted harbour sediments are expected. The use of TBT in wood preserving paints in Denmark is being phased out by a ban on sales and production issued June 1999. This regulation includes a total phase out in the middle of year 2000 (Nielsen 1999, pers. comm.).

Internationally, the regulation of TBT in antifouling paints for ships > 25 meters, is an issue for the United Nations organ, the International Maritime Organisation (IMO). They have proposed a regulation on marine use regarding the sale and paint applications in Year 2003 and a total ban in 2008. The process is ongoing and negotiations are continuing in the IMO at pres-

ent. Implementation of this ban is dependent on ratification processes by the membership countries during Year 2001.

In the EU membership countries, the antifouling agents in general, are due to are regulated by the so-called biocides directive, issued by the EU parliament in 1998. This regulation applies for all biocides, including antifouling agents, which after 14. May 2000 all new substances need to be approved prior to use. All biocides all ready on the market need to pass the approval process before a 10-Year period (Nielsen 1999 pers. comm).

Triphenyltin is not approved for use as fungicide but has been used in antifouling paints. Other organotin compounds than TBT and TPhT, are not at present regulated in Denmark.

6 Determination of organotin compounds in environmental matrices

The method development is described in paper I. In brief, a new extraction technique was implemented and a new detectortype installed on an existing GC system.

6.1 Scopes of organotin determination techniques

In order to carry out studies of organotin (OT) compounds in the marine environment the following objectives were set:

- To develop a robust analytical method that could quantify and identify phenyl-, butyl- and ethyltin derivatives.
- To implement extraction techniques of organotin from environmental matrices including seawater, surface microlayer, sediments, biota and solvent filled sedimentation traps.
- To improve the method so limits of detection are better than 1 ng Sn/L for aquatic samples and 1 µg Sn/kg for sediment and biota (based on biological effect concentration levels).

6.2 Introduction to organotin determination techniques

In order to measure a specific compound or group of compounds present in a matrix, it is important to investigate their inherent properties. The physical chemistry of organotin compounds is listed elsewhere in the previous chapter. An important feature for the capability for detection and quantification is the tin (Sn) atom, which is bonded to different organic ligands. Such compounds belong to an important class of chemicals, the so-called organometals. Naturally, analytical methods to determine OT compounds have been based on metal or other heteroatom determination techniques. Therefore many publications on analytical research include determination by atomic absorbtion spectrometry (AAS), mass spectrometry (MS) and lately also inductively coupled plasma mass spectrometry (ICP-MS).

Tin analysis based on heteroatom selectivity

If total amount of tin is measured, this does not specify how much of this is organotin or even less the amounts of TBT. For many environmental investigations, it is of crucial importance to know the amount of organic tin or even to specify the tin-species. Many methods determine the amount of organic extractable tin as described in Mortensen *et al.* (1996) and Fytianos & Samanindou, (1992).

An analytical method should be able to determine the different OT species also because large amounts of organotin com-

pounds are used for various laboratory products and reagents CAS 1998). This could interfere with the method in general and in worst case lead to bad limit of detections and erratic results.

A recent review (ICES 1998) describes the different approaches to the analytical techniques. As example the methods generally used for separation of OT compounds, extracted from marine sediments are illustrated in Figure 6.1.
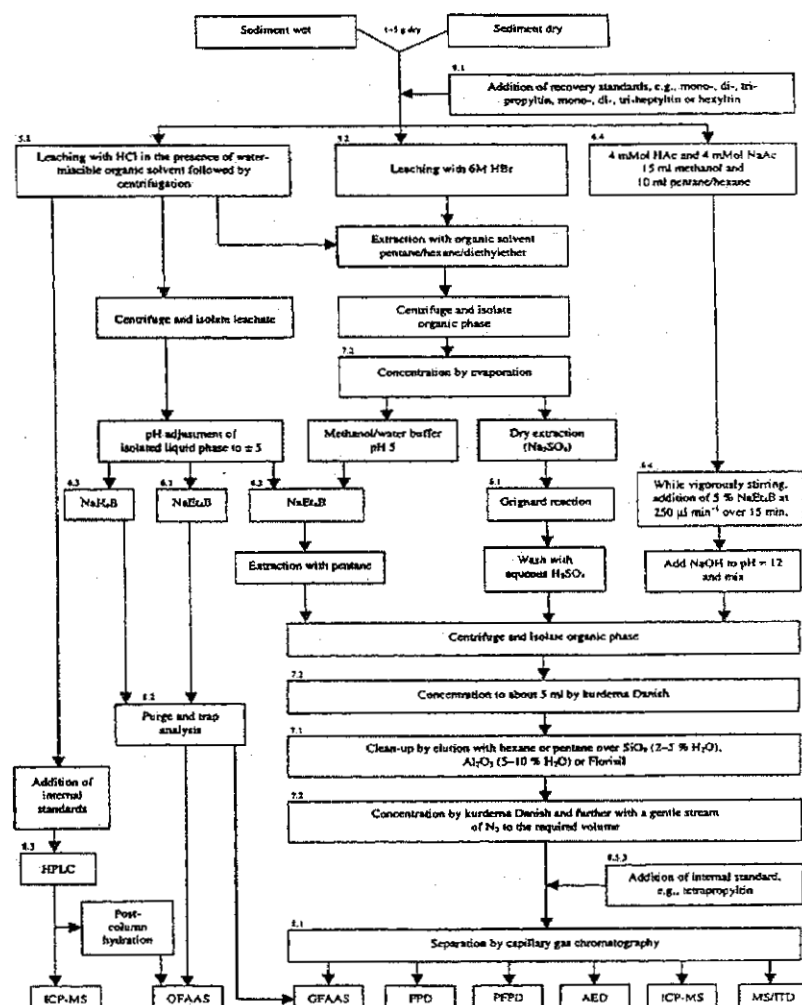
Figure 6.1 Overview of speciation techniques for organotin in sediments (ICES 1998)

Other reviews of the overall organotin speciation methods using liquid liquid extraction have been published by Dirkx *et al.* (1994), Ceulemanns & Adams (1995), Gomez-Ariza *et al.* (1995), Liu *et al.*, (1993).

6.2.1 OT extraction

The primary step is always the leaching of an analyte out of the complex environmental matrix. Examples of those techniques are: supercritical fluid extractions: (Kumar *et al.*, 1993; Liu *et al.*, 1993; Alzaga & Bayona, 1993; Shen *et al.*, 1991), acid extraction (Gomez-Ariza *et al.*, 1995; Desauziers *et al*, 1989; Lalère *et al*, 1995), alkaline extraction digestion by sodium hydroxide or extraction using tetra ethylammoniumhydroxide.

Acid extraction selected

In the present work, acid extraction was selected, because this technique is gentle to phenyltin compounds, without compromising the extraction efficiency for the other organotin compounds (Jantzen 1994, Quasimeme 1999).

Liquid/liquid extraction is the most widely used extraction technique (PAPER I). As these procedures include *in-situ* derivatisation a non-polar solvent was selected (*n*-pentane). Liquid/solid extraction techniques have been developed mainly for aquatic samples (Chiavarini *et al.* 1992; Alzaga & Bayona 1993) and lately automated solid phase microextraction (SPME) has been applied for organotin determination (De Smaele *et al.* 1996)

6.2.2 OT separation using HPLC

Separation techniques for the organotin compounds directly from aquatic samples has been performed using ion exchange or micellar liquid chromatography and ICP-MS (Garcia-Alonso *et al.* 1993; Kumar *et al.*, 1993; Nigge *et al.*, 1994; Inoue *et al.*, 1995; Rivas *et al.*, 1996). Direct injections, without time consuming work up procedures, are very tempting for any analytical chemist. These methods have shown their capabilities and were initially used for the certification of PACS-1 standard reference material. Nevertheless, there are some major drawbacks for organotin determination. Firstly the detectors for HPLC systems are, to date, not sensitive enough to meet the requirements for organotin determination in environmental samples, and secondly determination of organotins in complex, non-aquatic matrices as sediments and biota does need an extraction method. Finally, the separation power of HPLC is not always able to discriminate between all organic tin compounds (Rivas *et al.* 1996).

6.2.3 OT separation using GC

The advantages of organotin determination by gas chromatographic (GC) systems, is the availability of tin sensitive and selective detectors. The most frequently used are flame photometry (FPD), atomic absorption spectrometers (AAS) or mass spectrometry (MS). In addition,to a lesser extent the detectors electron capture detector (ECD) and atomic emission spectrometer (AES) have been used for environmental samples.

Sensitive detectors available for GC

For GC-FPD, the combustion of tin containing compounds in a hydrogen flame generates an analytical favourable flame signal with a sharp optimum at 590 nm. This can be filtered to meet higher selectivity using a narrow pass filter but on the expense of sensitivity. Furthermore the FPD is a simple and low cost detector and commercially available for any GC. Previously many researchers have used these systems for organotin determination (Greaves & Unger, 1988; Kawata *et al.*, 1993; Krull *et al.*, 1989; Maguire & Huneault, 1981; 1986; Aue *et al.*, 1992; Gomez-Ariza *et al.*, 1995; Aue & Flinn, 1980; Caricchia *et al.*, 1993; Michel & Averty, 1991 and Müller, 1984).

GC – AAS systems have also been applied in organotin speciation and they can get similar absolute minimum detectable levels (MDL). It is however a more complex system to implement, as it is not commercially available (Wilken *et al.*, 1994; Stallard *et al.*, 1989; Martin & Donard, 1995; Hansen, 1996).

"Tin has ten"
(stable isotopes)

Another successful and commonly used detector for gas chromatography is the mass spectrometer (MS). Tin has more than 10 stable isotopes, which results in very characteristic spectrograms formed by the tin "sisters". Nevertheless, there seems to be a lower OT sensitivity, than GC-FPD, when using GC-MS (e.g. Dirkx *et al.* 1994), probably due to the ten stable isotopes when using MS in *selected ion monitoring* mode (SIM). These problems have been overcome by recent developments in GC-MS (Ariese *et al.* 1997). Another general problem with tin determination is the formation of tin oxides on the internal surfaces of any detector type (detector fouling). Detector fouling is a problem for most detector types (Aue *et al.* 1992 and paper I), when analysing tin compounds.

GC-ICP-MS

Lately hyphenated techniques combining capillary GC with ICP and high resolution MS have become versatile multi-element determination technique for volatile organometals. (Garcia-Alonso *et al.* 1993; Kumar *et al.*, 1993; Nigge *et al.*, 1994; Inoue *et al.*, 1995; Shen *et al.*, 1991; Pritzl *et al.*, 1996; Rivas *et al.*, 1996; De Smaele *et al.*, 1996). One GC ICP-MS system was operational at our laboratory for research in environmental behaviour of organometallic compounds including organotin compounds. This system is somewhat cost expensive for routine tin speciation. Furthermore a major drawback was the analysis of phenyltin derivatives, which seemed to vanish in the high temperatures of the interface before reaching the plasma (see Pritzl *et al.* 1996).

6.2.4 Derivatisation of organotin compounds

Organotin compounds in aquatic solution and solid matrices are essentially non-volatile (Weidenhaupt *et al.*, 1998) and therefore not directly applicable for gas chromatographic instruments. Prior to injection, the compounds need to be transferred into a water-free organic solution and to be derivatised. The traditional method widely adapted is the so-called Tropolone/Grignard method. This method is seemingly the most widely distributed method, and the method recommended by the US-EPA.

The steps are: a) to extract the organotins to an organic phase by using a complexing agent (tropolone) and then b) to derivatise by means of a Grignard reaction.

A Grignard reagent is an agent donating organic ligands to inorganic tin. The resulting reaction is widely used industrially and experimentally for preparation of organotin compounds including *bis* tributyltin oxide (see e.g. Omae 1989). An example is shown in equation 6.1

$$4\,RMgCl \; + \; SnCl_4 \; \rightarrow \; R_4Sn \; + \; 4\,MgCl_2 \qquad \text{(Eq. 6.1)}$$
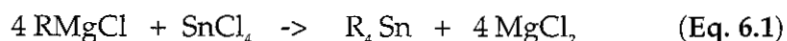
Grignard reaction

The Grignard reaction is not active in the presence of water, thus a method using tropolone as a complexation agent, is widely used to extract ionic organotins into an organic phase. The methods main drawback is the poor recovery of mono- and di-substituted derivatives. This is suggested to be related to the steric hindrance of the bulk ligand (Liu *et al.*, 1993). Direct derivatisation in the aquatic phase seems more favourable at first glance. This can change the physico-chemical properties severely, by the addition of organic groups to all ligands. The increase of Log K_{ow} by at least one order of magnitude facilitates the organic extraction. Two reagents have been used for direct derivatisation based on B (Boron): sodium tetrahydroborate (NaH_4B) and sodiumtetraethylborate ($Na(C_2H_5)_4B$).

NaH_4B has been successfully applied as a simple and fast technique for aqueous samples (see e.g. Astruc *et al.*, 1992; Martin & Donard, 1994; Ritsema & Donard, 1994; Quevauviller *et al.*, 1993; Martin & Donard, 1995;).

In-situ ethylation by sodiumtetraethylborate has been carried out mainly by European laboratories as published in a number of reports (Ceulemans *et al.*, 1993; Michel & Averty, 1991; Wilken *et al.*, 1994; Martin & Donard, 1995).

6.3 Methods used in the thesis

The method implemented for this thesis is described in paper I. The general background for the methods are given in this section.

6.3.1 *In-situ* ethylation and extraction

Prior to GC injection, the samples needed to be extracted into an organic phase and the tin compounds needed to be derivatised. Available publications indicated that *in-situ* derivatisation was more favourable, with less steps than the tropoplone complexation and Grignard reaction. Extraction using *in-situ* derivatisation with sodium tetraethyl borate ($Na(C_2H_5)_4B$) is in brief aquatic derivatisation and extraction. Schematic reaction is listed below.

The dramatic change of ionic alkyl- and aryltin compounds by ethylation into much more lipophillic ethyl derivatives does favour the use of non-polar extraction solvents as *n*-pentane or hexane instead of dichloromethane or ethylacetate. This method was also selected because there are no known natural bio-ethylation reactions to date, which could lead to erratic results. The high vapour pressure of *n*-pentane enables a low loss pre-concentration of organotin derivatives in the sample extracts. Evaporation of solvent was performed by rotation evaporator from 30 mL to about 1 mL. In case of ultra low levels of organotin compounds, another preconcentration step from 1 mL to 100 µL was carried out using a cool Argon gas flow (4.8). Internal standard addition

Sea water sample
↓
Volume quantification
↓
Addition of tri-n-propyltin as internal standard
↓
Argon gas anoxidation
↓
pH adjustment to 5
↓

In-situ ethylation (aq) of trialkyl-/-aryltin

or

In-situ ethylation (aq) of monalkyl-/-aryltin
↓
Triple Extraction in n-pentane
↓
Dried by Na_2SO_4
↓
(Cleanup on silica-gel® column)
↓
Rotation evaporation to 1 ml
↓
Argon evaporation to 100 µL
↓
Addition of injection standard
↓
Determination on GC-PFPD or GC- ICPMS

Figure 6.2. The analytical procedure for seawater samples.

6.3.2 Detection and quantification

As a logical consequence of the ethylation, the determination of e.g. TBT in a sample, is dependent on the ability to detect tri-*n*-butyl mono ethyltin. Furthermore, the separation from

other compounds needed to be adequate for determination thus using a suitable polarity on the GC column.

The pulsed flame photometric detector (PFPD) was a novel detector previously made commercially available and the manufacturers promised higher sensitivity and stability than the FPD. There were no publications on tin speciation on this detector, but keeping the tin sensitivity of the FPD in mind, the decision was made to purchase a PFPD. For extraction, a simple method was sought and the therefore *in-situ* derivatisation was selected for this work. Not every day novel GC - detectortypes reach the market. A very interesting development was the improvement of the conventional FP and FI detectors. The major change was the pulsed flame propagation in the pulsed flame ionisation (PFID) and flame photometric detectors (PFPD). To my knowledge PAPER I is the first publication for organotin speciation in environmental samples using the *pulsed* FPD.

Pulsed flame photometric detector
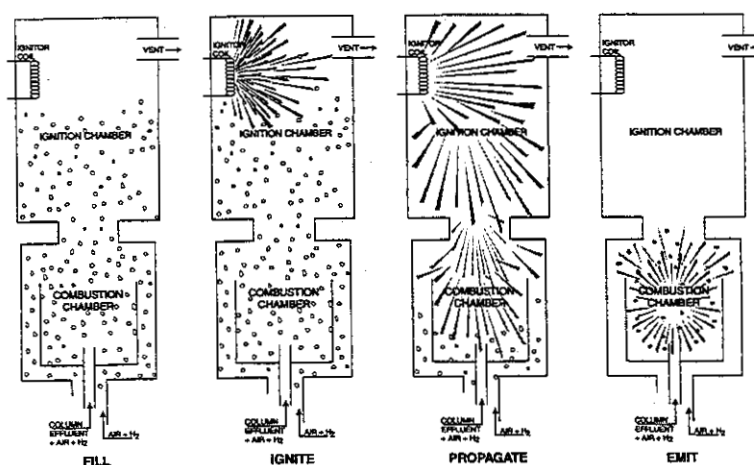
Figure 6.3. The working principle of the PFPD (© Varian Chromatography)

The working principle of the PFPD as described in fig. 6.3 is essentially flame propulsion running at a stoichiometric minimum. The light emission takes place in pulses allowing flame retention time to be a second parameter in selection and detection of analytes. Till now more than 28 heteroatoms can be determined and thus distinguished from the hydrogen flame. The exact timing of photo-multiplier delay and time of aperture opening together with filter choices can make the signal specific and sensitive towards single or groups of heteroatoms (Amirav 1999). Furthermore hence many heteroatoms like Sn can be separated from their carbon and hydrogen groups, a GC signal will consequently give a signal proportional to the amount of tin as illustrated in fig 6.4.

Figure 6.4. GC-PFPD chromatogram of around 15 ng Sn/peak ethylated organotin standard mix. Peak number: 1: MBT, 2: DBT, 3: MPhT, 4: TBT, 5: DPhT and 6: TPhT.

P and S Interference

As for the conventional FPD, interference from S and P can be experienced for some sediment. In some extracts, this interference have to be eliminated. This can be carried out during the preparation method or by enhancing the detector selectivity.

Peak tailing

The peak tailing of organotin compounds is suggested to be detector specific formation of tin oxides because phosphor and sulphur containing compounds do not tail unless the column is overloaded or damaged. The peak tailing is an illustration of the PFPD self cleaning capability. The integration of peaks is limited to the peak height quantification, because of the non-symmetric peak shapes.

Procedural blanks

Routinely also procedural blanks are prepared parallel to normal sample preparations. An example of a procedural blank spiked with tri-n-propyltltin (TPrT), is shown in fig. 6.5. Note the impurity of approximately 3 % di-*n*-propyltin (DPrT). The peak height relation between TPrT and DPrT is used to monitor the quality of the recovery standard solution and thus when to produce a new solution. This is in average done every 3 months.

Figure 6.5 GC-PFPD chromatogram of a procedural blank including recovery standard tri-*n*-propyltin (2) and 3 % impurity of di-*n*-propyltin (1).

6.3.3 PFPD Instrument evaluation

The major achievements of the PFPD in organotin determination are described in Paper I, but an update is appropriate at present.

Long-term stability

The long-term stability mentioned in the paper is continuing now 5 years after purchase. The only parts that are changed are 3 mm quartz combustor tubes every 6 months and crunch washers every 1 year. No detector cleanup has been necessary due to the inherent self-cleaning capability. A bad contamination can be cleared overnight by leaving the PFPD on. It is only turned off for routine maintenance, as it is now the workhorse of the antifouling research at NERI

Dual channel PFPD

A hardware upgrade was installed in the GC- PFPD system, by a second parallel connected electron multiplier. This was supplied by VARIAN for testing purposes, especially for gaining selectivity towards sulphur interference in sediment extracts. It enabled the photomultiplier signal to be simultaneously analysed in the time domain settings. For instance looking at sulphur in one channel and sulphur and phosphor in the other channel will leave out the sulphur interferences in a third recalculated chromatogram. This enables the PFPD to be heteroatom selective as mentioned earlier in this thesis.

6.3.4 Quality assurance

For internal quality control, PACS-1 sediments were analysed frequently and the method was accepted with recoveries better than 85%.

For external quality control, NERI participates in an international quality assurance programme for marine samples QUASIMEME. There have been 2 development exercises on analysis of butyltin and phenyltin compounds in biota (QUASIMEME 1998) and seawater, biota and sediments (QUASIMEME 1999). Results of the spiking experiments of biota, seawater and sediments are shown in table 6.1. As illustrated there are some large analytical variances with the method but nevertheless, these results are generally regarded as satisfactory at present state. Degradation of especially MBT and MPhT is regarded as a commonly encountered error in these spiking experiments.

Table 6.1 Own result for the QUASIMEME 1999 recovery spike experiments (in %).

Compound Matrix	TBT	DBT	MBT	TPhT	DPhT	MPhT
Blue mussels	120 ± 11	110 ± 17	310 ± 45[a]	25 ± 13[b]	60 ± 14	130 ± 25
Seawater	87 ± 13	96 ± 5	130 ± 48	125 ± 11	120 ± 16	120 ± 8
Sediment	85 ± 12	132 ± 15	45 ± 45	86 ± 12	131 ± 17	75 ± 3

[a]Calculation errors, [b]degradation of spike in mussel.

6.4 Method development summary

The methods for organotin measurements were developed and implemented. The range of organotin compounds vary from ethyl to phenyl derivatives in general at concentration levels:

In aqueous samples: from 0.2 ng Sn/L in seawater, to 2 mg Sn/L in ground water.

In sediments samples: from 0.2 µg Sn/kg DW in open water sediments to 6000 µg Sn/kg DW in harbour sediments.

In biological material: from 0.2 µg Sn/kg WW in whole body mussels from Greenland (Paper V) to ~2700 µg Sn/kg WW in livertissue from a flounder in the Port of Copenhagen (Strand and Jacobsen 2000b).

7 TBT and TPhT Single Dose Meso-cosm Fate Exeriments

A mesocosm experimental test system was selected for mimicking an organotin pollution incident in marine environment. The mesocosm systems were spiked with tri-organotin compounds and the concentration development was monitored for 16 days of duration. The details of this specific experiment is described in Paper II.

7.1 Experiments for environmental fate modelling

In order to study the fate of TBT and TPhT at environmentally realistic field conditions the objectives of this part of the project was to perform:

- Medium scale field experiments (mesocosms) including a sediment interface.
- Single dose simulation of a pulse release of OT from a ship
- Study the re-release of TBT from polluted sediments.

The results were later used for parameterisation of the modelling approaches in the technical annex. By means of achieving the objectives, the mesocosm experiments was performed in co-operation with other research groups using the same facilities. Geographically the experimental site was situated in a small-secluded cove, called Knebel Vig, about five miles from the Kattegat.

7.2 TBT and TPhT speciation and sorption in seawater

The fate of triorganotins (TOT) in the aquatic environment is mainly governed by sorption processes due to the low solubility in water (Fent 1996). The sorption behaviour of organotins is dependent on conditions of the aqueous media, as e.g. salinity and pH but also of the properties of the sorbate (suspended particles, algae). TOT both exhibit ionic and organic properties dependent on the aquatic conditions. Lipophillic characteristics and bioconcentration potentials are often modelled by the l-octanol/water distribution coefficient.
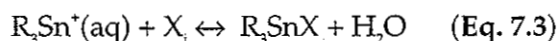
The pH gives following speciation:

$$R_3Sn^+(aq) + H_2O \leftrightarrow R_3SnOH + H^+ \qquad \text{(Eq. 7.1)}$$
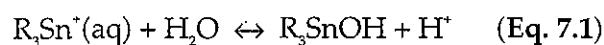
$$K_a = \frac{[R_3SnOH][H^+]}{[R_3Sn^+]} \qquad \text{(Eq. 7.2)}$$

K_a is the acid constant for TOT, R is an aryl or alkyl group. For TBT $pK_a \sim 6.2$ and for TPhT $pK_a \sim 5.2$ (Arnold *et al.*1997)

Another influence on speciation of TOT compounds, is the ion composition in the water phase.

$$R_3Sn^+(aq) + X_i \leftrightarrow R_3SnX + H_2O \quad \text{(Eq. 7.3)}$$

$$K_a = \frac{[R_3SnX]}{[R_3Sn^+][X^-]} \quad \text{(Eq. 7.4)},$$

where X is a halogen (Cl⁻, I⁻, Br⁻) or OH⁻ in seawater this is mainly OH⁻ and Cl⁻.

Consequently, in estuarine seawater with pH around 8 (greater than pK_a for both TPhT and TBT), the hydroxide non-ionic species is dominant (as shown in eq.7.3).

A model, including the aqueous ion composition and pH for the 1-octanol-water distribution is recently suggested by Arnold *et al.* (1997):

$$K_{OW} = \frac{10^{pH-pK'_a}(R_3SnOH) + \sum_i K'_i[X_i^-]K_{OW}(R_3SnX_i)}{1 + 10^{pH-pK'_a} + \sum_i K'_i[X_i^-]} \quad \text{(Eq.7.5)}$$

The sorption of TOTs to clay minerals is expected to be important in freshwater systems because of the negative charged clay and the kationic TOT (Weidenhaupt *et al.* 1997). In marine waters the sorption to organic suspended matter as e.g. algae's and bacteria's because TOT is more likely to be found as non-ionic TOTOH or TOTCl, (Stuer-Lauridsen, 1996; Laughlin *et al.*, 1986). In oligotrphic systems, on the other hand, TBT is mainly dissolved in the seawater column (Michel and Averty 1999).

The degradatio products DBT, MBT (from TBT), DPhT, and MPhT (from TPhT) are much more water-soluble than TOT and consequently they exhibit lower LogK$_{ow}$ values.

7.3 Background for mesocosm experiments

Medium sized marine enclosures, also called mesocosms, are defined as an experimental model system that in size is:
-   large enough to reflect a high degree of the complexity of a natural ecosystem, but
-   small enough to enable collection of representative samples.

For our experiments, we selected a size around 5 m³ of seawater.

The overall objectives of the marine mesocosm studies were to study near realistic intact ecosystems. As the system can not include the whole local ecosystem, it is broadly regarded as a study on community level responses to some external manipulation. Studies have often focused on nutrient level re-

sponses, as e.g. N, P, C and/or Si loading. (Lomstein *et al.* 1997) The mesocosm approach, if well designed, can reveal complex coupling on toxic response on many species at different trophic levels (Dahl & Blanck, 1996; Petersen and Gustavson 1998; Riemann *et al.* 1999)

For risk assessment of environmental toxicants, mesocosm experiments have been discussed by Shaw & Kennedy, 1996. The main difficulties with mesocosm studies from a scientific point of view, are the amounts of parameters to be controlled - especially, when working with a "close to" natural system.

In the research field of experimental environmental chemistry, not many mesocosm experiments have been carried out. This is possibly due to the large resource requirements and the low possibility to control these systems and maybe the difficulties sometimes to interpret the results. There is contradicting evidence of the benefits on the different experimental designs (Shaw and Kennedy 1996).

Several fate studies of organotin compounds in marine enclosures have however been carried out. In Spain by Tolosa *et al.* (1992) and in USA by Adelman *et al.* (1990), but never in estuarine brackish seawaters as the Kattegat estuary.

Environmental chemistry investigations of multiple compounds in large-scale freshwater systems have been carried out in Swiss lakes that are physically well described. This enables the researchers to obtain accurate mass balances of specific compounds. The hydrography of the lakes is described by energy balances by temperature development or mass balances of conservative tracers or conductivity. The obtained data are used for calibrating model parameters as inflow/outflow, mixing rates, evaporation of the lake. There is no artificial addition of chemical into the lake system, because most compounds of environmental concern can be found. But the shear size of this system makes it the largest known mesocosm experiments (Schwarzenbach *et al.* 1993 or Ulrich 1991).

7.4 Knebel Vig Mesocosm experiments

The experimental site was set-up in a shallow cove, Knebel Vig, adjacent to Kattegat, Denmark. The mesocosm enclosures were constructed in co-operation with the Water Quality Institute (WQI), Hørsholm, Denmark. The mesocosms consisted of 15 cylindrical nylon reinforced flexible polyethylene walls containing a volume of approximately 4500 litres of seawater. The cylindrical top was connected to a wooden pontoon construction. For 12 of these mesocosms, the pelagic enclosures, the bottom was tied off and for three, there was sediment contact through a 40 cm high aluminium cylinder with a diameter of 1.2 meters. The mesocosms with sediment interface were especially used for the TBT and TPhT fate experiments described in this thesis.

The set-up for ecotoxicological experiments in the pelagic mesocosm systems at Knebel Vig run in parallel with the fate study of the TOT, represent mainly, but not entirely, pelagic plankton communities, thus excluding macroalgae, fish and nesting birds. Macroflora and -fauna could introduce a large

heterogeneity into the system, and therefore disturb the balance of the experimental design. The sediment did however include filtrators as sand mussels and each mesocosm contained 10 starfish and 2 shore crabs (this study).

The results of the TBT effect studies in the Knebel Vig pelagic mesocosm experiments are published elsewhere (Gustavson *et al.* 1998; Riemann *et al.* 1999; Stenalt *et al.* 1998; Prior & Riemann 1998; Kusk & Pedersen 1997)

In paper II, is the outcome of the mesocosm experiments presented and discussed. Shortly, three sediment mesocosms were studied. They were each spiked with TBT, TPhT and a mixture of TBT and TPhT respectively. The concentrations of TOT compounds and their degradation products were followed over the period of 16 days. At day 6 the aqueous phase was exchanged with seawater from the bay, in order to study processes of both sorption (day 0 to 6) and desorption (day 6 to 16). The conclusions are that fate of TOT in this short experiment is mainly related to sorption and sedimentation processes. However, the processes are reversible driven by equilibrium partitioning. As a consequence, TBT and TPhT desorption from freshly contaminated sediments will occur. Other studies show that ageing of sediments does not influence the TBT partitioning behaviour so the findings could also be in the risk assessments of TBT contaminated sediments (Unger *et al.* 1988). Another result of the mesocosm studies show that the surface microlayer is concentrating both TPhT and TBT. There seems to be no rapid degradation of TBT and TPhT under these environmental conditions given in the experiments due to the low formation of degradation products.

7.5 Modelling of TBT and TPhT in marine mesocosms

Modelling the processes in mesocosm experiments gives an opportunity to assign processes and rates to specific overall processes. The objectives of the so-called "back-forecast" modelling of the mesocosms were:
a) to give a theoretical background for the understanding of TBT and TPhT fate processes,
b) to try to quantify them.

The specific objective was to build a simple model, which adequately describes the system. Such simplistic, but useful approaches in fate modelling of anthorpogenic compounds has been demonstrated in e.g. Yoshida *et al.*, 1983; Mackay *et al.*, 1983; McCall *et al.*, 1983; Mackay, 1994). In the technical annex, a description of the modelling of the mesocosm experiments is presented.

7.6 Introduction to environmental chemistry modelling

Successful modelling of TBT in a local area as e.g. in the Hai-He estuary has been carried out by Shu-Gui and co-workers. It is based on a compartmentalised Mackay level III model assuming constant input to the system. This work supports our

mesocosm experiments where the main fate is expected to be sedimentation. (Shu-Gui *et al.*, 1995). Another attempt to model TBT in a larger scale was carried out by Stäb and co-workers, where the Dutch waterways were modelled. This was a predicitve model to forecast future TBT concentration levels in all compartments including a large variety of biota The model verification is however not possible until future measurements are carried out (Stäb *et al.*, 1995).

Fate modelling of xenobiotic compounds in mesocosm systems is generally based on chemical unit operations as described in e.g. (Hansen & Søltoft , 1989) and in mathematical modelling of chemical systems and Elements of Chemical Reaction Engineering (Scott Fogler, 1992) combined in Environmental system analysis as in Schwarzenbach *et al.* (1993). Unit operations as mass transfer and energy transfers are generally applied in disciplines as chemical engineering. The description of an environmental system is somewhat more complex than the chemical reactor thus containing a larger degree of uncertainty. For instance important model parameters like the input of xenobiotic compounds to environmental systems like a real lake or estuary is often stochastic and measurements are often inadequate or erratic. This alone could compromise the applicability of environmental modelling. Thus, the assumptions for environmental models in particular need frequently to be based on rough estimates combined with general mathematical modelling of chemical systems. The basic process of designing a environmental model and the necessary assumptions will be introduced in the following section.
The paradigm for developing models for quantitative purposes is a stepwise function focused on finding the simplest model giving an acceptable result compared to the experimental data.
The developed back-forecast models, as shown in the technical annex, could be a basis for the development of predictive models as to estimate the fate of a toxic substance in the environment and estimate environmental concentrations.
This could, for TBT be applied for estimating environmental concentrations after a given dredge spoil or dumping of polluted sediments.

8 Organotin concentrations in the marine environment

In this chapter, a few results of authentic samples with concentration levels found in the marine environment will be discussed. This chapter is briefly an introduction to the papers III, IV and V.

As mentioned earlier the widespread use of TBT containing antifouling paints will probably cease in year 2003. As TBT is known to damage the marine environment and due to its high persistence in sediments, it is important to assess the timescale before concentration levels of TBT have fallen to an acceptable level in the marine environment.

This section is an estimate of the development of the TBT pollution level in the Danish marine environment. Papers III and IV include data of occurrence of organotins in the Danish marine environment related to shipping traffic and distances to hot spots. In paper V, measurements of TBT in blue mussels and sediments illustrate how widespread TBT contamination is.

8.1 Organotin in seawater

Not many measurements of the TBT content seawater from the Danish waters are available. Previous TBT measurements in the port of Copenhagen (Miljøkontrollen 1996) 19 and 46 ng Sn/L.

Recent spot-sample measurements (1999) in three marinas

Organotin in ports and marinas

near Copenhagen reveal that the aquatic concentrations of TBT are still high, although TBT has been banned for boats < 25 m for several years (Fig 8.1). These findings could indicate that there is an illegal use or there is desorption from sediments. The concentrations were comparable to, or higher than those found in the commercial port of Copenhagen. The port has more than 100.000 ships at call per year, but has also a inherent high water exchange, because it is situated around a natural channel between two islands. This could lead to washing out effects and thus lower concentrations in the waterphase through dilution.

It is worth noting that Vallensbæk is a recently constructed marina and therefore no high levels of TBT are expected in the sediments or water. The concentrations found in Vedbæk marina are the highest concentration levels recorded in harbours and marinas since the ban in 1991 (n > 23). It is comparable to concentration levels measured in slipways and shipyard waters of 122 ng Sn/L (unpublished data). A recent source for TBT is therefore suspected to exist in the marina of Vedbæk. This could be caused by illegal use of TBT, as more than 99 %

of the boats in this marina are < 25 meters. In a study from the French coastal waters, Michel and Averty (1998) measured 237 seawater samples. 50% of the TBT concentrations were 2 ng/L (as Sn) and 75% below 8.8 ng/L. Notably many marinas in the Mediterranean had higher concentrations of TBT. This was related to the high TBT concentration levels in sediments and to the non-effective reinforcement of the TBT restrictions (France 1982). Also, large fractions of the pleasure boats in the Mediterranean are > 25m and the hydrographical conditions yield low water exchange rates in these marinas (Michel and Averty 1998). Only at two stations, the values were comparable to the TBT concentrations in this particular Danish marina. The Danish TBT levels are similar to those reported in the beginning of the 1990'ies measured in Dutch marinas and found a general level ranging between 12 – 102 ng/L (as Sn). This Dutch study showed comparable values to the findings in the UK, France, Spain, the USA and New Zealand (Ritsema 1994).
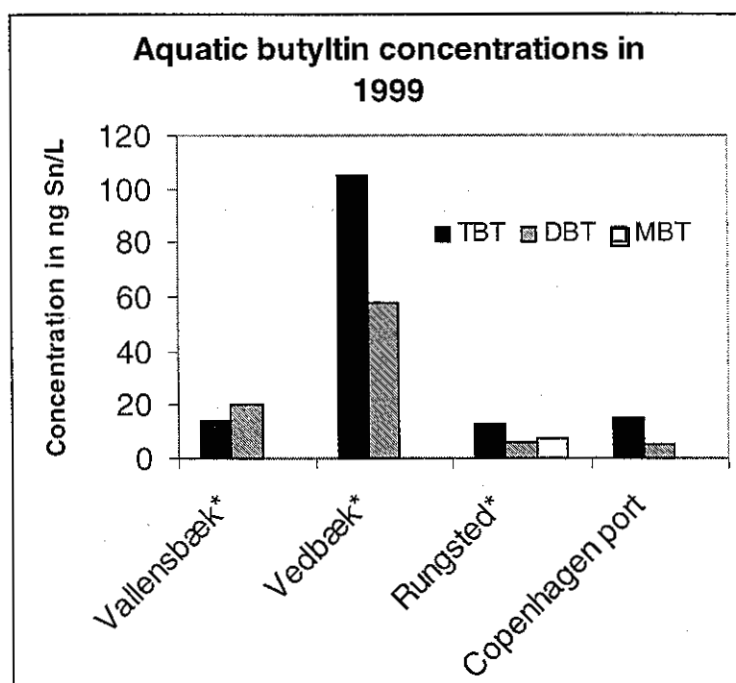
Figure 8.1 Butyltin concentration measured in summer 1999 from three boating marinas (marked *) and one commercial shipping port (Copenhagen).

Organotin in open waters

In open waters, concentration measurements are scarcer. In The Sound (Øresund) concentration levels were around 4 ng Sn/L in 1996 (Miljøkontrollen) and Kattegat 11-14 ng Sn/L in 1992 (measured as total organic extracable tin) (Mortensen *et al.* 1993).

A rough estimate of the possible concentration ranges for the open Danish marine area in 1998 (from Kattegat to the Western Baltic) is illustrated in the following equation:

Yearly input:	0.2 – 1.4 tonnes TBT (as Sn) (MST (1998).
Volume:	100 000 km^3
Est* $[TBT]_{aq}$:	0.2 – 1.4 ng Sn/L

*The calculation is based on TBT emission data from commercial shipping 1997(DK-EPA WR # 7, 1998 assuming TBT at steady state (input − output = disappearance (This work).

The TBT pollution in the Danish marine environment from a risk evaluation perspective

One of the recently introduced parameters is the PEC to PNEC ratio (Predicted Environmental Concentration / Potential No Effect Concentration) ratio. PEC/PNEC above one represents a potential risk from the specific chemical. As PEC value, the rough concentration estimate could be used, and as PNEC the value 0.5 ng Sn/L (NOEC for imposex) has been used (Gibbs and Bryan 1986). The resulting risk coefficient varies from 0.4 and 2.8. This high coefficient is supported by the findings of widespread imposex effects in the Danish waters (Strand and Jacobsen 1999*Accepted*).

8.2 Organotin in sediments

Unpublished recent results from marinas show that there still are considerable amounts of TBT dwelling in harbour and marina sediments. Because of being well sheltered, marinas in particular tend to have high levels of TBT in the sediments. In addition, shipyards and areas around slipways tend to contain considerable amounts of TBT in their sediments.

Organotin in sediments from ports and marinas

In harbour sediments, there is a continuous input of TBT from ships still painted with TBT containing antifouling paints. As shown in the mesocosm experiments the majority of TBT tends to accumulate in sediments. In marinas, the input is officially stopped since 1991, but TBT is present at levels similar to commercial shipping harbours (see Figure 8.2). Organotin measurements in marine sediments have been carried out ongoing for counties and port authorities, during the work with this thesis. The summarised concentrations in the period 1996-1999 are shown in Figure 8.2. There are differences towards high maximum levels at shipyards and commercial shipping ports. Surprisingly the contamination of marinas continues to be profound despite the partial ban on TBT use for boats. This is probably related to the high persistence of TBT in marina sediment, but illegal use of TBT could not be excluded.
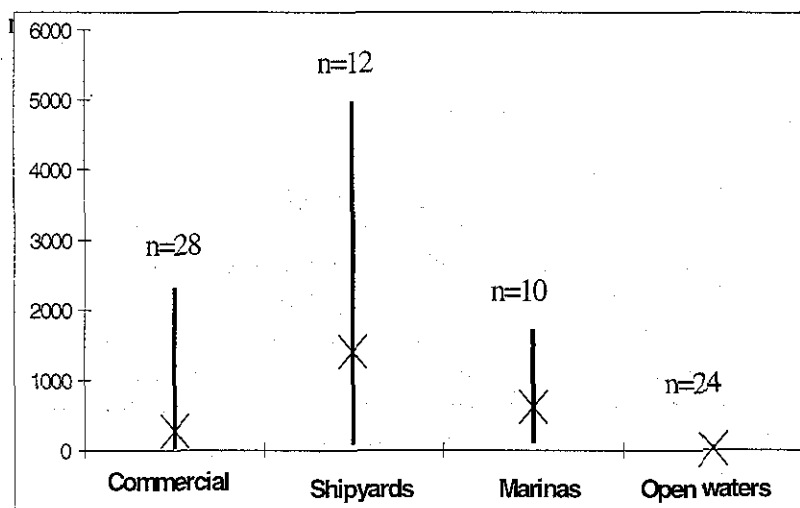
Figure 8.2 Measurements of TBT in sediment (μg Sn kg^{-1} DW) from various locations in the Danish waters 1996-1999. Bars indicate minimum, maximum, and average (X) concentrations.

In a typical marina the concentration levels are found to be between 162 and 1844 μg/kg (as Sn) (Andersson *et al.* 1998). In Figure 8.2 a typical chromatogram of a marina sediment shows that both TPhT and TBT as well as their degradation products are present. This indicates that TPhT also has been used in antifouling paints on yachts.
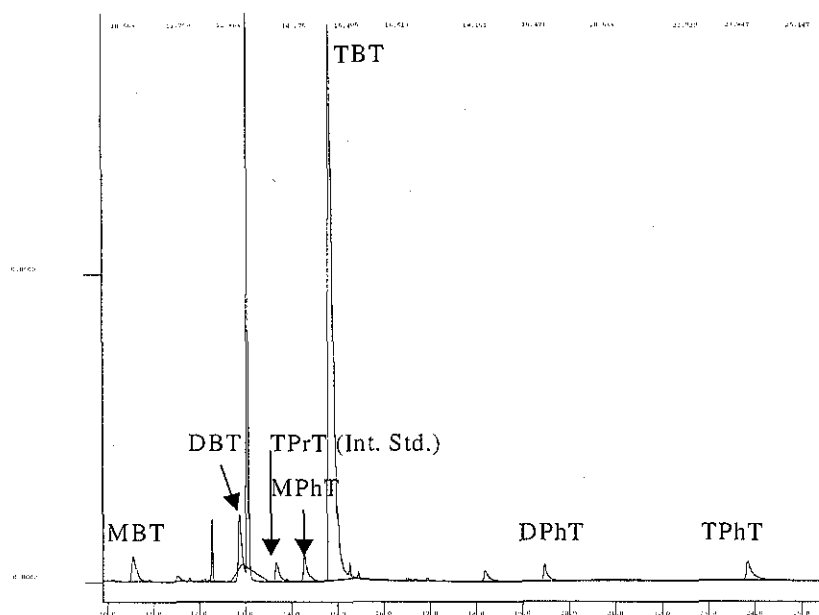
Figure 8.3 Chromatogram from sediments in a Danish marina September 1998.

TBT in sediments from open waters

The Danish waters are divided in three different marine areas: a) The North Sea area, which is a saline sea basin with tidal influence and b) the inner Danish waters, Kattegat and the Belt region, which generally is an estuary coastal brackish sea bordering between the North Sea and the Baltic and finally c) the western Baltic Sea. There are vast differences between the different areas. The western part has a high tidal influence and

- 35 -

high salinity (~35 psu), and the eastern most has no tidal influence and salinity (< 8 psu). I order to study if the TBT contamination would be uniformly distributed a small study was conducted in open marine sediments.

The measurements of TBT in sediments from the Danish open waters, away from hot spots, are indicated the righthand bar of in Figure 8.3. The concentrations range from below limit of detection (<0.2 µg Sn/kg DW) to around 66 µg Sn/kg DW. There seem to be regional differences regulated by sedimentation rates and shipping intensity.

The Wadden Sea has a high sedimentation rate and therefore a high degree of dilution of TBT and a medium rate of shipping density. The Sound has a high density of ships and lower sedimentation rate and thus not the same dilution of TBT as in The Wadden Sea. Photolytic and biological degradation of TBT is also suggested to be higher in the Wadden Sea than in The Sound. Based on these assumptions these two areas represent minimum and maximum background TBT concentration in sediments from the Danish marine areas.

For any contaminant there is a need to know the background concentrations at a dumping site, which mostly is situated in the open waters. TBT measurements are expensive and spot samples of sediments not always reveal the natural background concentration in the sediments, due to heterogeneity in the sediments. Consequently, there is a need for estimating background TBT concentrations in open marine areas. Logically the natural-background concentrations for a man made substance, as TBT, is nil. There seems to be a background level dependent on the organic content with linear relationships illustrated in fig. 8.4. Some data points are below limit of detection, but these also have equally low levels of organic content.
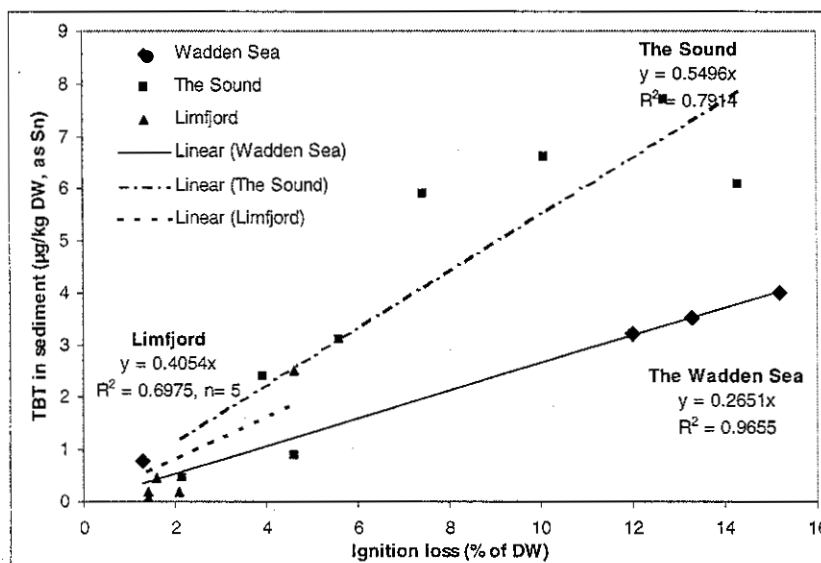
Figure 8.4 TBT concentrations in surface sediments distant from hot spots.

Linear relationships as shown in fig. 8.4, were all with significant positive trend, but intercepts were not significant different from 0. Therefore, all equations are forced through 0 for deduction of a generalised equation for the TBT background concentrations in Danish waters (1998-1999):

$$\bullet_{s,TBT} = (0.41 \pm 0.14) \bullet IL \ (\% \ of \ DW) \qquad \text{(E.q. 8.1)}$$

$\bullet_{s,TBT}$ *is the estimated background TBT concentration(as µg Sn/kg DW), and I.L is the ignition loss in % of the dry weight according to standardised method, DS 204.*

Important to notice is that generally concentration levels do not exceed 10 µg/kg DW (as Sn). The range covers 95 % of the data, but at low values, < 2 %, of ignition loss, the uncertainty of this method is high. Limitations are of course in cases where there are point sources in the vicinity. Such point sources could be anchorage for ships, off shore sewage outlet or harbour dredge spoils recently deposited. Still recommendations are to use measurements of background levels, but in case of time and resource limitations, it is always more inexpensive to measure ignition loss than TBT concentrations. It is merely a guideline for estimating TBT contamination in the specific area.

8.2.1 Butyltins in sediment cores

As shown in paper IV sediment cores from The Sound reveal historical trends of butyltin contamination. TBT could almost be recognised as a conservative tracer to determine the age of non-disturbed sediments. Assuming constant sedimentation rate and TBT loading during the last 3 decades, the first order half lives in sediments is calculated to be around 10 years. This is similar to findings in other temperate climates as Canada (Stewart and Thompson, 1996). If on the other hand the loading has been changing throughout the period, the sediment profiles merely are a picture of the general loading. In this case the match in a relatively undisturbed sediment change in the surface layer either due to increasing sedimentation or to declining TBT concentrations and depositions.

8.3 Organotin compounds in biota

Biota ranging from blue mussel, and whelks, sediment feeding mussels to fish, sea otters, birds and marine mammals were analysed. Concentration levels varied between 0.2 µg Sn/kg (as WW) in blue mussels from Greenland (see paper V) to livers of harbour porpoises at 2200 µg Sn/kg (as WW) (Strand and Jacobsen 2000b *in prep.*).

In papers III IV and V, TBT and TPhT concentrations in biota and sediments are measured both in Swedish - Danish waters and in Arctic coastal waters off the Greenland West Coast. The contents of TBT and degradation products in biota near a shipping route were higher than the contents were further away. This indicates that TBT emissions originate from ships painted with TBT containing paints.

This study was not focused how biota affects the fate or how TBT affects the biota. However, this methodology is used for the support of TBT effects studies in the Danish marine environment (See Strand & Jacobsen, accepted for publication in Marine Ecology Progress Series)

9 Conclusions

Analytical procedures for GC detection of organotins in complex environmental matrices were developed. A novel detector type was implemented and optimised for tin heteroatom determination and quantification.

The analytical method was applied on environmental materials (water, biota and sediment) at environmental relevant concentrations. The current limit of detection allows determination of organotin compounds in practically all samples from the Danish marine environment. In addition, it allows determination of compounds in compartmentalised fate experiments at environmental relevant concentration levels. Mesocosm enclosure experiments revealed reversible sorption/desorption processes at experiment. Desorption rates of TPhT and TBT from polluted sediments showed that re-mobilisation of these compounds is possible. The mesocosm experiment was used for constructing an environmental chemical fate model. The model was also used for predicting the fate of TBT sorbed in sediments.

The method developed was applied for environmental investigations of OT compounds and the occurrence in seawater, sediments and mainly marine biota.

10 References

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10.1 List of abbrevations

Abb.	Explanation
AAS	Atomic Absorption Spectrometry
AES	Atomic emission spectrometry
BAF	Bioaccumulation factor
BCF	Bioconcentration factor
DBT	Dibutyltin
DK	Denmark
DOC	Dissolved organic carbon
DPhT	Diphenyltin
DPrT	Dipropyltin
DW	Dry weight
ECD	Electron capture detector
EPA	Environmental protection agency (US or DK)
FID	Flame ionisation detector
FPD	Flame photmetric detector
GC	Gas chromatography
GF	Graphite furnace (for AAS)
HPLC	High performance liquid chromatography
HRGC	High resolution gas chromatography
ICP	Inductively coupled plasma
IMO	International maritime organisation (UN org.)
K_a	Acid constant
K_{ow}	Octanol water distribution constant
L.O.D.	limit of detection
MBT	Monobutyltin
MDL	Method detection limit
MPhT	Monophenyltin
MS	Mass spectrometry
$NaEt_4B$	Sodium tetraethylborate
OT	Organotin
PFID	Pulsed flame ionisation detector
PFPD	Pulsed flame photometer detector
POC	Particulate organic carbon
POM	Particulate organic matter
$R_xSn^{(4-x)+}$	X alkyltin ion (X=4, anionic)
SFDB	Solvent filled dialysis membrane bag
SML	Surface microlayer
Sn(IV)	Sn^{4+} ,tin(oxidation level IV)
SPMD	Semi permeable membrane device
TBT	Tributyltin
TOT	Total organotin
TPhT	Triphenyltin
TPrT	Tripropyltin
UN	United Nations
WW	Wet weight

11 Technical Annex: Environmental fate experiments and modelling of organotin compounds

Modelling of the TBT and TPhT mesocosm experiments was carried out in order to get more precise information about the fate of these compounds in a small artifical enclosure mimicking natural reactions and processes.

11.1 Modelling Theory

The modelling used in this section is based back-forecast simulations. The steps are: designing a plausible model using border limitations and start values from the mesocosm experiments and rate constants from literature. Upper and lower limits of rate constants or functions are tested and compared after each simulation to the measured values.

11.1.1 Reactor theory

The mesocosm can be compared to a continuous stirred tank reactor system based on the assumption that input to the reactor vessel is completely distributed instantaneously. This is merely a mathematical assumption whereas realistic larger systems, as in a mesocosm scale will not be well mixed. The mixing rate is important to the system due to its relatively large size and deep cylindrical shape. The fate of tin-organic pollutants by single dose addition is modelled by a compartmentalised mass balance model.

$$\frac{dM_A}{dt} = (-r_A) \cdot V \cdot C_A \qquad \text{eq. 11.1}$$

Where M_A is the number of moles of substance A in the reactor and r_A the rate of which A converts (e.g. degradation) and V the volume and C the concentration of compound A.

11.1.2 Mass transfer between phases

The main driving forces of mass transfer processes are 1. The differences in concentrations from equilibrium concentration and 2. the diffusion through a laminar boundary layer.

$$-\frac{dC_A}{dt} = -r_A = kC_A^a \qquad \text{eq. 11.2}$$

Where C_A is the concentration of compound A where ($C_A = M_A/V$).

11.1.3 Sorption to Particulate matter

The sorption of triorganotin compounds to particulate matter is generally described by the distribution coefficient K_d. Kd is an

overall distribution coefficient giving a rough estimate because the heterogeneity of sediments and particulate matter. The definition according to Schwarzenbach *et al.* 1993

$$K_d = \frac{C_{om} \cdot f_{om} + C_{min} \cdot A + C_{ie} \cdot s_{ie} \cdot A + C_{rxn} \cdot s_{rxn} A}{C_{w,neut} + C_{w,ion}} \quad \text{eq. 11.3}$$

Where C are concentrations, A areas, f are fractions and the denotations are: om: organic matter, i.e. ion exchange capacity, min mineral surfaces, rxn reversible bonded active surfaces, Cw are water concentrations of the respectively neutral (neut) and ionised (ion) fraction of the compound. In the case TBT the speciation given in recent work by Weidenhaupt and co-workers (See Weidenhaupt *et al.* 1997) the TBT is mainly present as TBT-hydroxide at the conditions in the experimental area. (pH at 8.2, salinity at 18-22 psu. The ionised fraction can be eliminated, as well as the ion exchange capacity fraction

An empirical K_d is determined using Schwarzenbach *et al.* 1993 and Arnold *et al.* 1997:

Kd is empirically established by the ratio between dissolved concentration and the particulate bound or sorbed concentrations at equilibrium:

$$K_{dX} = \frac{Xsorbed}{Xdissolved} \quad \text{eq. 11.4}$$

Where X denotes the model compound.

The process is based on equilibrium partitioning weed reaction rate k_2

$$\frac{dX_{dissolved}}{dt} = -k_2 \cdot (K_{dX} - \frac{X_{sorbed}}{X_{dissolved}}), \quad \text{eq. 11.5}$$

where k2, is a constant rate containing diffusion.

11.1.4 Sorption to the mesocosm walls - film theory

The plastic (PE) material of the mesocosm walls are considered to be an important sink for substance scavenging and release - especially when the substance has a affinity for organic material. The sampling of relevant mesocosm wall material is not possible during the experiment, due to leaks. Supplementary laboratory test where conducted in order to estimate the uptake rate of compound dissolved in the water to the mesocosm walls and following also the desorption was estimated from this experiment. The experiment is described in appendix section &&.

The processes influencing the uptake to the plastic walls that are considered important are:

- The difference in concentrations in water phase (dissolved) and on the surface of the mesocosm walls (driving force, $\nabla(X,Y)$)

- The equilibrium constant $K_{wall\,x}$ derived from microcosm laboratory experiments
- The mixing rate (thickness of rate limiting boundary layer)
- linear equilibrium adsorption is assumed

$$K_{wallX} = \frac{X_{wall}}{X_{dissolved}}$$ eq. 11.6

K_{wallX} between walls and water denoted the substance X , X_{wall} is the substance X sorbed to the wall (e.g. ng TBT/m^2 wall (as Sn)) and $X_{disssolved}$ at equilibrium.

The size of the rate limiting laminar boundary layer between water column and mesocosm walls (see figure XX influenced by the water mixing rate (empirically the Eddy mixing rate), the mesocosm wall surface area A.

The model adapted to this mesocosm system is thus:

$$\frac{dX_{wall}}{dt} = (K_{x,wall} - \frac{X_{wall}}{X_{diss}}) \cdot k_1$$ eq. 11.7

Where X is TBT or TPhT in mg total in mesocosm, $K_{wallexp}$ is the experimental established equilibrium partitioning between wall and water concentrations. K_{wall} adapted to the mesocosm is normalised to volume and area. Eddy is a calculation of the mixing rate within the mesocosm and thus a velocity rate and dependent on wind shear and waves. For simplicity, this is only called wind shear.
The starting condition is Xwall = 0 and Xdiss = 7 mg Sn.

11.1.5 Sedimentation

Sedimentation is an essential process in modelling lipophillic xenobiotic compounds in the marine environment especially working on substances with high affinity for particulate organic matter (high $logK_{ow}$). Particulate bound sedimentation of a compound is suggested in Schwarzenbach *et al.*. (1993)

$(1-f_w)k_s = v_s\ r_{sw}\ C_s$ eq. 11.8

f_w is the fraction of the substance dissolved in water, where v_s is the velocity of the solid s, r_{sw} is the rate between solids and water concentrations of the compound, and C_s is the concentration of the substance adsorbed to particles.

In this study the sedimentation process is described based on this equation and converted (first order sedimentation rate)

$$\frac{dXsed}{dt} = k'sed \cdot Xsorbed \;, \qquad\qquad eq. \; 11.9$$

Where Xsed is the amount of compound in sedimentation fraction, Xsorbed is a function of the partitioning between dissolved compound X and the sorbed fraction. The sedimentation rate was also measured in the experiments (see previous chapter).

11.1.6 Desorption

It is not possible to separate desorption of TBT and TPhT from the mesocosm walls and the mesocosm sediments can in this model. This is the logic consequence of not being able to sample from the mesocosm walls. The general equation is the same as for the sorption, using the experimentally established K_{wall} between water and mesocosm wall again using the equilibrium partitioning theory assuming reversible sorption.

11.1.7 Degradation

The degradation of TBT is known to be a sequential de-butylation and the TPhT degradation is known to be a sequential de-arylation (Fent 1996). Most of the degradation rates in literature are pseudo first order rates so this assumption is used in building the models. The degradation is not assigned to a specific process as biological degradation, hydrolysis or (in) direct photolysis in the surface microlayer. Therefore, any degradation could maybe solely be related to abiotic processes, because this specific habitat, Knebel Vig, has not been highly polluted with TBT. The presence of biota adapted to TBT metabolism seems unlikely. The formula is based on the assumption that only the dissolved fraction can degrade. In the desorption experiment a bio-film is established on the mesocosm walls which contributes to the degradation of TBT. Consequently degradation rates can not be assumed constant while a TBT tolerant and TBT consuming microbial community is developing. The (pseudo) first order kinetics in these model constructions are all based on this simple equation:

$$r_{degradation,diss} = -degrate_X \cdot X_{diss} \qquad\qquad eq. \; 11.10$$

In the case of DBT formation also a TBT fraction deriving from the mesocosm walls need to be accounted for based in this equation:

$$r_{degradation,wall} = -degrate_X \cdot X_{wall} \qquad\qquad eq. \; 11.11$$

The formation of DBT could also be a desorption from the mesocosm wall material, but the laboratory experiments do not support any DBT leaching or desorption from the PE material. As mentioned the PE is much likely to contain di- and mono-organotin compounds.

11.2 Model construction

The models are built on some general assumptions, because not all parameters where possible to determine or within the economy of the project to be monitored.

- 4500 litres bulk water
- 15 m² of PE mesocosm enclosure walls
- No evaporation of compounds
- No water exchange through the sediment bottom of the bag
- No leaching of organotin compounds from the mesocosm materials
- No export of organotin compounds on sampling equipment (Polyethylene is known to have a sorption capacity for organotin compounds)
- Constant mixing rate
- linear and reversible sorption
- First order degradation (pseudo)
- No diffusion within sediment

11.2.1 Compartmentalisation

The models are based on partitioning equilibrium constants and the differences from equilibrium as driving forces. In these models equilibrium is never reached because the time window is relatively small (16 days). The overall model description is based as earlier mentioned on mass balance of the tin species. The mass balance is monitored by a sum of stocks function built into the model.

The mass balance equation is as follows:

$$\frac{dA}{dt} = I_0 - P_{sorb} - Sed(P)_{sed} - Sed_{sorb} - Deg - Wall_{sorb}$$

11.12

The total amount of substance A is given by: The input I at time 0 (single dose addition of substance)
A sorbs on particulate matter P (organic or inorganic), Sedimentation on particulate matter Sed(P)$_{sed}$ or direct sorption (Sed$_{Sorp}$), Deg is degradation (in this case a pseudo first order rate de-butylation and de-phenylation A -> B-> C-> D (Sn(IV))), Wall sorption is the sorption to plastic walls is dependent on the eddy mixing of the mesocosm and the boundary layer between wall and well mixed compartment.

The result of the compartmentalised model is be a dynamic multiple - box mass balance with 7 coupled first order linear differential equations. The solution to the system is solved by using numerical approaches. The model description is shown in detail in appendix. The initial conditions, rate constants and boundary conditions are described in the following section.
The coupled differential equations are given in equations 11.13 to 11.19

$$\frac{dTBTdiss}{dt} = TBT\square desorp(t) - TBTwall(t) - TBTsorb(t) - TBTdegr(t) - TBTexpequ(t)$$

$$\frac{dTBTsediment}{dt} = TBTsed(t) - TBTdesorp(t)$$

$$\frac{dTBTsorbed}{dt} = TBTsorpt(t) - TBTsed(t)$$

$$\frac{dTBTwall}{dt} = TBTwallsrop(t)$$

$$\frac{dDBTdiss}{dt} = TBTdegr(t) - DBTdegr(t)$$

$$\frac{dMBTdiss}{dt} = DBTdegr(t) - MBTsorp(t) - MBTdegr(t)$$

$$\frac{dSn(IV)}{dt} = MBTdegr(t)$$

Table 11.1 The coupled first order differential equations for the TBT sediment mesocosm model.

11.3 The Modelling software

The modelling software used in this work, STELLA° is produced by High performance Systems Inc. The basic concepts are numerical solutions to dynamic models. The system is a user-friendly, windows®-based interface, giving advantages as easy to approach and easy for other than the programmer to comprehend the system almost at one glance. The basic assumptions and process variables are easy to understand through connections with arrows and processes.

In this work, the focus has been on mass balance equations and partitioning equilibrium compartmentalisation. The modelling software is described in appendix. The basic principles and solutions are not different to any numerical model tools. The user interface is somewhat more start-up friendly for non-programmers and is recommended for easy to use and to overview.

11.4 Results and discussion

Most of the removal rate of TBT could be assigned to physical-chemical processes as sedimentation to the seafloor and sorption to wall material. The biotic and a-biotic rate of degradation and thus DBT formation plays a minor role in these mesocosm experiments of natural- like systems.

11.4.1 Modelling of TBT in sediment mesocosm -part 1 sorption

The modelling was performed by using Stella II° software. The results of the modelled and experimental values are illustrated below in the figure and tables. The TBT sorption describe the fate of TBT as sorption processes to particulate matter (8 %) and sedimentation (38 %) and as wall sorption (15 %). The rest is still in

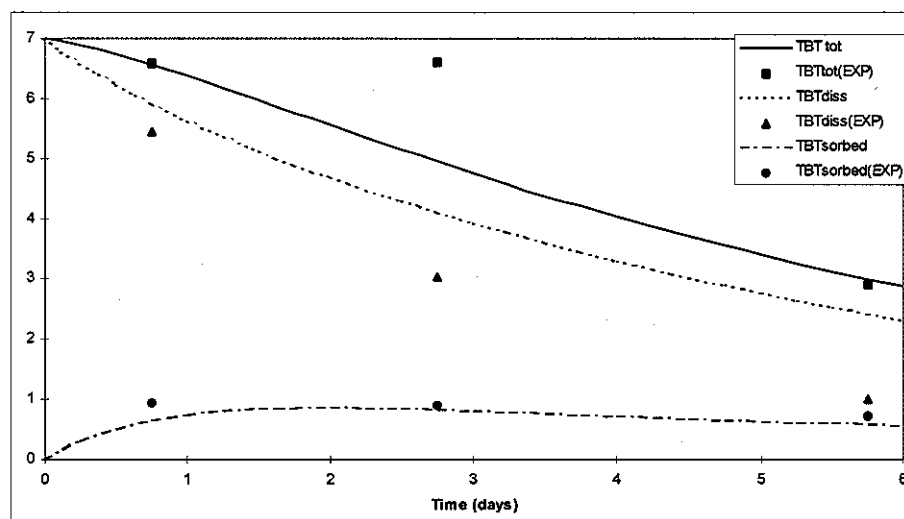solution or degraded to DBT. These values are used for starting conditions in the desorption experiments.

Figure 11.1a. Modelled and experimental results of the TBT meso-cosm study part 1 sorption (see previous chapter for raw -data)
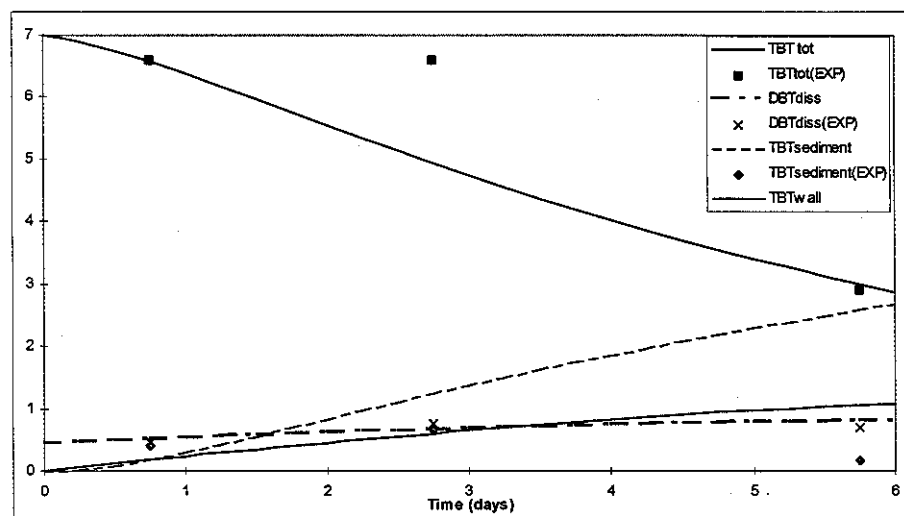

Figure 11.1b Modelled and experimental results of the TBT meso-cosm study part 1 sorption (see previous chapter for raw -data)

Table 11.2 Some rate constants, ranges and mass fluxes derived from the TBT modelling

Constant, rate or process (c), (r) or (p)	unit	Output	Output min-max
Calculated Kd (c)	$L\ kg^{-1}$	5000	1000-10000
Kwallexp (c)	m	0.21	021
Kwall (c)	$mg_{wall}\ mg^{-1}_{dissolved}$	0.53	0.53
Sorption to wall (p)	$mg\ d^{-1}$	0.16	0.08-0.24
Sedimentation rate (p	$mg\ d^{-1}$	0.56	0.28
TBT degradation rate (r)	d^{-1}	0.025	0.02-0.03
DBT degradation rate (r)	d^{-1}	0.005	0.0-0.01

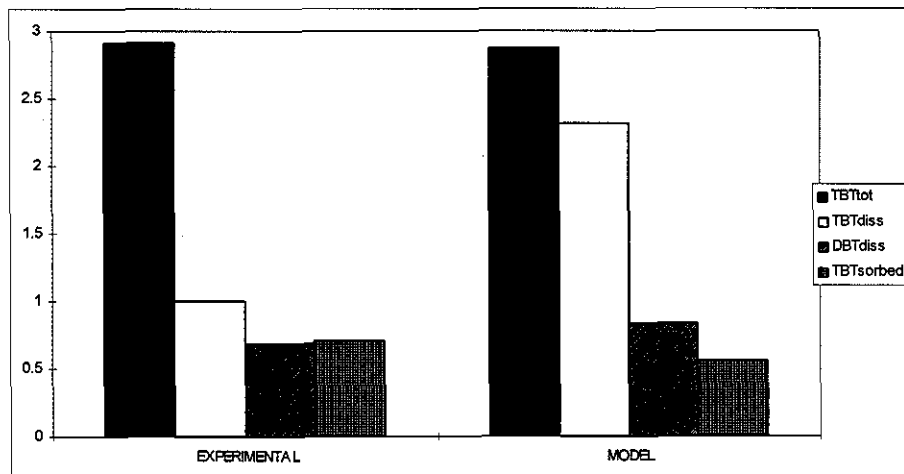| MBT degradation rate (r)	d^{-1}	0	0
Desorption from sed (p)	mg d^{-1}	0	0

Figure 11.2 Comparison between experimental and modelled outputs.
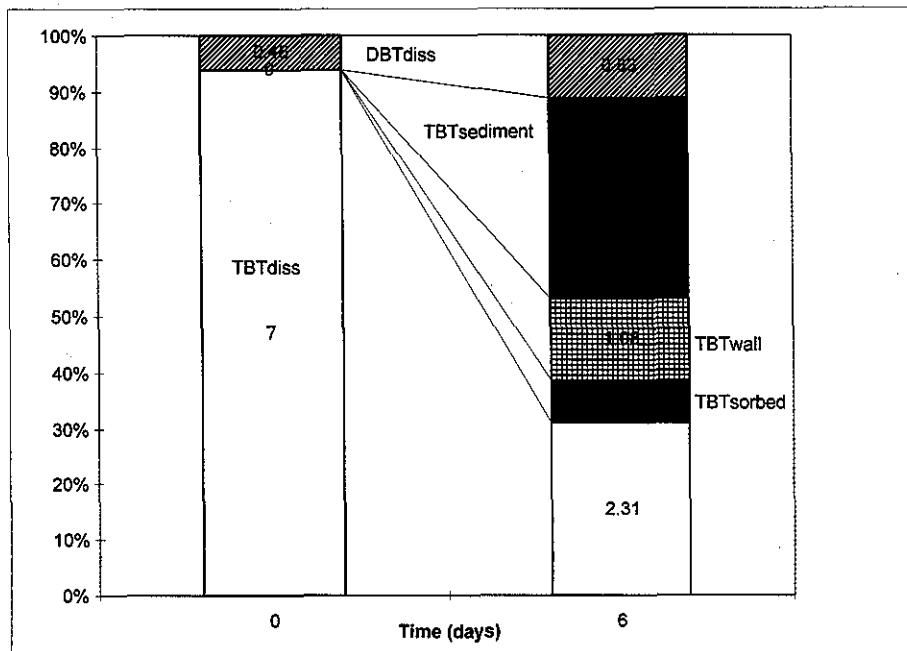

Figure 11.3 The results of the sorption modelling study with a suggested distribution to compartments. TBT or DBT diss: TBT or DBT in the dissolved phase (<0.4 μm), TBT sorbed: TBT sorbed to particulate matter (>0.4 μm), TBT wall: TBT sorbed onto wall material,

The results from this study indicate that the majority of TBT is removed through sorption to surfaces and/or fall out through sedimentation processes. The degradation to dibutyltin seems to be a first order process with half life around 25 to 30 days. This is amongst the slowest degradation rates recorded. The high persistence of TBT in Knebel Vig is suggested to be lack of potential microbial activity on systems able to metabolise this compound.

11.4.2 Modelling of TBT in sediment mesocosm -part 2 desorption

The desorption modelling was carried out using the generated rates from the sorption experiment and the start conditions given by the assumptions:

- 97 % of the bulk water is changed (sorbed and dissolved fractions 97 % removed)
- no change in degradation rate (pseudo-first order rates)
- No evaporation of compound
- No export on sampling equipment

The modelling was carried out sequential as maximum and minimum estimation of desorption from polluted sediments. The maximum rate was established from a over estimation of sediment fraction (25 % of TBT ending in the sediment after the sorption experiment. Two models were established in this task and the evaluation of the experiment was a goodness of fit in order to be able to compare the two model choices:

A: No desorption from mesocosm walls
B: No desorption from sediments
C: Sediment and wall desorption

This will give a maximum experimental value for desorption of TBT from natural marine sediment in the Knebel Vig cove in an enclosure. The predictive power and the general assumptions for further modelling will be discussed in the following chapter, when one needs to carry out risk assessment for dredge sediments. The inputs for that section are based on these assumptions.

A: No desorption of TBT from mesocosm walls:

The model of desorption was designed in order to quantify the amounts of TBT originating from the sediment and the amounts origianting from the wall material sorbed fraction.
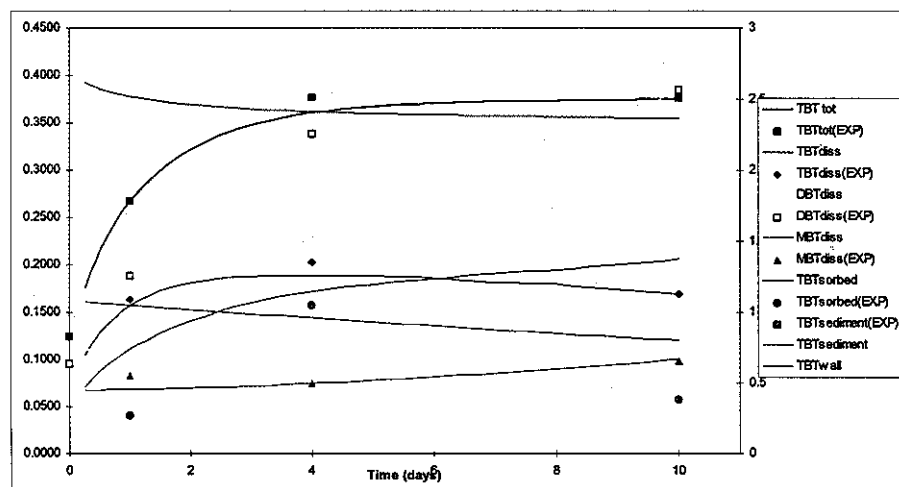
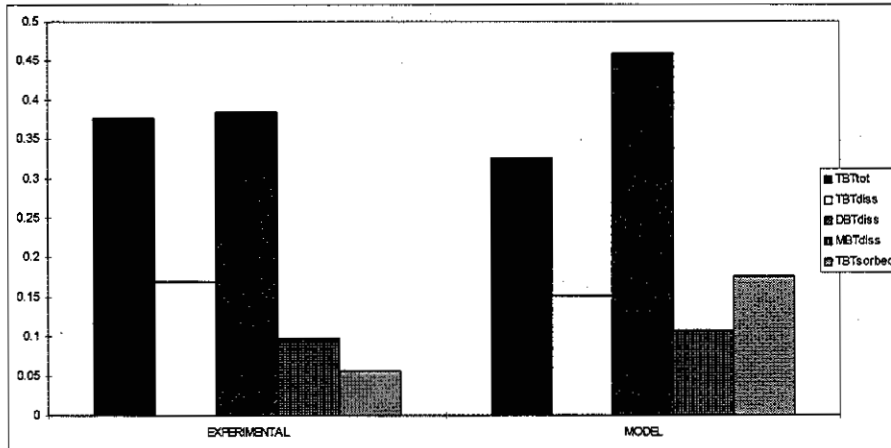*Figure 11.4 Model and experimental of the TBT desorption experiment.*
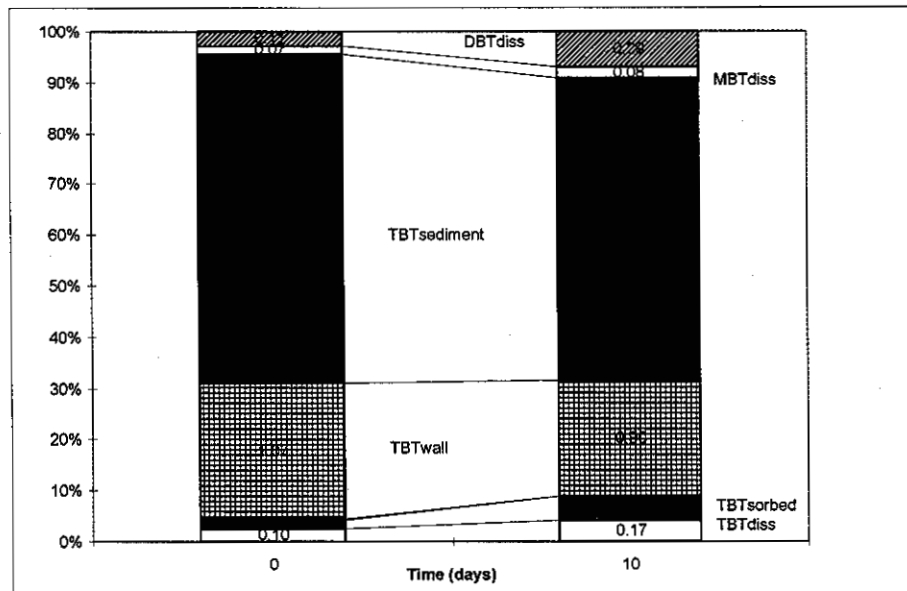

Figure 11.5 No wall desorption

Figure 11.6 The fate of TBT during 10 days desorption period.

Table 11.4 The rate constants in model (d⁻¹)

k_1 (d⁻¹)	0.00	Model goodness of fit:	(Residuals)²
k_2 (d⁻¹)	15.00	Total	0.05809
k_3 (d⁻¹)	0.01	TBT $_{tot+diss}$	0.01070
TBT $_{degrate}$	0.03	TBT $_{tot+diss+sorbed}$	0.03808
k_{sed} (d⁻¹)	0.60		

The maximum sediment associated TBT desorption rate derived from these experiments is between 0.2 mg/(m² day) at the start and 0.087 mg Sn/(m² day) at the end of the 10 day period.

B: No desorption from the sediment

The desorption from wall only model does not seem to fit the experimental data well as shown in figure 11.10. One reason to this could be a fast desorption rate due to high bulk water mixing and

movements of the bag. The days after the desorption experiment started a 3 day period with high winds (10-15 m/s) destroyed another mesocosm system. The rapid decrease towards the end of the model phase does not fit the data well and this model is therefore not accepted as acceptable description of the system.
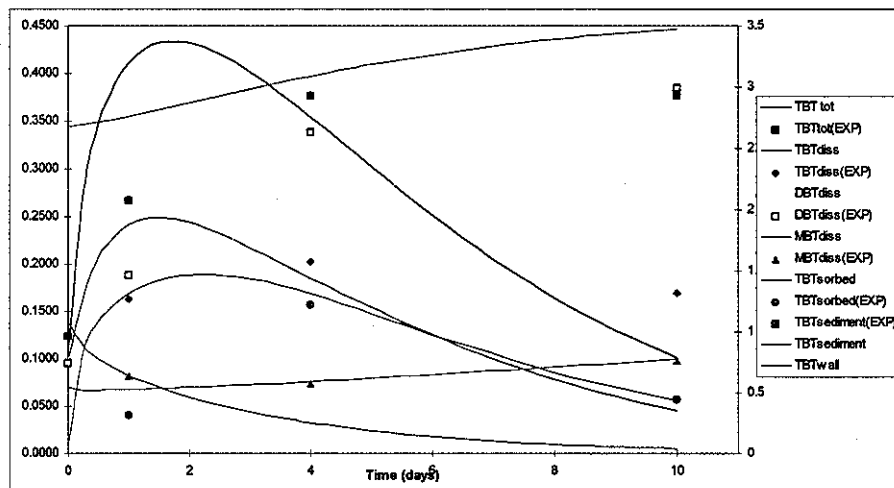

Figure 11.10 Simulation run clearly diverts from the experimental results by indicating that important processes, as sediment desorption, are not included.

C: Sediment and wall desorption in combination

Both models A and C seem to be able to describe the experiments reasonable well (see figures 11.7 and 11.8 and 11.11 and 11.12). A maximum desorption from these freshly spiked sediments is 0.01 d^{-1} and this would give a half-life in the sediment of around 70 days. The modelling shows an equilibrium between water concentration and release resulting in a much longer half life in the sediment.

The rates of sedimentation are estimated and compared to the experimental.

The best fit is the combined model which in also makes sense. There is likely to be a rapid desorption from the mesocosm walls. As the rate is high the sediment desorption takes over and the dominating desorption process towards the end of the experiment is the sediment desorption.
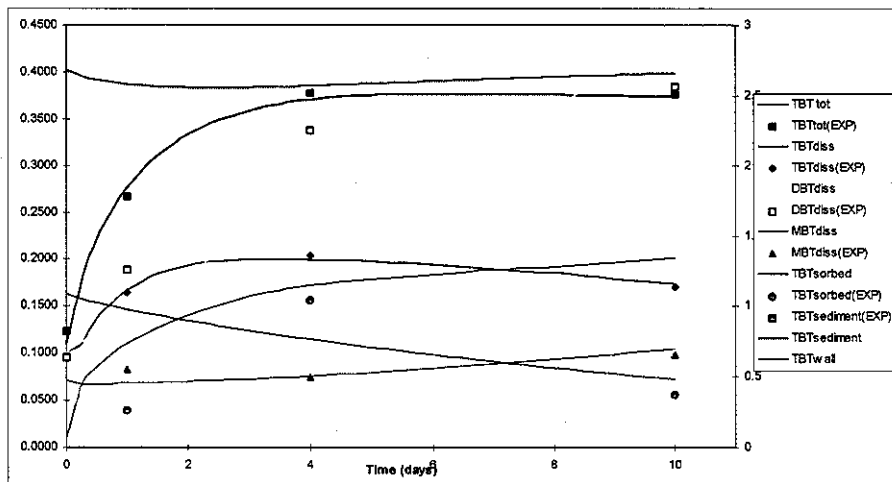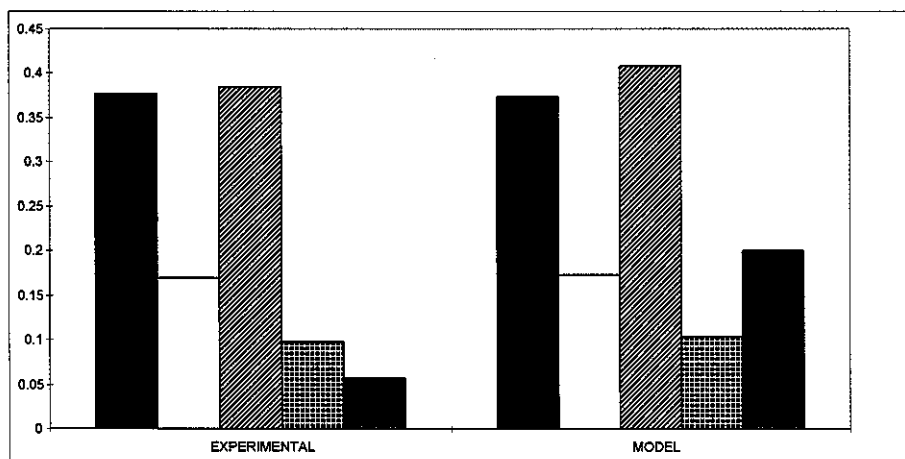
Figure 11.11

Figure 11.12 Model and experiment of the combined desorption
model. Legends: TBTtotal (▇) TBT dissolved (▢), DBT dissolved
(striped), MBT dissolved(squares), TBT sorbed (▇).

	No wall desorp	Combi
Total	0.05567	0.05033
TBT $_{tot+diss}$	0.01063	0.01035
TBT $_{tot+diss+ sorbed}$	0.03575	0.03619
k_1	0.00	0.0095
k_2	2.00	2.00
k_3	0.01	0.0075
TBTdegrate	0.03	0.04
k_{sed}	0.60	0.60

Table 11.5 A comparison of the two best describing models. The
goodness of fit is the squared residuals between model and experi-
ment.

The mass balances and the fate of the dissolved TBT is shown in
figure 11.13. This model describes the resulting fate, which in-
cludes the actual transport processes (sedimentation and desorp-
tion). The removal of the overlying water would result in a larger
removal rate from the sediment as well as the contribution from the

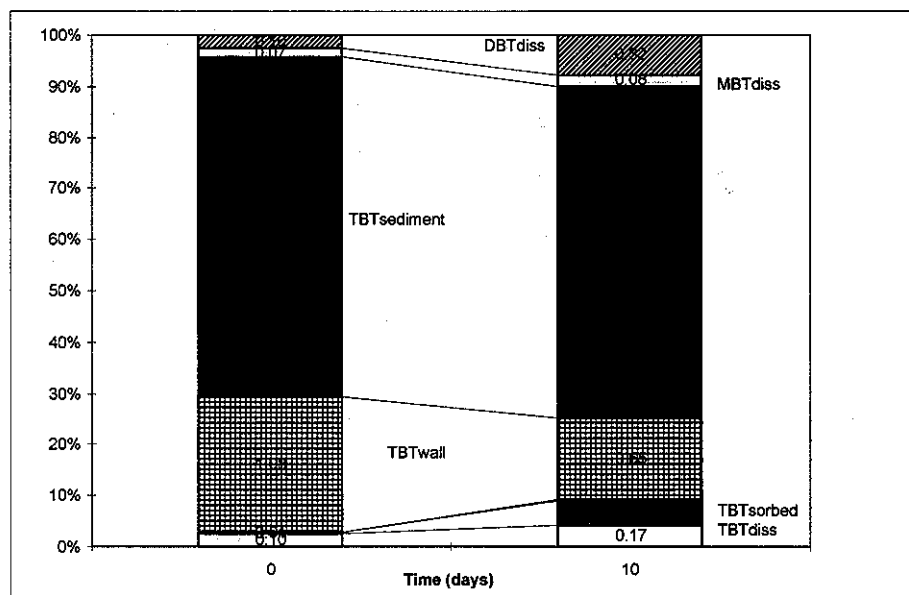mesocosm walls is included in the net sediment concentration of TBT.

Figure 11.13 The mass balance for TBT in the desorption experiment. A mass transfer from sediment and wall sorbed TBT towards DBT, and TBT sorbed is hereby postulated.

The conclusions of the modelling results are in general:

- There will be a desorption from polluted (freshly spiked) sediments, depending on water concentrations.
- Desorption rates of TBT are from 0.08 to 0.2 mg $m^{-2}d^{-1}$ (as Sn) for pristine marine areas (dumping sites).

A TBT desorption rate of 0.08 to 0.2 mg $m^{-2}d^{-1}$ will eliminate TBT from this specific sediment for a period of time with half lives between 50 and 100 days. But the sediment pool is lower than normal harbour dredged sediments of at least on order of magnitude higher concentrations. 100 to 10000 μg/kg DW (as Sn).

A major uncertainty is the mesocosm capability of simulating mixing rates as also found in the environment.

It has to be noted that the rates calculated in this work are maximum rates based on experiments and modelling in order is used for risk assessment by dredging TBT polluted sediments. These experiments show that there are risks for desorption of TBT from these sediments. The rates are closely linked to the TBT concentration in the sediment (and the water is expected to be low around dumpsites) and the distribution coefficient between water and sediment.

11.5 Modelling conclusions

The modelling as a process is a strong tool for deriving rates and creating a good perspective by combining the environmental chemistry with the mathematical modelling.

- The main removal processes for organotin compounds in the marine environment are sorption and sedimentation processes under relatively calm conditions as in enclosed systems as harbours or shallow coves
- Degradation rates for TBT - estimated half lives - in sea-water between 14 and 35 days
- There will be TBT and TPhT desorption from freshly spiked sediments.
- The physicochemical properties of the compounds is important especially when choosing the materials on equipment and walls of enclosures - the results could be biased due to unrealistic sorption processes.

PAPER I
Jacobsen, J.A., Stuer-Lauridsen, F. and Pritzl, G. (1997): Organotin Speciation in
Environmental Samples by Capillary Gas Chromatography and Pulsed Flame
Photometric Detection (PFPD) Appl. Organometallic Chem., 11, pp 737-741.

PAPER II
Jacobsen J.A. and Stuer-Lauridsen, F. Sorption and desorption rates of tri-*n*-
butyltin (TBT) and triphenyltin (TPhT) in marine enclosure experiments
(Submitted to *Environmental Toxicology and Chemistry*)

PAPER III
Jacobsen, J.A., Strand, J., Pedersen, B & Granmo, Å (Subm. 2000) Organotin
compounds in Biota in the Shipping Strait between Sweden and Denmark
(Øresund) (Submitted to:*Chemosphere*)

PAPER IV
Jacobsen J.A., and Strand, J.(Subm. 2000) Depositional Profiles of Butyltin
Residues in Marine Sediments from the Sound Between Sweden and Denmark,
(Submitted to *Environmental Technology*)

PAPER V
Jacobsen, J. A. and Asmund, G.(2000) TBT in marine sediments and blue mussels
(*Mytilus edulis*) from Central-West Greenland *Science of the Total Environment*,
245, 131-136.

Table of contents:

1.1 PAPER I

Jacobsen, J.A., Stuer-Lauridsen, F. and Pritzl, G. (1997): Organotin Speciation in Environmental Samples by Capillary Gas Chromatography and Pulsed Flame Photometric Detection (PFPD) *Appl. Organometallic Chem.*, 11. pp 737-741.

Organotin Speciation in Environmental Samples by Capillary Gas Chromatography and Pulsed Flame Photometric Detection (PFPD)

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Pulsed flame photometric detection (PFPD) for gas chromatography was applied to organotin compounds as standards and in environmental samples. Ethylated organotin species (n-propyl-, n-butyl- and phenyl-) were extracted from spiked artificial seawater and from an environmental sample. Selectivity towards tin is shown in the analysis of highly polluted seawater samples from a commercial port where no significant interferences are found. The self-cleaning capability and long-term stability of PFPD is shown in this work during 140 days of continuous operation. The absolute limit of detection for this capillary GC–PFPD technique ranged from 0.2 to 0.4 pg (Sn) for tetraethyl- to tetraphenyl-tin, allowing determination of sub-nanogram/litre concentrations of organotin compounds. © 1997 by John Wiley & Sons, Ltd.

INTRODUCTION

Organotin compounds are used in a broad variety of industrial processes and products as accelerators, PVC stabilizers, coatings, polymers, cross-linking and as biocides.[1,2] One of the most species-specific toxic substances deliberately released to the marine environment is the organotin antifouling agent tri(n-butyl)tin (TBT),

which is mainly used in the paints applied to subsurface areas of ships. The first effects on non-target organisms (oysters) were found by Alzieu and co-workers at the beginning of the 1980s.[3] TBT is toxic at approximately 1 ppt (ng l^{-1}) in seawater, and has caused a decline in dog whelks (*Nucella lapillus*) around the United Kingdom.[4–6] Recently effects arising from TBT in the open North Sea have been reported and related to shipping traffic intensities.[7]

The scope of this work was to implement an analytical method for the simultaneous determination of organotin species from ethyl to phenyl derivatives in environmental samples at concentration levels of ecological concern. Over the last two decades a large number of analytical techniques have been developed and applied to the determination of organotin compounds in environmental matrices. The separatory power of gas chromatography (GC) in combination with tin-selective and -sensitive detection methods such as flame photometry (FPD) is widely used.[2] Nevertheless, self-contamination of important parts of the photometer by tin oxides and other low-volatility and inert oxides is a major concern, especially when analysing environmental samples.[8] The detection of organotin compounds by GC–FPD can encounter interferences from sulphur- and phosphorus-containing compounds, that may be abundant in environmental samples, and therefore analysis of biota and harbour water samples requires a highly selective method. Interferences have been reduced using dual-channel FPD, but self-contamination still remains.[8]

Pulsed flame photometric detection (PFPD) is suggested to be self-cleaning by the pulsed flame propagation principle and, furthermore, may have better selectivity and higher sensitivity towards elemental tin detection as proposed by the developers Amirav and Jing).[9]

In this work PFPD has been successfully

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1.2 PAPER II

Jacobsen J.A. and Stuer-Lauridsen, F. Sorption and desorption rates of tri-*n*-butyltin (TBT) and triphenyltin (TPhT) in marine enclosure experiments (Submitted to *Environmental Toxicology and Chemistry*)

Sorption and Desorption Rates of Tributyltin (TBT) and Triphenyltin (TPhT) in Marine Sediment Mesocosm Experiments

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Abstract – Tri-n-butyltin (TBT) and triphenyltin (TPhT) sorption and desorption

experiments were undertaken at environmentally realistic conditions in marine

mesocosm enclosures. The experimental contained seawater was exchanged to

simulate dumping of polluted sediments in a pristine environment. Both

compounds sorb strongly to particulate matter and the main removal process in

this system was sedimentation. Total sedimentation rates were estimated betweem

1.3 and 20 ng Sn cm^{-2} day^{-1} for TBT and between 1.1 and 6.6 ng Sn cm^{-2} day^{-1}.

Desorption of TBT and TPhT from sediments to the entire water column, were

suggested to be dependent on equilibrium partitioning. The fastest release

immediately after water phase exchange was determined as a linear regression

slope estimate. Initial desorption rates ranged from 0.81 to 1.6 ng Sn cm^{-2} day^{-1}

for TBT and from 0.26 to 2.2 ng Sn cm^{-2} day^{-1} for TPhT. Resuspension rates

were also determined as the total amount of compound released to the water

column. Sediment interaction rates of TPhT were quantified for the first time in

this study. No significant degradation rates could be determined. The main fate

processes for TBT and TPhT derived from these the experiments are suggested to

be sorption to particulate matter, sorption to sediment and sedimentation.

INTRODUCTION

The active ingredient in many marine antifouling paints, tri-*n*-butyltin (TBT), is perhaps the most toxic substance ever deliberately introduced into natural waters [1]. Triphenyltin (TPhT) has been used in antifouling paints in combination with TBT, but is most commonly used as fungicide in agricultural crop protection [2]. Numerous findings show elevated concentration levels of organotins (OT) in both freshwater and marine environments. [3,4]. TPhT was detected for the first time in harbour environments in Spain by Tolosa and co-workers [5]. Recent measurements of Danish marinas show detectable concentrations of TPhT [6,7]. Due to their sorptive behaviour and persistence in sediments, OT´s accumulate in sediments [8,9]. This is, however, a reversible process and sediments may become sources of water column OT. when exposed to polluted sediments [10]. Adsorption and desorption experiments of TBT and degradation products have been estimated in field experiments in Pearl Harbour, Hawaii, by Stang & Seligman [10]. TBT adsorption rates were 0.57 ng TBT $cm^{-2} day^{-1}$, but TBT desorption from harbour sediments was insignificant. From laboratory experiments Unger and co-workers reported reversible sorption and desorption processes of TBT, which were strongly dependent on the partition coefficient between sediment and water (Kd) [9]. Langston and Pope [11] showed that sorption processes of TBT were dependent on partitioning equilibrium (Kd) of TBT and sediment characteristics. At present no adsorption and desorption rates for phenyltin compounds from sediments have been established.

Distribution studies of radioactively labelled TBT in marine enclosure conditions have been carried out by Adelman and co-workers [12], where the main fate process was suggested to be degradation.

The main objectives of our study were to study the environmental behaviour of TBT and TPhT under realistic conditions. To our knowledge, this is the first study on TPhT desorption rates. A marine mesocosm approach was chosen to ensure environmental complexity, presumably including all non-hydrodynamical processes.

MATERIAL AND METHODS

Mesocosm

The mesocosm enclosure materials consisted of nylon reinforced polyethylene, chemically controlled not to contain OT substances (as e.g. photolytic stabilisers). The dimensions were 4 meters of depth and 1.2 meters in diameter resulting in a volume of approximately 4.5 m^3. The open bases of the cylindrical enclosures were attached to galvanised Fe cylinders with a diameter of 1.2 m, a height of 0.4 m. The foundations of the cylinders were pushed approximately 10 cm into the estuarine sediment, at a water depth of approximately 4 m (Fig.1). The enclosure walls were then lifted to the surface and attached to a pontoon arrangement as described elsewhere [13].

Site characteristics

The experimental site was a small wind-protected cove situated at Jutland, Denmark (Fig.1) described earlier in [14]. The salinity was 20 parts per thousand (ppt). The temperature was 18 °C at the start of the experiment and 23 °C at the end. The nominal amount of OT compounds spiked to each of the three enclosures were 7 mg (as Sn), giving a concentration of approx. 1.6 µg/L (as Sn) in the mesocosms. The individual mesocosm volumes varied and thus there are variations in the concentration levels of OT compounds at day 0 were from approximately 1.3 to 2.4 µg /L (as Sn).

Sampling

The following compartments were sampled at day 1,3,6,7, 10 and 16, in addition total

water samples were taken at days 0 and at beginning of the desorption period day 6 +

4 hours: Integrated water samples of the mesocosm water column was collected using

a 3.5 m hard polypropylene tube with internal diameter of 3.5 cm (approx. 2.3 L),

which was submersed into the mesocosm and closed with a rubber plug at the top.

The pipe was retrieved, shaken three times and the first sample was discarded. The

procedure was repeated and an aliquot was poured into a 1 L sample flask. The

sampling frequencies are outlined in Table 1. The water samples were filtered using a

pressurised Teflon[®] filtration system with 0.4 μm polycarbonate membrane filters

(MicroPore, USA). The particulate fraction (filters) were kept individually in PE

containers at < -20 °C. The dissolved fraction (filtrate) was acidified and kept at < 5

°C until analysis. Surface micro-layer (SML) samples were collected using a 50 by 50

cm square "Garrett" screen, 0.4 mm stainless steel wire and mesh size of 1.12 mm, as

described by [15]. The screen was vertically submersed into the water column,

aligned horizontally and retrieved while carefully collecting the surface microlayer.

The sampling was repeated 7 times giving approximately 400 mL of sample, covering

approx. 1.75 m^2, corresponding to a SML thickness of 230 μm. The SML sample was

stored in a 500 mL Pyrex glass bottle preserved with 2 mL HCl (30% Suprapur,

Merck). Each screen was dedicated to the same mesocosm throughout the

experimental period. The screens were rinsed in acetone (Merck, p.a.) and distilled

water after each sampling occasion. All aqueous samples (1L) were acidified with 2.5

mL HCl sample and stored cool and dark. For recovery experiments samples of the

cove were collected and spiked with TBT and TPhT.

The sediment traps consisted of open top cylindrical glass tubes with a 3.9 cm diameter and a height of 43 cm. In each mesocosm, three traps were placed for the sorption period and three new trpas were placed after exchange of water. The traps were placed upright in each tray. To avoid biological activity in the traps 50 mL dichlormethane (Merck, p.a.) was added to each trap prior to placement at the sediment surface. Sediment traps were retrieved individually, shaken vigorously and 0.5 mL HCl (Suprapur®, Merck) was added for preservation. The traps were kept dark and cool until analysis.

Analysis of OT compunds

All aqueous samples were prepared as previously described [16]. In brief: pH adjustment to 5 ± 0.5 using a solution of 10% sodium acetate and 20% sodium hydroxide (Merck, p.a.) in milli-Q water. Each 400 mL water sample was filled into a 500 mL separator funnel and the oxygen was stripped off by a gentle argon gas flow for ten minutes. *In situ* ethylation was carried out by adding 500 µL of a 10% sodium tetraethyl borate (Fluorochem Ltd, UK) in water free methanol (Merck, p.a.) solution, vigorous shaking for more than 10 seconds and followed by a reaction time of ten minutes. The organic extraction was carried out by addition of 10 mL *n*-pentane and vigorous shaking for one minute. After phase separation, the organic phase was collected. The ethylation and extraction step was repeated 3 times. The excessive water in the combined extracts was dried by addition of anhydrous sodium sulphate (Na_2SO_4). The extracts were pre-concentrated to 100µL by solvent evaporation using nitrogen gas flow.

Filter samples were spiked with internal standard (tri-n-propyltin, Aldrich), acidified and extracted by whirly mixing and ultra-sonification in one hour followed by pH

adjustment and triple in-situ ethylation extraction. The extract was cleaned on activated silca gel columns and dried on sodium sulphate (Merck p.a.). This method was originally developed for biota at our laboratory and was modified to cover the preparation of other solid samples as sediments, 0.4 μm membrane filters and mesocosm wall material).

The procedure for the sediment traps was internal standard addition, pH adjustment to 1 (all OTs speciated as ionic compounds) and the 50 mL dichloromethane (Merck, p.a.) was evaporated by argon gas. The remaining water sample was filled into separator funnel and the sediment trap was rinsed 3 times in acidified water, which was added to the sample. The remaining procedure followed the water sample preparation.

Instrumental equipment

The system for OT speciation determination consisted of a Varian 3500 gas chromatograph (GC) equipped with a Varian 1077 split/splitless injector operated in splitless mode for 2 minutes, and a Varian pulsed flame photometric detector, (PFPD) (Varian Chromatography, Walnut Creek, CA, USA), as described prevoiusly in [16]. The capillary column used for OT separation was a 0.25 mm x 30 meters RTX-5 (5% polarity, cross-bonded) with a film-thickness of 0.1 μm (Restek Corp., USA). The injector was lined with a quartz frit-splitter also from Restek Corp. USA. Calculations of signal responses were performed on Varian Star 4.5 software based on peak height and retention time. For confirmation of tin standards and selected samples, verifications were performed on a Varian 3400 GC and Saturn IV ion trap mass spectrometer (Varian Chromatography, Walnut Creek, CA, USA).

Laboratory experiment for determining mesocosm wall sorption

An initial laboratory experiment was setup to measure the sorption of TBT and TPhT

to the mesocosm wall material. Two 10 liter glass bottles were filled with 10 liter

artificial sea-water at 20 ppt, prepared from distilled water and sodium chloride and

pH adjusted to 8.2 by sodium hydroxide (Merck, p.a.). 2000 ng Sn/L TBTCl was

added to each bottle. After overnight equilibration time, the mesocosm wall was

submerged into each of the flasks. The material area of experiment A consisted of

0.025 m^2 and the area of B was 0.1 m^2 (double sided). The flasks were stirred with

Teflon coated magnet (5 cm length) at 300 revs min^{-1}. The temperature was 22 $^{\circ}$C and

pH 8.2 throuhout the experiment. Analysis was carried out as described earlier in this

section.

Quality assurance

There are no certified reference materials at experimental relevant concentration

levels for butyltins. For phenyltin compounds, no certified materials are available to

date. Recovery of PACS-1 standard reference-material gave the following recoveries

for butyltin compounds: MBT 89 ± %, DBT 104 ± and TBT 102 ± %. The laboratory

participates in the QUASIMEME program on butyltin and phenyltin in the

environmental matrices seawater, sediment and biota with satisfactory results [17].

RESULTS

The mesocosm experiments were carried out in two sections: (a) simulation of an

organotin spike into an marine aquatic system (sorption) and (b) simulation of an

organotin polluted sediment in an unpolluted water body. The results of the

concentration developments in all three mesocosm experiments are shown in Figure 3,

4 and 5. The figures are divided into phases and an expanded view is presented for a better magnification of the desorption experiments. The results of an additional PE wall material experiment was carried .

Laboratory testing of TBT sorption to wall material

In order to estimate the maximum amount of TBT sorbed to the mesocosm wall material a simple microcosm experiment was conducted. In two glass flasks of each 10 L articifical seawater (20 psu NaCl, Merck, p.a.) was spiked with

Mesocosm experiments day 0 to 6 – sorption period

This section will present the results from the sorption period for all three mesocosms. In general, all experiments show decreasing concentrations of tri-organotins in the aqueous phases during the initial 6 day period. The nominal and actual concentrations of TBT and TPhT are shown in Table 1. The differences between nominal and measured concentrations in the three mesocosms are believed to reflect the differences in filling volumes. For the TPhT mesocosm, the walls were visibly concave due to incomplete filling. The initial concentrations of the degradation product DBT and DPhT are due to impurities (approx. 6% as Sn) in the TBT and TPhT standards. All the mesocosm experiments show decreasing aqueous OT concentrations for both totals, dissolved and particulate sorbed. The mass balance for TBT is shown in Figure 2, which reveals a residual fraction of between 15 and 50%, which not could be accounted for in these experiments. Sampling of sediments and wall material could not be carried out in order not to disturb the overall system. A compartment as the surface micro layer, a pre-concentration of all OT compounds could be reported, but with less than 0.1% of the total TBT and TPhT present, this fraction is not an

important sink for OT. The concentration ranges are shown in Figure 3, 4 and 5.

Recoveries from TPhT and the mix mesocosm were not sufficient for performing

determination of the particulate sorbed fractions. The decrease in the parent

compounds concentrations follows apparent a first order rate.

The sedimentation of TBT and TPhT in the sediment traps is shown in figures 3-5.

The highest sedimentation rate is at day 3 for the TBT mesocosm. The sediment traps

at day 1 from TPhT and Mix mesocosms were lost during transport. A large initial

sedimentation is expected since the OT concentration will be lethal to a large part of

the pelagic biota. The sediment traps recovered at day 6 all show decreasing

concentrations compared to the day3. For TBT, the sedimentation rates are calculated

from 1.3 to 20 ng Sn cm^{-2} day^{-1}.

Desorption experiments

The results of desorption experiments are shown in all right hand panels in Figures 3,

4 and 5. Unfortunately, as for the sorption period, the particulate sorbed fraction of

TPhT could not be extracted from the 0.4 μm filters, thus no data of are shown in

Figures 4 and 5. In general, the aqueous concentrations of tri-OT increase until an

apparent equilibrium is reached after about 10 days. DBT levels are still increasing

the end of the experiments. In the mixed OT mesocosm there is desorption of OTs

into the aquatic phase, however, an accidental rip in the mesocosm wall material on

days 7 and again at day 8, caused a dilution of analytes during the desorption period.

The material was repaired and after this, OTs increased again in the watercolumn

Figure 5. Extra samples were collected and analysed (total aqueous pases) and thus

extra data points are exhibited in Figure 3.

The compound desorption from the wall material could not be excluded when calculating the sediment desorption rates. The initial desorption rates are calculated from the linear regression estimates.

DISCUSSION

In order to assign the resulting concentration developments in these mesocosm experiments to general processes we used a simple one-box mathematical model of the systems. The model assumes no degradation hitherto the low build-up of degradation products. The mass balance is described in equation 1 and Figure 2. Mainly there is a large mass of TBT which could not be accounted for.

$$M_{single-dose} = M_{dissolved} + M_{part.\ sorb.} + M_{sediment} + M_{material} \tag{1}$$

The single-doses were added to the system as TBTCl and TPhTCl, the initial total concentration at day one yields the volume of the mesocosm enclosures. The sorption to particulate material is considered instantaneous driven by the distribution coefficient Kd and the concentration and characteristics of the suspended material. After the initial mixing and sorption to particulate material of less than one day, the larger scale processes as sedimentation and sorption to surfaces are expected to occur.

Mesocosm experiments day 0 to 6 – sorption period

The calculated (pseudo) first order disappearance rates for our study are presented in Table 2, are based on solutions to first order reactions:
$$C_t = C_0\, e^{-kt} \tag{2},$$

k is the removal rate (day^{-1}), t: time (in days) and C_0 is the initial concentration at day zero. The resulting half-lives ($t_{1/2}$= ln2/k) range from 1.0 to 2.0 days for TBT and 2.5

to 4.6 days for TPhT. For TBT, this is considerably faster than most reported

biodegradation rates in the water column [3,8], and the increase of degradation

products could not account for this disappearance rate of parent compounds. Adelman

and co-workers [12] calculated first order removal rate for TBT from 10 to 20% day^{-1}

(half-lives of 3.5 –6-9 days). Evaporation is, in our experiments, not considered to be

important due to the low vapour pressure 10^{-3} Pa (20 °C) for TBT and the calm

weather throughout the sorption period (low wind shear). The likely fate processes of

OT in our mesocosms are related to physical processes as sorption to suspended

particulate material (algae and bacteria), sediment and wall material and

sedimentation of particles [17]. From the laboratory experiment it could be estimated

that that a maximum 15 % of the TBT could to be assigned to mesocosm wall. No

tests were performed on TPhT sorption to the wall material.

Stang and Seligman [10] estimated a TBT to sediment sorption rate at equilibrium of

0.23 ng Sn cm^{-2} day^{-1}, whereas in this study the calculated sorption rate is 3.4 ng Sn

cm^{-2} day^{-1}. The calculations are based on the disappearance (residual) of TBT divided

by the total surface of the mesocosm sediment and material surface, assuming equal

sorption characteristics in both material and sediment. The differences in sorption

rates could mainly be explained by the aqueous phase concentration development,

which shows that our mesocosm system was at equilibrium during the sorption

period.

The sedimentation processes are important TBT removal in these experiments. The

driving force of sedimentation is probably compound toxicity and thus an elimination

of algae and bacteria's in the water column as shown in [19]. However, the sorption

directly to sediment and mesocosm wall material should also be taken into

consideration. The sorption onto wall material was estimated, from our laboratory

experiments, to account for a maximum of 15% of the loss from the aqueous phase.

However, in our experiment the estimated first-order disappearance rate for TBT of

0.35 day^{-1} is supported by earlier studies by Adelman *et al.* [12].

Mesocosm experiments day 6 to 16 – desorption period

For TBT desorption is estimated to be 0.81 to 1.6 ng Sn cm^{-2} day^{-1} and for TPhT

between 0.26 and 2.2 ng Sn cm^{-2} day^{-1}. In addition, re-suspension rates for TBT and

TPhT have been calculated (Table 2) from the concentration development in the total

water phase. The rates are three folds higher than the calculated desorption rates

possibly due to particulate matter in suspension. The initial desorption rates for TBT

have not earlier, to our knowledge been quantified for a medium scale enclosure

system. Studies by Unger *et al.* [9] show desorption of TBT from marine sediments

were experimentally established to exhibit a steep initial phase and a linear slower

phase. Desorption of TBT was postulated to be dependent on reversible partitioning

equilibrium processes depending on Kd for the specific sediment. Other in-situ

experiments dispute the desorption of TBT from marine sediments [10], but as noted

recently by Langston and Pope [11], the low of TBT desorption could possibly be due

to near-equilibrium conditions. Our study supports that TBT sorption and desorption

processes are reversible and shows that this applies for TPhT.

CONCLUSIONS

This is the first study of organotin desorption from natural sediment to include TPhT

The Sorption and desorption processes are shown to be reversible and depending on

equilibrium partitioning (Kd). Rates of sorption and desorption were estimated from the enclosure experiments.

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Tables

Table 1. Nominal and measured initial concentrations of OT in the mesocosm experiments. The amounts and concentrations are given as Sn.

| | | Mesocosm | |
	TBT	TPhT	Mix (TBT & TPhT)
Organotin added	7 mg (as Sn)	7 mg (as Sn)	3.5 mg each (as Sn)
Nominal initial concentration	1.56 µg L^{-1}	1.56 µg L^{-1}	0.78 µg L^{-1} each
Measured initial concentration[a]	1.4 µg L^{-1}	2.4 µg L^{-1}	TBT: 0.57 µg L^{-1} TPhT: 0.76 µg L^{-1}
Recovery in %	90	154	TBT: 72 TPhT: 97

[a]Measured 18 hours after spiking, [b]water phase was exchanged over a 4 hours.

Samples were taken immediately before and after renewal.

Table 2. Calculated sorption and desorption rates derived from the mesocosm experiments

Mesocosm Compound	TBT	TPhT	TBT&TPhT
Sorption experiment			
Dissolved phase halflives[a] *in days*			
TBT	2.0		1.0
TPhT		4.6	2.5
Sedimentaion rate[b] *ng Sn cm^{-2} day^{-1}* (range)			
TBT	1.3 - 20		1.5 – 5.1
TPhT		3.1 – 6.6	1.1 – 1.7
Desorption experiment			
Desorption halflives[c] *in days*			
TBT	0.6 - 0.9		1.1 – 1.4
TPhT		2.5 – 2.8	0.8 - 1.7
Initial Desorp. rate[d] in *ng Sn cm^{-2} day^{-1} (Linear)*			
TBT	0.81		1.6
TPhT		2.2	0.26
Resuspension halflives[e] *in days*			
TBT	0.7 - 0.9		1.0 – 1.3
TPhT		0.46	0.9 – 1.2
Initial Resusp. rates[d] in *ng Sn cm^{-2} day^{-1} (Linear)*			
TBT	2.4		0.87
TPhT		7.0	1.1

[a]Calculation of first order removal rates, no degradation (as observed), [b]estimated from the ratio between sediment trap and mesocosm sediment area (1:950), [c]assuming (pseudo) first order rates, [d]Total phase resuspension including dissolved phase, [e]Resuspension is the total water phase concentration development (max. estimate).
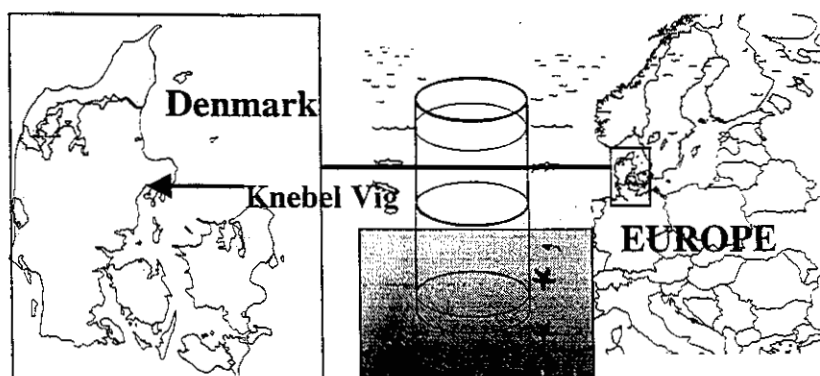
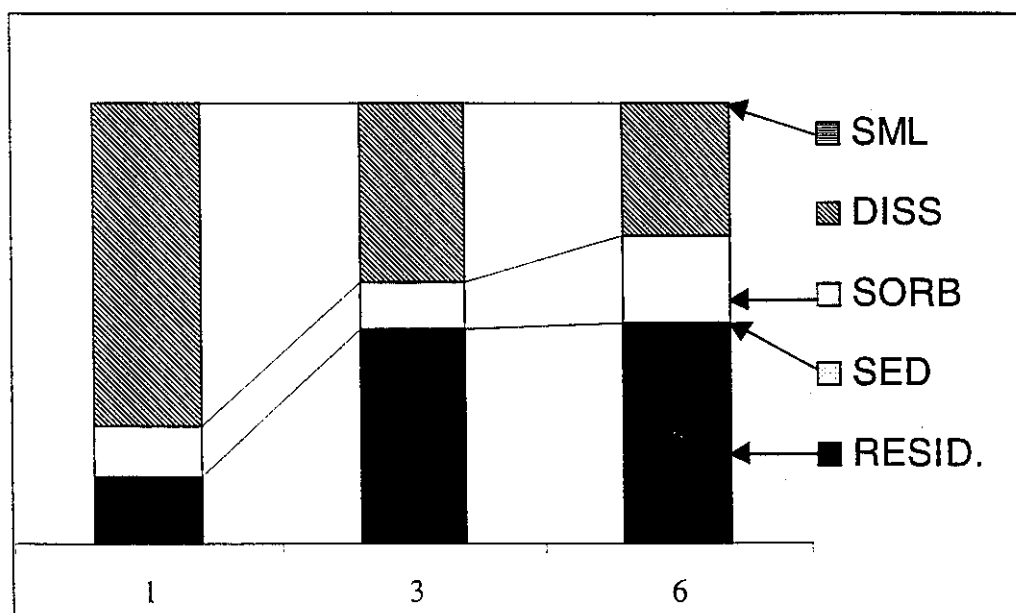Fig.1. The temporary mesocosm experiment facility at Knebel Vig, Jutland, Denmark.

Fig. 2. Compartmentalised view of TBT (100% = 7mg TBT, as Sn) in the TBT mesocosm sorption period (days 1, 3 and 6). Legends: SML: suface-microlayer, DISS: dissolved, SORB: sorbed on particulate material > 0.45 μ, SED: calculated sedimentation, RESID: unknown residual.
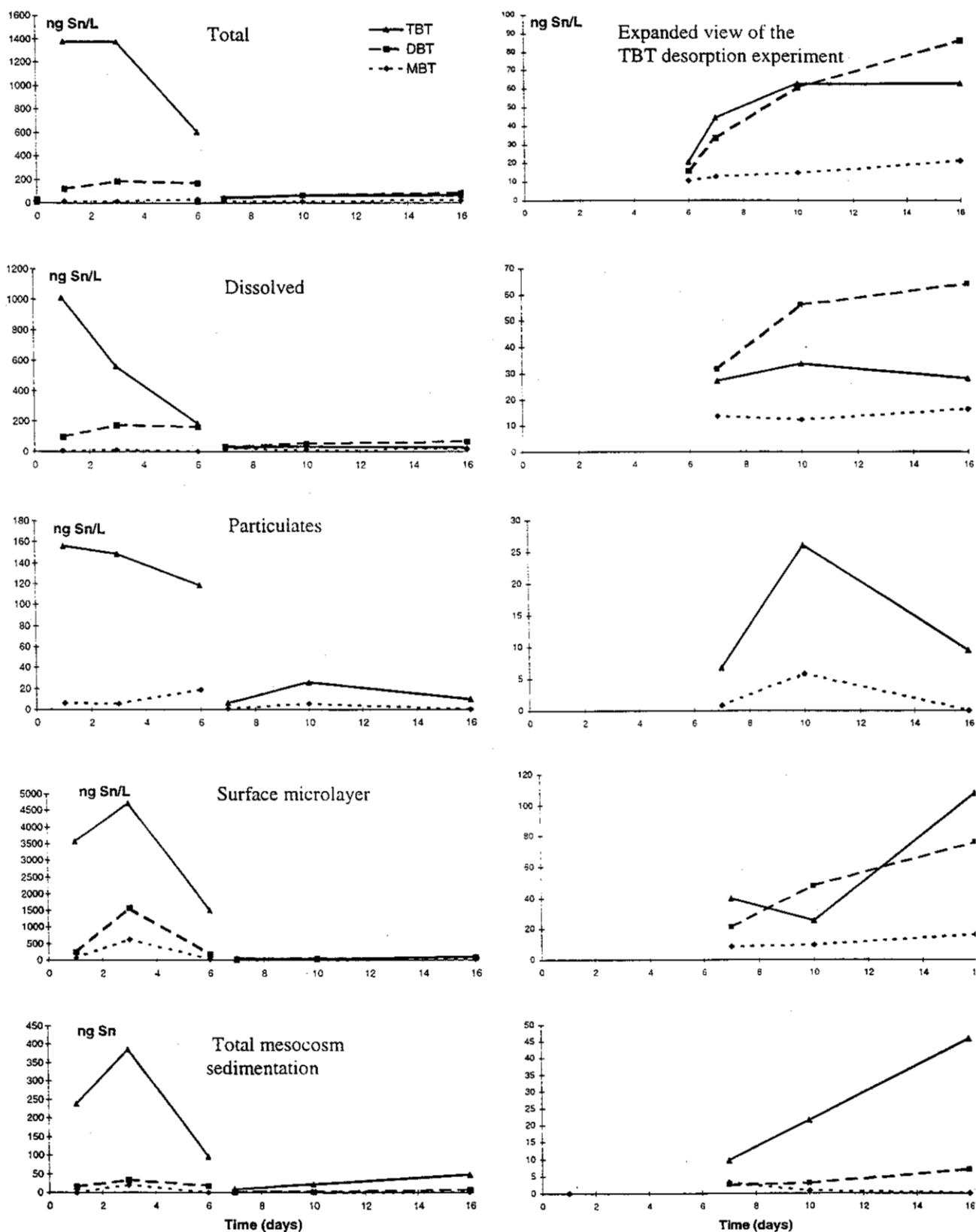
Fig. 3. TBT mesocosm experiment. 5 compartments were measured. Right side of figure is an expanded view of the desorption experiment. Total is the total aqueous

phase, dissolved is < 0.4 µm filtrate, particulate is the retained OT on a 0.4 µm filter, the trapped sedimentation is the total sedimentation into one sediment trap.
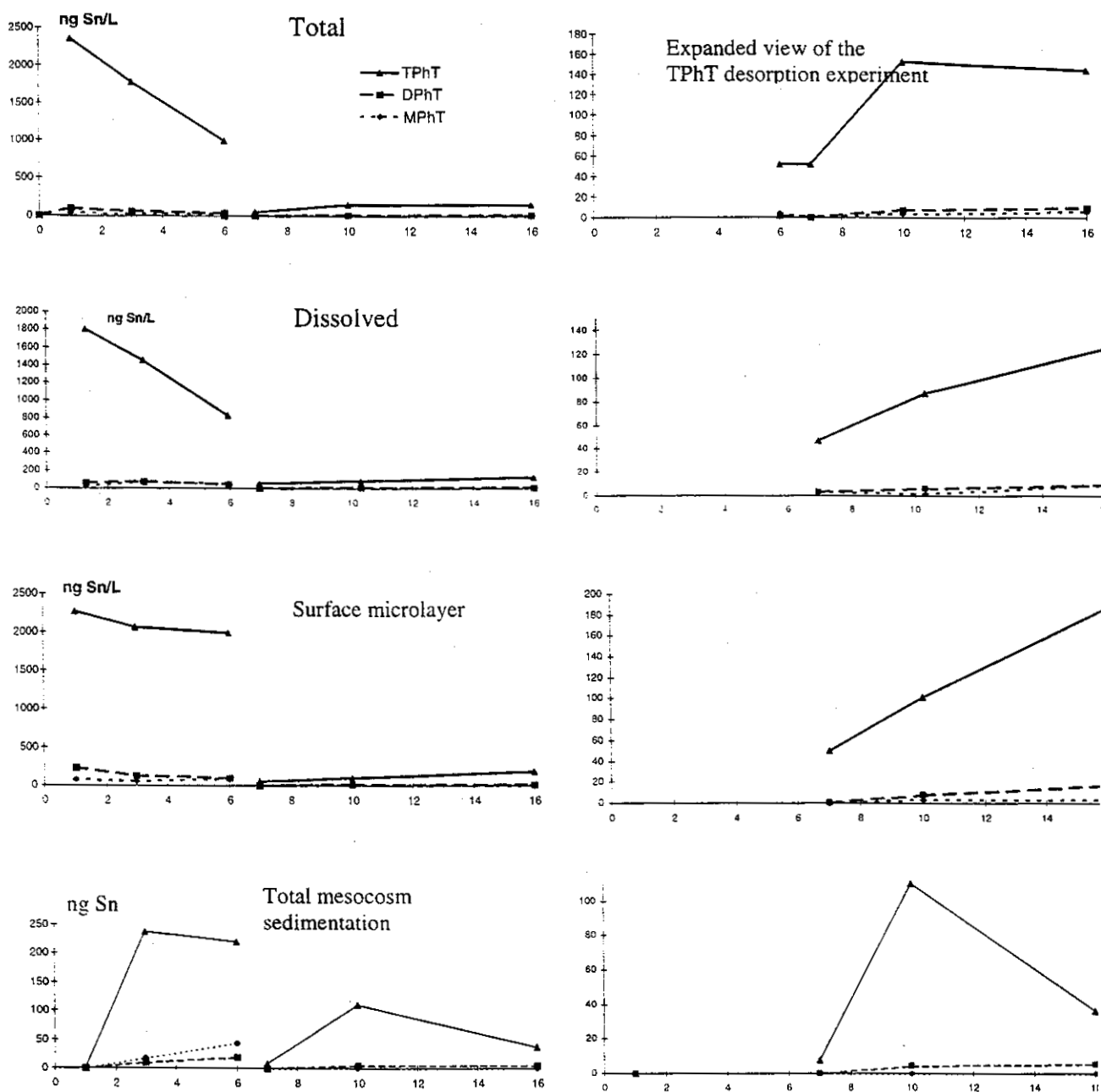
Fig. 4. TPhT mesocosm experiment. Right side panels shows the expanded view of the desorption experiment. Total is the total aqueous phase, dissolved is < 0.4 μm filtrate, the trapped sedimentation is the total sedimentation into one sediment trap.
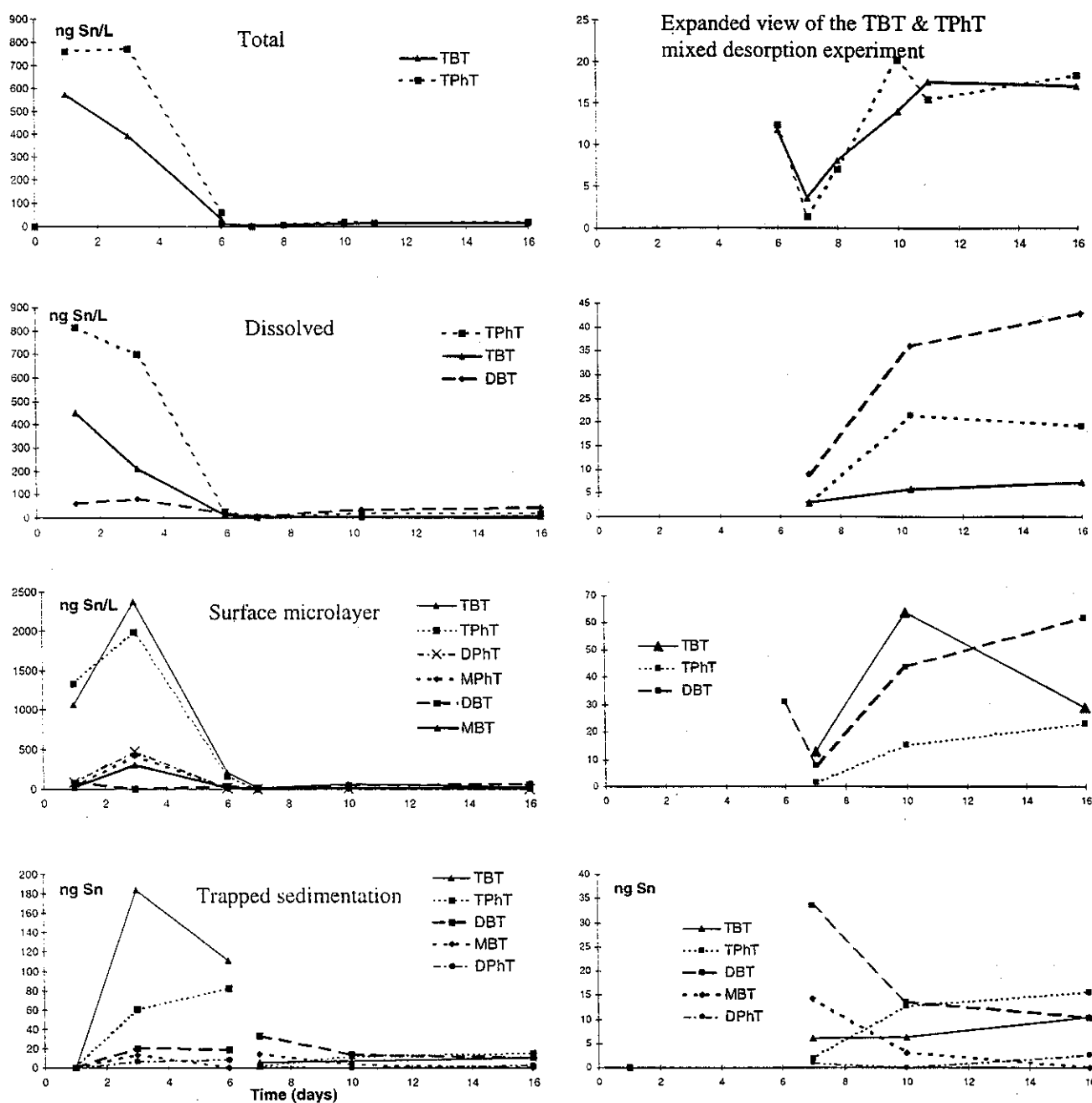
Fig. 5. TBT and TPhT mixed mesocosm experiment. Right side is an expanded view of the desorption experiment. Total is the total aqueous phase, dissolved is < 0.4 μm filtrate, the trapped sedimentation is the total sedimentation into one sediment trap.

1.3 PAPER III

Jacobsen, J.A., Strand, J., Pedersen, B & Granmo, Å (submitted) Organotin compounds in Biota in the Shipping Strait between Sweden and Denmark (Øresund)

Organotin Compounds in Sediment and Molluscs from the Shipping Strait between Sweden and Denmark (Øresund)

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Abstract

In order to establish knowledge of the tributyltin (TBT) pollution distribution in the sublittoral zone of the narrow shipping strait (the Sound, Øresund) between Sweden and Denmark. Sediment and benthic biota samples were collected over two transects across and along the Sound. The bivalves Nuculana pernula, Cardium echinatum, Arctica islandica, Musculus niger and the gastropods common whelk, Buccinum undatum, and red whelk, Neptunea antiqua, were collected. The samples were analysed for organotin compounds TBT and degradation products dibutyltin (DBT), and monobutyltin (MBT) using GC-DC-PFPD. In sediments the TBT levels ranged from 0.9 to 7.7 ng g^{-1} dry weight with a fine correlation between sediment organic fraction and the TBT content ($r^2 = 0.90$). TBT was detected in all of the collected animals from the area with concentrations ranging from 0.7 ng g^{-1} wet weight in B. undatum to 84.6 ng g^{-1} wet weight in N. pernula. All organotin concentration levels are normalised to tin (Sn) to facilitate the comparison between parent compounds and degradation products. N. pernula was found to be an ideal monitoring organism for sediment pollution levels.

Introduction

The antifouling agent tributyltin (TBT) is extremely toxic, especially for marine molluscs. The compound has caused severe effects on coastal oyster populations in France in the early eighties (Alzieu et al., 1986) and on dog whelks, Nucella lapillus, around the United Kingdom (Gibbs and Bryan, 1986). In agreement with these findings, several studies show that many other gastropod species are sensitive to triorganotins, especially TBT (Langston, 1996). The severe effects of TBT on marine snails at very low concentrations (below 1 ng l^{-1} (Bryan & Gibbs, 1991), have led to international recommendations on chemical and biological monitoring programs for TBT. The areas to be monitored are especially heavy shipping straits in order to improve our knowledge how widespread the effects of TBT are in the more open sea areas.

The narrow and shallow straits between Denmark and Sweden are important transportation routes between Europe or countries overseas and the rest of Scandinavia, the Baltic countries or Russia. The shipping traffic is channelled through the Great Belt (Storebælt) and through the Sound (Øresund). In 1995 the total number of ships larger than 50 gross tons passing these parts of the Danish waters exceeded 50 000 (Danmarks Statistik, 1997). In addition to the commercial cargo shipping, the local ferry-traffic is an important part of the regional infrastructure and consequently has to be considered as a major TBT source.

The TBT contamination in Tokyo Bay and in the Strait of Malacca, areas with intense shipping and ferry activity, was recently investigated by Hashimoto and co-workers (Hashimoto et al., 1998). The organotin and TBT concentrations in Danish - Swedish near coastal and harbour waters has earlier been investigated (Kure and Depledge, 1994; Mortensen et al., 1995; Miljøstyrelsen, 1993). Studies of the North Sea by ten Hallers-Tjabbes et al. (1994) showed a positive correlation between shipping intensity and incidences of imposex in common whelk (Buccinum undatum), indicating the widespread contamination of TBT originating from ship. A similar study in the northern part of the Sound showed that 20-44 % of B. undatum and 100 % of Neptunea antiqua had developed imposex, indicating that this area also is contaminated with TBT (Strand and Jacobsen in press).

TBT has a relatively high affinity to particulate matter (Meador et al., 1997, Weidenhaupt et al., 1997, Fent, 1996). TBT is therefore expected to partition to

organic matter of which most will scavenge to the sea floor by sedimentation. Therefore, the levels in sediments are expected to give an integrated value of the TBT concentrations in the area. Consequently, shipping lanes are expected to have higher TBT concentrations than more remote areas, due to the continuous TBT input from shipping traffic. An increased concentration is also expected to be found in the water phase. However, due to the strong and fluctuating current in the Sound this could be more difficult to measure than to measure the sediment and biota concentrations. The aims of the present study were:

1) To measure TBT and the degradation products dibutyltin (DBT) and monobutyltin (MBT) in biota and sediments from the narrow sound, the Sound, between Denmark and Sweden

2) To identify suitable species for studying bioavailability and distribution of TBT and degradation products in the Baltic and North Sea regions.

Materials and Methods

Sampling

The stations were planned as two transects, one across the shipping lanes and, one along the Sound, in the sublittoral zone at depths from 20-28 meters. The sampling stations selected for the transect perpendicular to the shipping lane were approximately 1 km apart (stations 1 to 8, west to east). The stations at transect parallel to the shipping lane were approximately 7 km apart (stations 9 to 12, north to south). The stations are pinpointed in Fig 1. The samples were collected during cruises in July 1997 and again in November and December 1997. An initial screening study was carried out where benthic species were caught at a station on the northern approaches to the Sound (see station P in Fig.1). At each station two trawl deployments were performed using a 5 mm mesh frame trawl 40 cm X 80 cm to collect benthos and sediment. The sediment samples were collected from the bulk of the trawl and sieved to a fraction less than 2 mm. The animals were collected after sieving the sample (approximately 40 kg, 5 minutes of trawling at a speed of one knot). The benthic fauna species collected were identified, registered, stored in plastic containers (at $< 5^{\circ} C$) and frozen within 8 hours after sampling. Positions were

determined by differential global positioning system (DGPS) at the beginning and at the end of each trawl.

[**Fig.1**]

Sediment and biota parameters

The dry weight of the sediments and the biota was determined by drying at 110 °C to constant weight and the organic fraction in sediments was determined by measuring the percent ignition loss at 550 °C in four hours.

Chemical analysis

The analytical chemical methods for this study, present the current state of the art at NERI and include quantificationof organotin using a modified VARIAN 3500 gas chromatography and dual channel pulsed flame photometer detector (GC-DC-PFPD). The analytical method is previously described in Jacobsen *et al.* (1997). In brief, the sediment (fraction less than 2 mm) or the biota (ultra turrax® homogenised) were spiked with a recovery standard (tri-n-propyltin from Johnson-Mathey, Germany), acid ultrasonic digested, followed by pH adjustment (pH=5±0.5), *in-situ* ethylation and extraction to an organic solvent. Solvent clean-up procedures were performed using silica gel® in order to minimise the GC contamination. This method is optimised for organotin speciation and can therefore quantify organotin compounds from ethyl to phenyltin derivatives. There were no certified reference materials with a biota matrix at the time of analysis. An important part of the quality assurance used was therefore the participation in the QUASIMEME development exercise on organotin compounds in biota (butyl and phenyl derivatives) with satisfactory results (QUASIMEME, 1998).

Results and Discussion

Concentration levels in sediments

Table 1 shows the TBT levels in sediments from the Sound versus the organic fraction, measured as ignition loss. The concentration range is between 0.9 and 7.7 ng g^{-1} as dry weight (DW, normalised to Sn). The affinity for TBT to sorb to organic

fraction is supported by the significant relationship between TBT sediment concentration levels and the organic fraction ($r^2 = 0.90$). The linear relationship is presented in Fig. 2, where the linear regression line has a significant ($p < 0.0041$) positive trend. This indicates that TBT in marine sediments primarily associates to the organic fraction, which is in line with findings in other studies (Meador *et al.*, 1997 and Weidenhaupt *et al.*, 1997). The slope is suggested to be general for this local region, and mirrors the TBT loading combined with the organic sedimentation rate in the area.

DBT and MBT were below the limit of detection (0.2 - 0.4 ng g^{-1}) at all stations. Propyl- and phenyltin compounds were not observed in this study.

TABLE 1
Sediment concentrations at 6 stations in the Sound in ng g^{-1} as dry weight normalised to Sn. Data also refer to Fig. 2.

Station[a]	n[b]	TBT in sediment[c] ng g^{-1} (DW)	Sediment organic fraction % of sediment dry weight
1	2	1.3 ± 0.0	4.0
4	2	2.6 ± 0.5	6.3
5	1	0.9	4.6
9	2	1.0 ± 0.1	1.9
10	1	6.1	14.3
11	1	7.7	12.7

[a] The station numbers refer to Fig. 1., [b] n is the number of independent sample preparations performed, [c] average ± standard deviation within the same sample.

[**Fig. 2**]

Species dependent accumulation of butyltin compounds

The butyltin concentrations in benthic organisms from the same station in the Sound area (marked as P in Fig.1) are presented in Fig. 3. One of the investigated species, the sediment-feeding bivalve *Nuculana pernula,* is found to accumulate butyltins one order of magnitude more than the filter-feeding bivalves, *Arctica islandica, Musculus niger* and *Cardium echinatum.* The neogastropods *Neptunea antigua* and *Buccinum undatum* have even lower concentrations of TBT and the TBT/DBT ratio is smaller than one (see Fig. 3).

[**Fig. 3**]

Data from Fig. 3 could indicate that many of the analysed bivalves have a reduced capability to degrade TBT since the ratio between TBT and the degradation product is above one. The differences in concentration levels among bivalves are likely to be related to the feeding strategy, as also discussed in Langston and Burt (1991). The deposit feeders probably selectively ingest the organic rich (and hence also TBT rich) fraction of the sediment. and consequently increase their exposure to organic associated contaminants as e.g. TBT (Meador et al., 1997; Forbes et al., 1998). Our study strongly supports that TBT deposited in marine sediments still can be bio-available.

Due to their high bioaccumulation N. pernula was selected for the further investigation of butyltin distribution in the region, although this species is not abundant in the entire area, but restricted to saline waters and depths greater than 20 meters. However the main habitat of N. pernula is coincident with the important shipping areas in northern and central parts of the Sound.

Distribution of butyltin in Nuculana pernula in the Sound

Two transects were sampled, see Fig. 1. The contents of butyltins in N. pernula are shown in Fig. 4 and Fig. 5. The transect from east to west shows the highest values in the mid shipping lane and towards the Swedish coast. This could indicate a higher level of TBT or a higher bioavailability of TBT in the middle of the shipping lane. The higher TBT content towards the Swedish coast could be explained by the industrial port of Höganäs or higher organic sedimentation rates given by the hydrological and geological conditions.

[Fig. 4]

[Fig. 5]

The north-south gradient is more significant, which could be due to higher shipping activities across the Sound, such as ferries and from the major ports of Copenhagen and Malmø. The area outside Copenhagen is well sheltered and used as a long-term large vessel anchorage. These ships will therefore also contribute to a higher TBT loading in this area. Another reason for the higher TBT level in N. pernula in the

southern part of the sampling area, could be the higher organic content and thus the higher TBT concentrations (as dry weight) in those sediments (see Fig. 2).

TABLE 2
TBT concentrations (as Sn) in sediment (derived from TABLE 1 and normalised to organic fraction), in *N. pernula* and the concentration ratios between sediment and *N. pernula*. The dry weight for *N. pernula* was (14.3 ± 0.7) % (n=5).

Station[a]	$C_{sed,OC}$ TBT in sediment[b] ng g^{-1} (OC, as Sn)	$C_{N,DW}$ TBT in *N. pernula* ng g^{-1} DW (as Sn)	CR_{DW} Concentration ratio $C_{N,DW}/C_{sed}$	CR_{OC} Concentration ratio $C_{N,DW}/C_{sed,OC}$
1	31.1 ± 0.6	315	242	10.1
4	40.7 ± 8.5	364	140	8.9
5	19.6	287	319	14.8
9	50.7 ± 2.4	385	385	7.6
10	42.7	412	68	9.7
11	60.6	587	76	9.6
Avg.		392	205	10.1
St.dev.		106	131	2.45

[a]The station numbers refer to Fig. 1, [b]average ± standard deviation (See Table 1.)

[Fig. 6]

In Fig. 6 the relationship between the TBT concentration in sediment normalised to the organic fraction and the TBT concentration *in N. pernula* indicates that there is a positive trend. The linear regression trend is significant at $p < 0.017$ (assuming normal distributed data). Based on those data a concentration factor between sediment and *N. pernula* is calculated in Table 2. The formula based on the TBT concentration in *N. pernula* is suggsted to be used to estimate the bioavailable concentrations of TBT in the sediments by using equation 1.

$$CR = [TBT_{Nuc,DW}]/[TBT_{sed,OC}] \cong 10.1 \pm 2.45, \quad (Eq. \ 1)$$

CR is concentration ratio in the Sound, TBT $_{Nuc, DW}$ is the concentration in N. pernula on dry weight basis, TBT$_{sed,OC}$ is the TBT concentration in sediment normalised to the organic content.

TBT is accumulated efficiently in *N. pernula,* with concentration ratios between TBT in sediment (DW) and organism between 68 and 385 (see Table 2). Another deposit feeding organism, the bivalve *Scrobicularia plana,* accumulates TBT at a ratio of around 9, or almost 1 to 2 orders of magnitude less than *N. pernula* (Langston and Burt, 1991). Other marine species that can accumulate TBT are summarised in Table 3. It should be noted that the TBT levels in sediments are compared to dry weight and not to organic content so the listed species dependent pre-concentration ratios are only indicative.

TABLE 3
Comparison of species dependent TBT concentration ratio (CR) between organism dry weight and sediment dry weight

Species	Location	CR$_{DW}$ Concentration ratio $C_{N,DW}/C_{sed.}$	Reference
Nuculana pernula	Øresund DK/S	68 - 385	This study
Crassostrea virginica	Chesapeake Bay, USA	4 - > 110	Espourteille *et al.* (1993)
Scrobicularia plana	Southern England	5 - 95	Langston and Burt (1991)
Detrivore amphipods	Lab	97	Meador *et al.* . (1997)
Detrivorrous polychaete	Lab	31	Meador *et al.* . (1997)
Mytilus galloprovincallis	Korea	4-7	Hwang *et al.* 1999
Crassotra gigas	Korea	4-7	Hwang *et al.* 1999

It should be emphasised that the high body concentrations of TBT in *N. pernula* could have a toxic effect, but nothing is known about effects on this species. For future assessment of the TBT pollution trend, a study of the long-term depuration or elimination rate of TBT from *N. pernula* could be relevant. Further investigations on the TBT toxicity, the possible impact on benthic communities and the ecosystem are therefore important.

Conclusions

TBT and primary degradation product DBT was detected in all of the collected biota samples from the Sound. In sediment samples, only TBT was detected.

The concentration of TBT in sediments and *N. pernula* strongly relates to the sediment organic fraction. The distribution of butyltin compounds in *N. pernula* from the Sound show higher levels towards the major harbour and anchorage areas. If there is a trend perpendicular to the shipping lane is somewhat unclear.

N. pernula was found to be an ideal monitoring organism for butyltin distribution in open and sublittoral Swedish and Danish waters, due to high accumulation potential.

Acknowledgements

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common whelk (*Buccinum undatum*) and redwhelk (*Neptunea antiqua*) in Danish waters.

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CAPTIONS TO FIGURES

Fig. 1. Map of the study area, the Sound, between Sweden and Denmark. The station numbers are shown next to the legend (+).

Fig. 2. The relationship between organic content in the sediment, measured as percent ignition loss, and the TBT concentration in sediments, measured as ng Sn g^{-1} (as Sn) dry weight and as Sn from 6 stations from the Sound.

Fig. 3. TBT (■) and DBT (□) concentrations in ng g^{-1} (wet weight, as Sn) in different species of molluscs from the same position from station P (pilot) in the northern parts of the Sound. All species were homogenised, sub-sampled and analysed (n) times. Homogenates consisted in total of (i) number of individuals: *Buccinum undatum* n=3, i=8; *Neptunea antiqua*: n=2, i=2; *Arctica islandica*: n=2, i=6; *Musculus niger*: n= 1, i=5; *Cardium echinatum*: n=1, i=2; *Nuculana pernula*: n=1, i=10. Only at n > 1 standard deviation bars are shown.

Fig. 4. Concentrations of TBT (■) and DBT (□) in *N. pernula* at a 12 km transect across the northern approaches to the Sound from west to east. Each bar represents 10 individual *N. pernula* pooled and homogenised (except station 8, where only 2 individual *N. pernula* were captured). The homogenates were sub-sampled and analysed once or twice (marked with standard deviation bars).

Fig. 5. Concentrations of TBT (■) and DBT (□)in Nuc*ulana pernula* at a transect from north to south. The station "1-8" is an average of stations 1 - 8 at the west to east transect shown in Fig. 4 and marked with standard deviation. The rest of the bars bar represents 10 individual *N. pernula* pooled and homogenised. The homogenates were sub-sampled and analysed once or twice (marked with standard deviation bars).

Fig. 6. The TBT concentration levels in: *Nuculana pernula* as a function of the TBT levels in the sediment and normalised to the organic fraction.
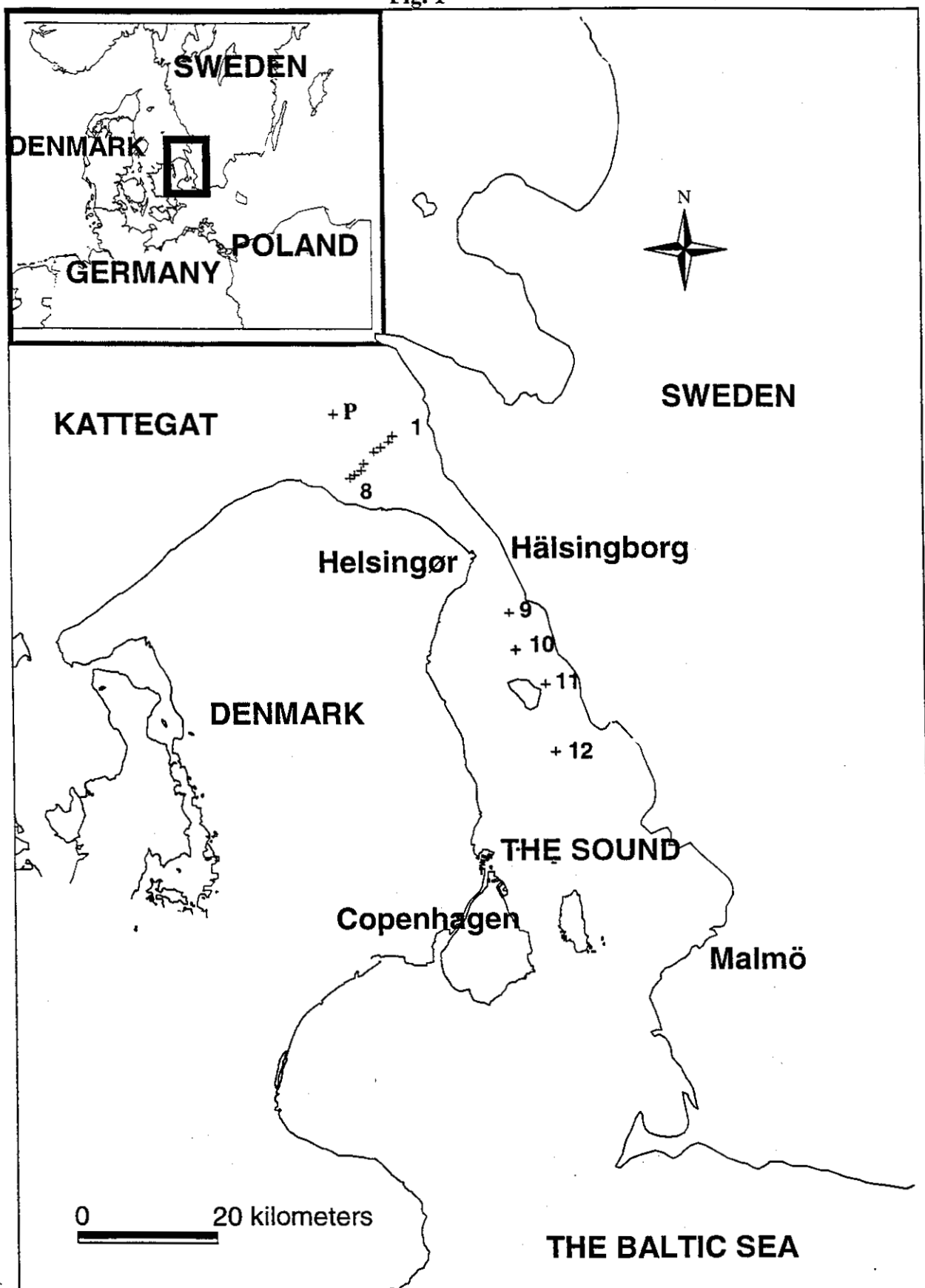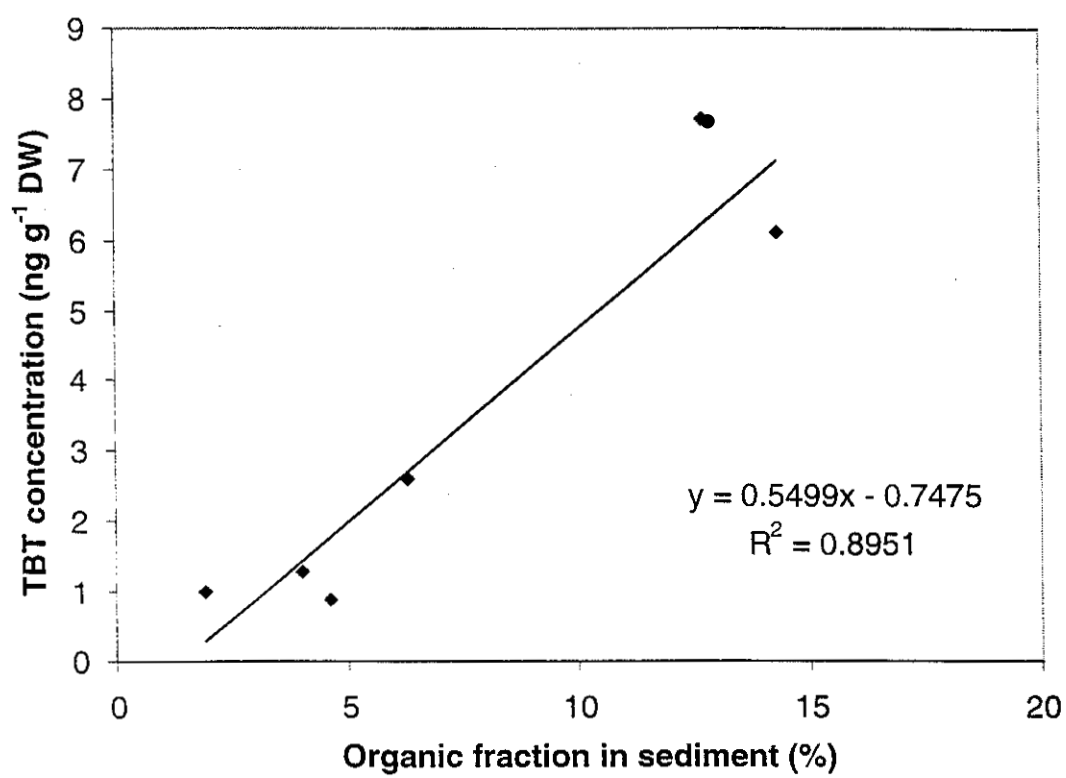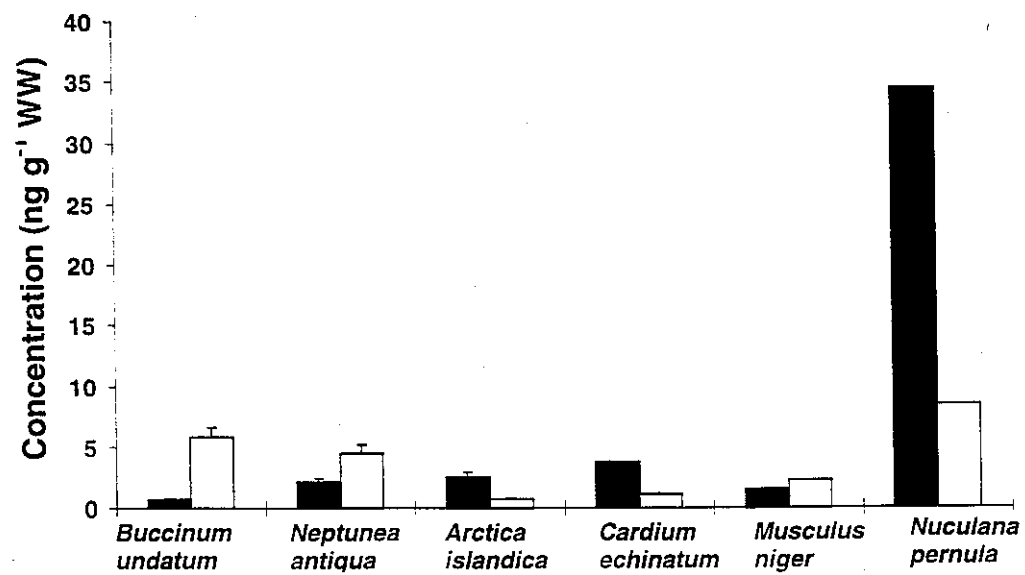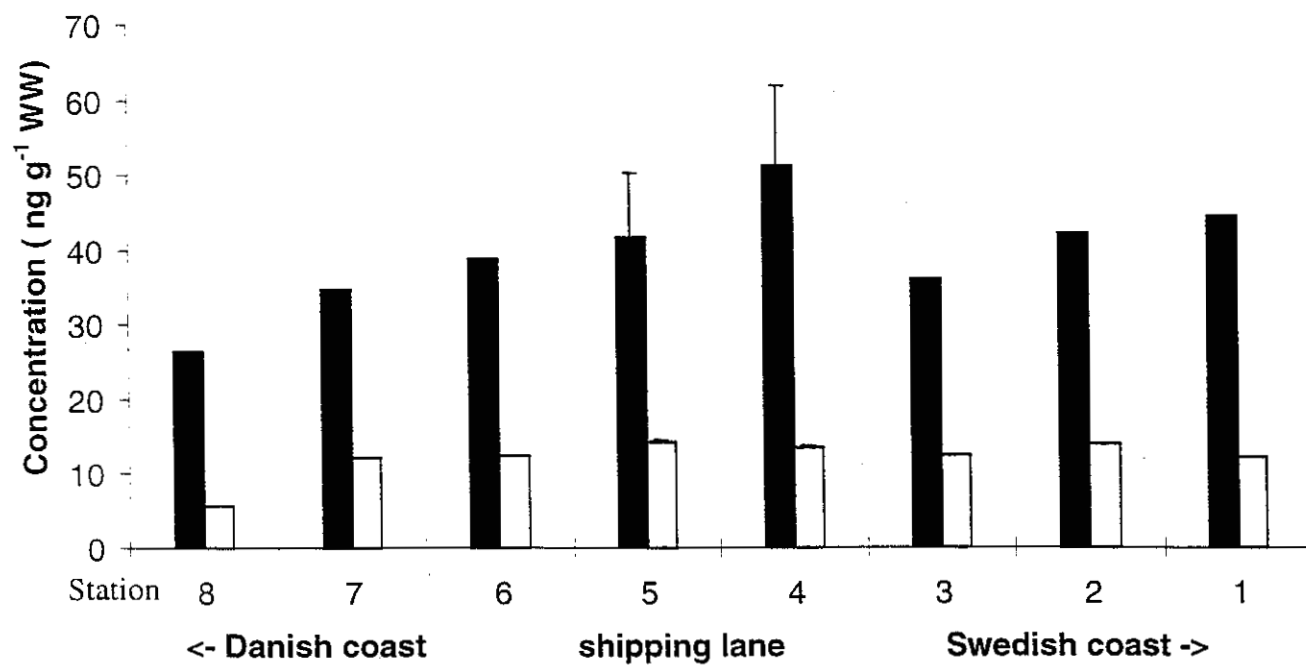
Fig. 1

Fig. 2

Fig. 2. Scatter plot of TBT concentration (ng g⁻¹ DW) versus Organic fraction in sediment (%), with the regression equation $y = 0.5499x - 0.7475$ and $R^2 = 0.8951$.

Fig. 3

Fig. 4

Fig. 5

Fig. 6

y = 6.5619*x* + 123.29
R^2 = 0.7945

X-axis: TBT concentration (ng g^{-1} organic fraction)
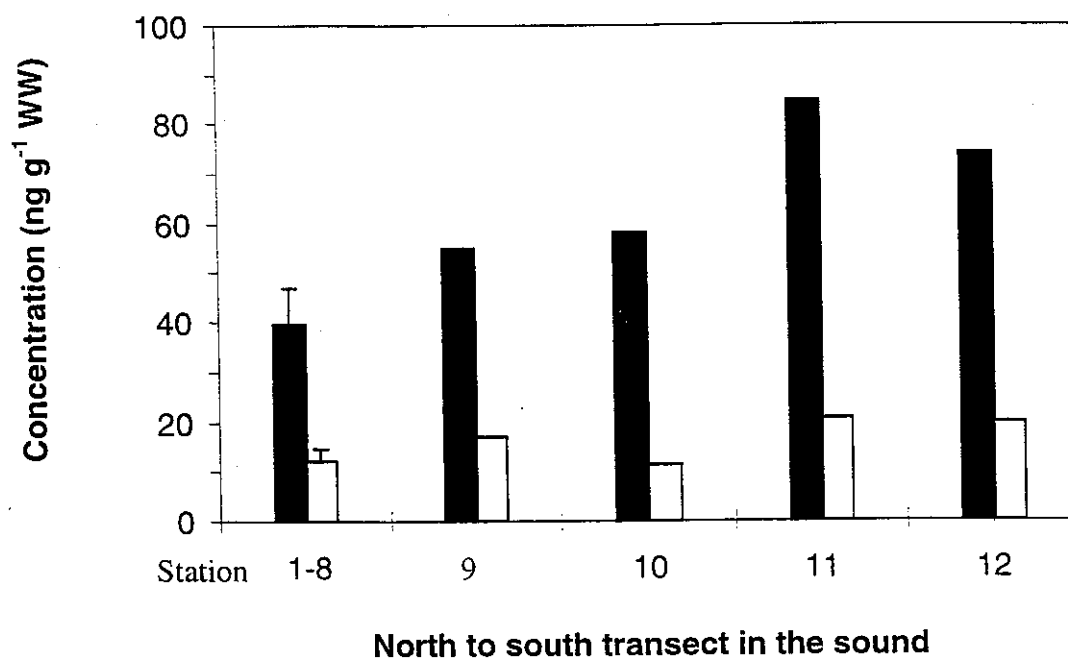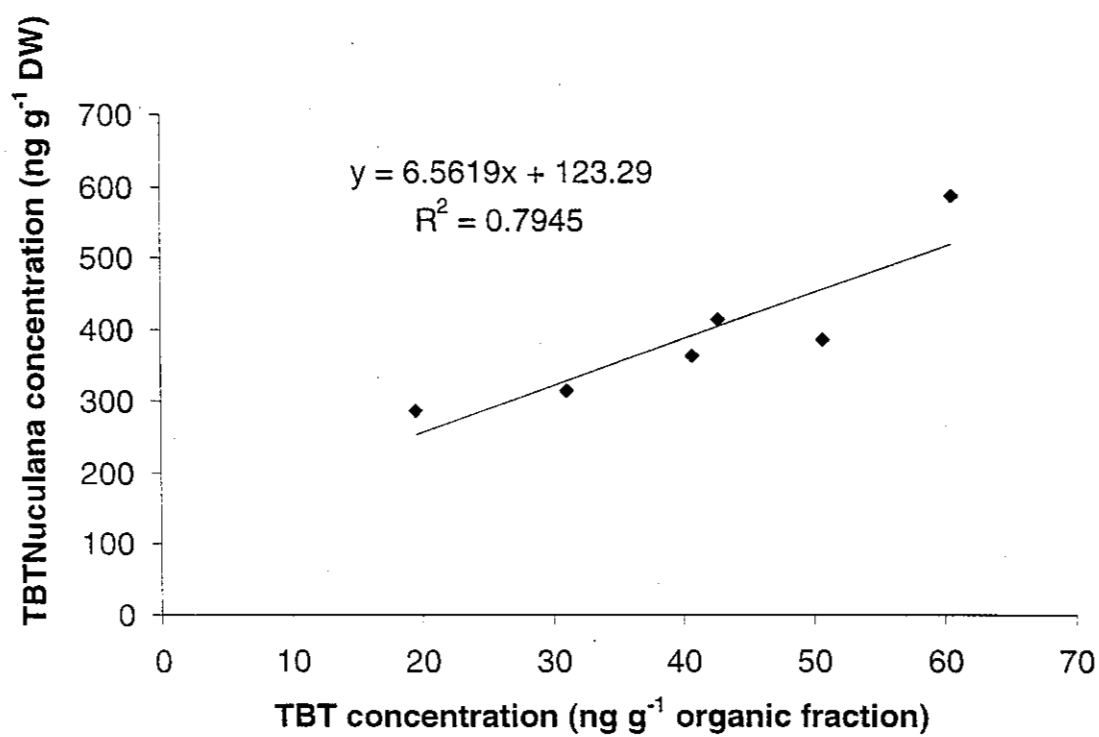Y-axis: TBTNuculana concentration (ng g^{-1} DW)

1.4 PAPER IV

Jacobsen J.A., and Strand, J.(Subm. 2000). Depositional Profiles of Butyltin Residues in Marine Sediments from the Sound Between Sweden and Denmark. (Submitted to *Environmental Technology*)

DEPOSITIONAL PROFILES OF BUTYLTIN RESIDUES IN MARINE SEDIMENTS FROM THE SOUND BETWEEN SWEDEN AND DENMARK

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ABSTRACT

Marine sediment cores, from the estuarine waters between Sweden and Denmark, were collected and the content of butyltin and phenyltin residues were measured. The cores contained tri-*n*-butyltin (TBT) ranging from below limit of detection < 1 μg kg^{-1} DW to 24 μg kg^{-1} DW. All organotin concentrations are normalised to tin atoms (Sn) in order to facilitate comparisons between butyltin species. Only small amounts of TBT degradation products, dibutyltin (DBT) and monobuytltin (MBT) were found, possibly due to the low degradation rates in sediments. No triphenyltin or its degradation products were detected. Calculated first order TBT degradation rates in sediment indicate half lives between 8.8 and 10.2 years. The low occurrence of degradation products indicates even slower degradation. There are indications of declining TBT concentrations in the surface sediments, probably due to legislation and reduced use of TBT for boats < 25 m.

INTRODUCTION

Tri-*n*-butyltin (TBT) is perhaps one of the most toxic substances deliberately introduced to the marine environment. Originally, TBT was marketed as an environmental friendly substitute to non-degradable and toxic heavy metals such as copper, mercury, arsenic and lead in antifouling paints. The total degradation of TBT into the less toxic inorganic tin, as well as carbon dioxide and water, is considered an environmental sound solution. Nevertheless, TBT degradation rates in the environment seem longer than first expected based on laboratory studies [1, 2, 3]. Furthermore beginning evidence of severe environmental problems emerged, as effect studies from Arcachon bay, France, shell anomalies and reduced growth in the pacific oyster caused by TBT pollution from local boating activities ceased the production of oysters [4]. Simultaneously the widespread occurrence of imposex in UK populations of dog-whelks, *Nucella lapillus*, was linked to TBT pollution. These findings called for restrictions on the TBT use, especially in fragile coastal marine environments [5]. The sources of TBT were regulated as the near global restriction banned the use of TBT for boats < 25 m in length. In Sweden and Denmark, this legislation was effectuated in 1989 and 1991, respectively. Nevertheless the effectiveness of this regulation has been much debated hitherto the use of TBT containing antifouling paints on ships > 25 m and imposex has recently reported to be related to shipping intensities in the open North Sea [6]. Commercial shipping is still considered to contribute with around 0.2 to 1.4 tons TBT per year (as Sn) (in 1998) to the inner

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1.5 PAPER V

Jacobsen, J. A. and Asmund, G.(2000) TBT in marine sediments and blue mussels (*Mytilus edulis*) from Central-West Greenland *Science of the Total Environment*, **245**, 131-136.

ELSEVIER

TBT in marine sediments and blue mussels (*Mytilus edulis*) from central-west Greenland

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4000 Roskilde, Denmark*

Abstract

Concentrations of butyltin compounds were investigated in the bivalve *Mytilus edulis* (five sites) and marine sediments (three sites) near the largest town, Nuuk, in Greenland. In seven of the eight samples the extremely toxic compound tributyltin (TBT) was detected. The concentrations of tributyltin and degradation products in the bivalves were close to 1 μg kg^{-1} wet weight (ww), calculated as Sn, which is lower than those found in Iceland and the Faeroe Islands. In sediments the concentration of TBT ranged from below the limit of detection of 1 μg kg^{-1} to 171 μg kg^{-1} dry weight (dw), calculated as Sn. which is comparable to levels found in Europe. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: TBT; Butyltin; Bivalves; Sediments; *Mytilus edulis*; Arctic environment

1. Introduction

Organotin compounds are used in a variety of industrial processes and products as, for instance chemical reaction catalysts, PVC stabilisers, and biocides. One of the most toxic substances delib-

erately released to the marine environment is the organotin anti-fouling agent tributyltin (TBT) which is mainly used in the paints applied to the sub-surface areas of ships. The first effects on non-target organisms, oysters, were found by Alzieu and co-workers in the beginning of the 1980s (Alzieu et al., 1986). TBT is toxic (sub-lethal) at approximately 1 ng Sn l^{-1} in seawater, and has caused a decline in dogwhelk populations (*Nucella lapillus*) at a number of sites around the UK (Gibbs and Bryan, 1986). Recently, effects

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