UNIVERSITY OF SOUTHAMPTON

FACULTY OF ENGINEERING SCIENCE & MATHEMATICS

School of Chemistry

The remediation of tributyltin-contaminated dredgings and waters

by

Evgenia-Varvara Gkenakou

Thesis for the degree of Doctor of Philosophy

December 2008

UNIVERSITY OF SOUTHAMPTON

ABSTRACT

FACULTY OF ENGINEERING, SCIENCE & MATHEMATICS

SCHOOL OF CHEMISTRY

Doctor of Philosophy

THE REMEDIATION OF TRIBUTYLTIN-CONTAMINATED DREDGINGS AND WATERS

by Evgenia-Varvara Gkenakou

Tributyltin (TBT) is a pollutant, mainly introduced to the environment as a marine anti-fouling agent. The aim of this work was to assess and develop sustainable and cost-effective remediation technologies for TBT-contaminated dredged materials. For this purpose, analytical methods were developed for sediments and sediment leachates.

For the sediments, a triple extraction followed by derivatisation and measurement by gas chromatography with pulsed flame photometric detection was employed, avoiding the lengthy concentration step of the organic layer. The TBT detection limit of *ca* 0.04 mg Sn/kg in sediment was below the suggested limit of 0.1 mg/kg for sea disposal of TBT-contaminated dredgings (OSPAR Commission). For the leachates, derivatisation and extraction into hexane was used. Also, a new procedure, with the potential for automation, was developed for the simultaneous analysis of multiple water samples, based on *in situ* extraction and derivatisation on C_{18} solid phase extraction cartridges. No legislative limits existed for TBT in leachates, therefore the detection limits of *ca* 6-10 ng Sn/L achieved were regarded satisfactory, as they were below or similar to the EQS for coastal and estuarine waters or freshwaters (2-20 ng/L TBT). A pilot investigation was carried out on a dockyard to evaluate the use of X-Ray fluorescence as a screening method for the presence of TBT in sediments. Due to tin contamination such a technique was not suitable for the site examined.

Incineration was found to remove TBT but it would incur very high costs. Ultrasonic destruction was not effective enough, even on TBT-spiked water solutions. Carbon products, pure clays, organically modified clays, zero valent iron, fly ash and cements were screened for their abilities to prevent TBT leaching, using a leaching test. The best performer was a powdered activated carbon product which, even mixed with cement that increases the leaching of TBT, delivered a TBT-free (< 5 ng Sn/L) leaching test result 33 days after the mixing. The result showed that this technique could provide a solution for the immobilisation of TBT in contaminated dredgings by mixing this relatively low-cost, multi-purpose and inert additive, with or without cement according to the site specific requirements.

Table of Contents

DECLARATION OF AUTHORSHIP

I, Evgenia-Varvara Gkenakou, declare that the thesis entitled

The remediation of tributyltin-contaminated sediment dredgings and waters

and the work presented in the thesis are both my own, and have been generated by me as the result of my own original research. I confirm that:

- this work was done wholly or mainly while in candidature for a research degree at this University;
- where any part of this thesis has previously been submitted for a degree or any other qualification at this University or any other institution, this has been clearly stated;
- where I have consulted the published work of others, this is always clearly attributed;
- where I have quoted from the work of others, the source is always given. For the reproduction of any images permission was granted, apologies for any omissions. With the exception of such quotations, this thesis is entirely my own work;
- I have acknowledged all main sources of help;
- where the thesis is based on work done by myself jointly with others, I have made clear exactly what was done by others and what I have contributed myself;
- none of this work has been published before submission

Signed: ………………………………………………………………………..

Date:……………………………………………………………………………

Acknowledgements

I would like to thank my academic supervisor Dr. Alan G. Howard, my industrial supervisors Bill Gush and Simon Bamford, for giving me the chance to be part of this interesting project, and also Land and Water Ltd and the Knowledge Transfer Partnership programmes for their funding and support. I should also mention the companies Steetley Bentonite and Chemviron-Calgon that generously provided us with materials to test.

I would also like to thank my supervisor for his advice and for correcting numerous drafts of the thesis, the members of my group Huyong Xuan, Supamathree Bunprapob, Natthakarn Ketkoom, Mohammed Algaradah, Luca Vescovo and Awad Al-Rashdi for their help and cooperation, Dr. Ian Croudace from the National Oceanography Centre for his help with the XRF part of my work, Dr. Andreas Danopoulos and his group for their help and for providing training with the glove box and the staff of Chemistry Stores for always being cheerful and willing to help.

I wish to also thank all the friends I made in Southampton for the great time we had together and even when a long time will have passed and we are all scattered around the world they will still be in my heart. And all my extended family and especially Lily, Leonidas, Telamon, Max and Laura and of course Areti, Thomas and Anna for the stimulating conversations and encouragement.

A big thank you is due to my beloved sister Melina for her support and encouragement. My much-loved partner in life Christos always has been there with his advice, his continuous help and caring, his practical and morale support and his patience and I thank him, as without him this work would not have been possible. I am grateful to my wonderful parents Yannis and Martha for their encouragement to be the best I can in life. To them I dedicate this thesis.

Abbreviations

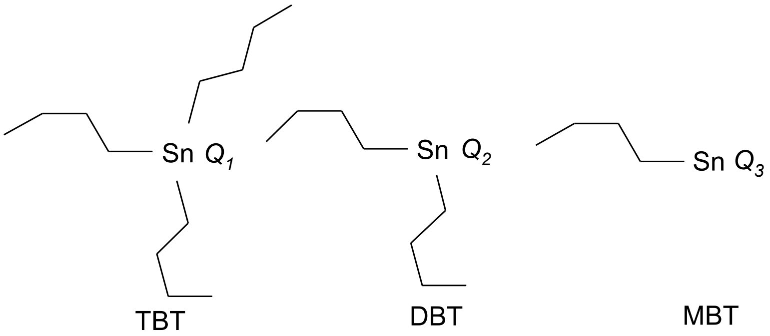
AAS	atomic absorption spectroscopy
AcOH	acetic acid
AcONa	sodium acetate
APDC	ammonium pyrrolidinedithiocarbamate
CRM	certified reference material
DAF	dissolved air flotation
DBT	dibutyltin
$DBTEt_2$	dibutyldiethyltin
DCC or DCCT	diethyldithiocarbamate
DCM	dichloromethane
DEA-DCC	diethylammonium diethyldithiocarbamate
DHDBT	di(n-butyl)di(n-hexyl)tin
DMD	dimethyldioxirane
DMeBT	di(n-butyl)dimethyltin
EQS	environmental quality standard
ETAAS	electrothermal AAS
EtOAc	ethyl acetate
EWC	European waste catalogue
FID	flame ionisation detector
FPD	flame photometric detector
GAC	granular activated carbon
GC	gas chromatography
HG	hydride generation
HPLC	high performance liquid chromatography
ICP-MS	inductively coupled plasma mass spectroscopy
IMO	international marine organisation
LC	liquid chromatography
LEI	laser enhanced ionisation
LLE	liquid-liquid extraction
MBT	mono(n-butyl)tin
$MBTEt_3$	mono(n-butyl)triethyltin
MHTBT	mono(n-hexyl)tri(n-butyl)tin
MIP-AES	microwave induced plasma atomic emission spectrometry
MS	mass spectroscopy

NaDCC	sodium diethyldithiocarbamate
OPC	ordinary Portland cement
OSPAR	Oslo Paris convention
PAH	polyaromatic hydrocarbons
PDMS	polydimethylsiloxane
PFPD	pulsed flame photometric detector
PTV	programmed temperature volatilisation
RPLC	reversed phase liquid chromatography
RSD	relative standard deviation
SFE	supercritical fluid extraction
SGV	soil guideline values
SPC	self-polishing copolymers
SPE	solid phase extraction
SPME	solid phase microextraction
TBT	tri(n-butyl)tin
TBTCl	tri(n-butyl)tin chloride
TBTEt	tri(n-butyl)ethyltin
TBTF	tri(n-butyl)tin fluoride
TBTH	tri(n-butyl)tin hydride
TBTO	tri(n-butyl)tin oxide
TCyT	tri(n-cyclohexyl)tin
TEA	triethylamine
TeBT	tetra(n-butyl)tin
THMBT	tri(n-hexyl)mono(n-butyl)tin
TPeTCl	tri(n-pentyl)tin chloride
TPrTCl	tri(n-propyl)tin chloride
TPrTEt	triethyl(n-propyl)tin
TBTOH	tri(n-butyl)tin hydroxide
XRF	X-ray fluorescence
ZVI	zero valent iron

1 Introduction

1.1 Introduction

One of the most common contaminants in the dredgings from ports, harbours and marinas is tributyltin (TBT). TBT compounds are organic derivatives of Sn(IV) with three covalent bonds with n-butyl (C_4H_9-) groups and one with Q which can be a halide, oxygen, or a part of a polymer (Figure 1).



Q_1, Q_2, Q_3 = Cl^-, F^-, O^{2-}, polymers

Figure 1. Structures of tributyltin (TBT), dibutyltin (DBT) and monobutyltin (MBT)

TBT was largely introduced in the natural environment as an anti-fouling agent in paints used for the hulls of boats, and other structures to be used in the marine environment. Marine bio-fouling, the accumulation of algae and shellfish on the surface of marine vessels, can have a significant impact on the friction against the water increasing the fuel consumption of ships by up to 77%[1]. It also increases the need for maintenance and produces waste. According to some estimates, 70-80% of the commercial ships in operation worldwide have used TBT-containing paints.[2]

TBT enters the marine environment by two main mechanisms. The first is by leaching out of the paint, by diffusion, directly into the water column. Most of it is believed to be adsorbed on the sediment, due to the high sediment-water partition coefficient of TBT. The other entrance route is the discharge of wastewater from dockyards, where ship maintenance activities, like sandblasting and repainting, take place. This TBT is contained in paint flakes, which are heavy and settle into the sediment and accumulate in adjacent areas. The paint flakes leach TBT into the water constantly, as TBT is very persistent in nature and has a half life of 1-20 years.[3] The degradation products of TBT are the less toxic compounds of dibutyltin (DBT) and monobutyltin (MBT) (Figure 1).

Organotins were used as antifoulants in quantities of about 3,500,000 kg per year globally. The use of organotin compounds in other industries constitutes an additional source of butyltin compounds in the environment. They have been used as polymer stabilisers, catalysts for polymer production (polyurethanes, silicones, esters), in material and textiles protection, as wood and stone preservatives, disinfectants and also as agricultural products (biocides).[4]

1.2 Chemistry of the tributyltin-containing paints

The marine biofouling problem has been known since ancient times. Ancient Greeks used to cover the hulls of their ships with mixtures based on tar and wax as well as lead to avoid bio-fouling.[5] Since the 1950s and a report by Van de Kerk and co-workers[6] about the toxic properties of compounds containing TBT, scientific research has focused on TBT-based paints as anti-fouling agents. Tri-organotins became very popular because they had a wide range activity, they did not cause the galvanic corrosion of aluminium hulls that other metal-containing paints did and they were colourless so they were the ideal substrate for any colour of paint.[4] The main organotin compounds that have been used as antifouling agents are: bis-tributyltin oxide (TBTO), triphenyltin fluoride (TPTF), tributyltin fluoride (TBTF), tributyltin chloride (TBTCl) and TBT self-polishing copolymers (SPC).[7]

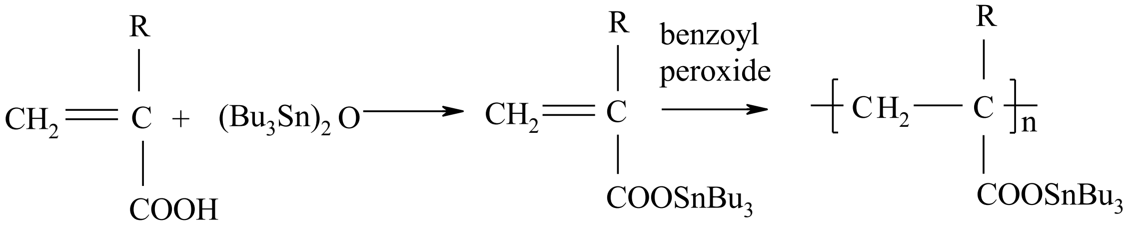
The most important characteristic for the antifouling effectiveness of the triorganotin compounds is their leaching rate from the paint film. If the leaching rate is too low the compound fails to create a protective cover of the material. On the other hand if the leaching rate is too high then the compound will be quickly spent, making it unsuitable for long-life use. The contamination caused will also be greater in that case.

The solubility of an organotin compound is related to its leaching rate. The higher its solubility in water the higher its leaching rate from the hulls of the boats to the water. TBTO has the highest solubility (Table 1). It easily migrates from the paint film and therefore has a short activity period. Nevertheless, its compatibility with other biocides and stability under a wide range of pH conditions has made it the most popular antifouling agent.

Organotin compound	*Solubility in seawater*
TBTO	8-10 ppm
TBTF	6 ppm
TPTF	1 ppm

***Table 1. Solubility of organotin compounds in seawater*[4]**

The above organotins were used as free-association paints i.e. they were initially dispersed within the paints and their release was uncontrolled. The revolutionary TBT-self polishing copolymer (SPC) compound was obtained by the reaction of TBTO with a polymeric system, typically acrylic or methacrylic acid according to Omae[4] (Figure 2).



R=H, Me

Figure 2. Formation of TBT-self polishing copolymer

The product has the characteristic of being easily hydrolysed by sea water as the paint contains a hydrophilic carboxylate group. The TBT moiety is cleaved from the copolymer exposing a new layer even if the boat is at zero speed.[7, 8]

The next step in the evolution of TBT-based paints was the incorporation of TBT into a siloxane polymer (Figure 3) where the hydrolysis cleaves the tin-oxygen silicon bond (Figure 4), according to Omae[4].

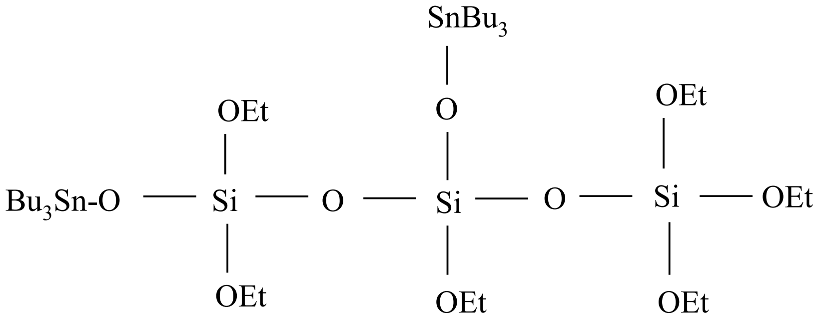


Figure 3. Structure of the polysiloxane TBT copolymer

$$\equiv \text{Si-OSnBu}_3 + \text{H}_2\text{O} + \text{Cl}^- \longrightarrow \equiv \text{Si-OH} + \text{Bu}_3\text{SnCl} + \text{OH}^-$$

Figure 4. The cleavage of the Si-TBTO bond from the paint and the release of TBT in the water

The results of the self-polishing innovation are that the leaching rate of the antifouling agent is now controlled, giving up to 3 years without need for dry-docking, and a fresh smooth layer is exposed after the erosion process, reducing the friction on the boat's movement.[4]

1.3 Toxicity of TBT

Inorganic tin is not considered toxic but its organic compounds are[9]. The toxicity of organotins varies according to the nature and number of organic groups attached to the tin atom. It is established that it is mainly the triorganotins, R_3SnQ (R= organic group, Q= counter ion), that pose a threat to the aquatic organisms. Trimethyltins are toxic to insects, triethyltins to mammals, tributyltins to fish, algae, mussels, molluscs and fungi, triphenyltins to fish, molluscs and fungi and tricyclohexyltins to mites and fish.[10] An increase in the number of carbons of the carbon chain is combined with a decrease in toxicity. It should be noted that the toxicity of the organotin compounds does not seem to depend on Q (Cl^-, F^- etc)[4], unless this is toxic on its own. In studies of animal proteins this has been attributed to the fact that trialkyltins have been found to form complexes with amino acids where the counter ion Q is not involved, according to [4]. The nature of Q may determine the toxicity of an organotin compound indirectly, as it influences the physical-chemical properties such as solubility in water or organic solvents and volatility.

The toxicity of TBT compounds is associated mainly with the chronic toxicity of low level TBT concentrations in the marine environment but TBT can also be lethal to marine organisms in very high doses (0.04-16 μg/L). According to research that started during the 1970s, after a drop in cultured oyster populations in Arcachon Bay in France[11], even extremely low levels of TBT in water can adversely affect sensitive non-target species.[10] TBT has been quoted to be one of the most toxic compounds introduced to nature by man.[12] More specifically, 1 ng/L of TBT can be harmful to algae, zooplankton, molluscs and the larval stage of some fish.[10, 13, 14] In the UK the species mainly affected are the common dogwhelk *Nucella lapillus* and the periwinkle *Littorina littorea.*[13]

The most common toxicological consequence of TBT poisoning is the phenomenon of imposex (imposed sexual organ), which is attributed to the endocrine disruptive action of the TBT compounds. Imposex is defined by the development of male sex characteristics in female gastropods (Figure 5), causing failure of the species to reproduce and thus a drop in populations or even local extinction.[13-17] According to Omae[4], up to December 1998 more than 140 species of gastropod were affected by imposex.

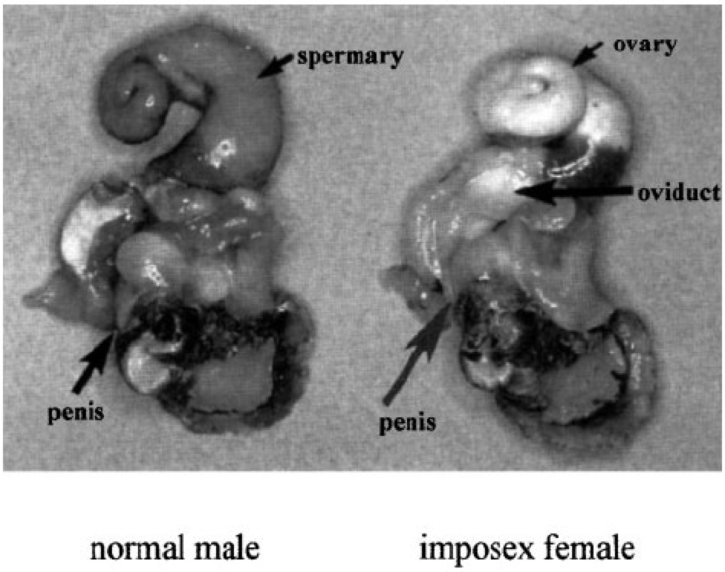


Figure 5. Imposex on rock shell Thais clavigera [4]

For mammals, the acute oral median lethal dose (LD_{50}) for TBT is 112-349 mg/kg[4] (rats) and it is higher than that of $Et_3SnOCOMe$ (LD_{50}= 4 mg/kg)[10], which is the most toxic tri-organotin to mammals. In humans, accidental occupational exposure to TBT has been found to cause irritation of the respiratory tract, eyes and skin. Nausea and vomiting have been reported after suspected inhalation of TBTO. Other reported symptoms are tiredness, headaches and loss of the sense of smell.[14] A tentative acceptable daily intake (ADI) of 1.6 μg/kg per day was adopted by Japan. No significant data have been found regarding carcinogenicity, teratogenicity or mutagenicity of TBT.[14]

Other butyltin contaminants are DBT and MBT, which are mainly introduced to the environment as degradation products of TBT. Recently, leaching of DBT from PVC water pipes was established as another common source of butyltins.[15-17] DBT and MBT are generally regarded as less toxic than TBT in the aquatic environment, but they are still of environmental concern (DBT LD_{50}=100 mg/kg, MBT LD_{50}=2140 mg/kg in rats)[10].

1.4 Occurrence and fate of TBT in nature

TBT enters the marine environmental mainly contained in paint flakes or in free suspended form in water. It then partitions between the paint flakes, the water, the sediments and any organic matter. According to data compiled for tributyltin compounds by the International Programme on Chemical Safety[18], concentrations of TBT of up to around 1.6 μg/L have been found in seawater and estuaries, 7.1 μg/L in freshwaters, 26.3 mg/kg in coastal sediments, 3.7 mg/kg in freshwater sediments, 6.4 mg/kg in bivalves, 1.9 mg/kg in gastropods and 11 mg/kg in fish. These data are useful in order to obtain a rough picture of the magnitude of the contamination, even though it is not clear if the data express suspended or total concentration for the water samples.

In Figure 6, the ranges of TBT concentrations encountered in marine systems are shown. The partitioning of TBT between the different parts of the water-sediment-tissue system has been studied and the results assist in the understanding of the fate of TBT in the marine system, as well as the difference in the concentrations encountered in water, sediment or tissue samples.

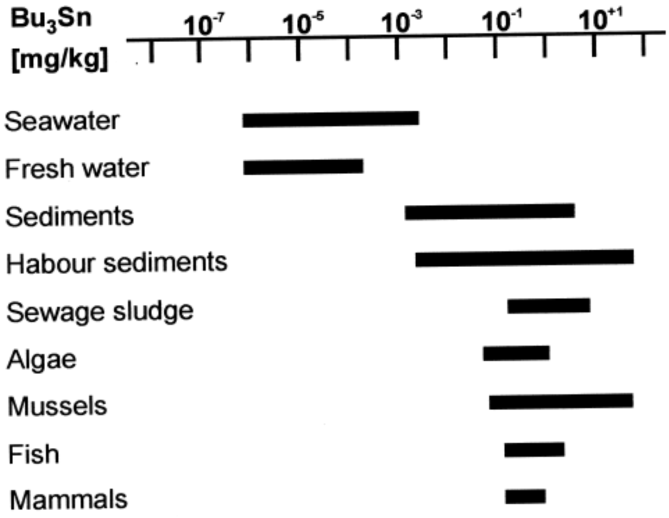


Figure 6. Ranges of concentrations of TBT (mg/kg) in the environment (from Ref[10] with kind permission from Elsevier)

In natural waters, TBT will form complexes with inorganic ions such as chloride, hydroxide and nitrate as well as organic compounds. According to Arnold *et al*[19] the pKa of TBT is approximately 6.25, so 50% of the TBT is in its ionic form at pH 6.25. In the same study it was calculated that TBT in solution occurs 93% as a hydroxide, under conditions present in seawater (pH=8, ionic strength =0.5 M).

The levels found within each category of environmental samples vary significantly (Figure 6). The octanol-water partition coefficient (Kow) can be used to explain the wide range of concentration values of neutral lipophilic organic compounds in water-sediment-tissue systems[20]. As the lipophilic compounds are expected to have an affinity for the lipid of tissue similar or proportional to that for octanol, their accumulation on tissue and the organic matter of the sediment could be predicted.[20] Studies on the Kow values for TBT report that these are highly dependent on the pH. This can be expected, as the strength of the lipophilic character of TBT is reduced with the pH, due to the increase of its ionic nature. In seawater (pH~8), values of $\log_{10}$ Kow from 3.7 to 4.4 were determined, while Kow values were one order of magnitude less at pH 6.[19, 21, 22]

In data compiled by Meador[23] from studies of laboratory experiments carried out in both seawater and freshwater, a correlation between the total organic carbon content of the sediment and the partition of TBT in a water-sediment system has been found. The values for the water-sediment partition coefficient Kp vary widely, so it is normalised for the organic content. The values for the normalised partition coefficient (Koc) show that $\log_{10}$ Koc is 4.3 to 5.0[24-28]. According to Meador [23], models that are used to predict the Koc from the Kow for lipophilic compounds are successful in the case of TBT, which is attributed to the lipophilic character of TBT under the pH conditions in natural waters.

Complexing of the TBT with the mineral fraction of the sediment has also been found.[29] A study by Poerschmann *et al*[28] on the partition of TBT between water and ashed sediment showed that only 26% partitioning occurred compared to that for the whole sediment. According to that study, the percentage recorded is indicative of the lesser contribution of the mineral content to the total partitioning of the TBT on the sediment, compared to the contribution of the organic matter. Since the ashing changes the nature of the inorganic phases, perhaps more work would be necessary to establish the extent of the contribution of each phase to the complexing.

The partitioning of TBT between sediment and water is difficult to calculate in an open marine system, as the water acts as an infinite sink for the TBT and equilibrium will not be achieved. Values of Koc and Kp (the partition coefficient of TBT between the overlaying water and the sediment) from the field, therefore vary significantly. Kp values of 5×10^{2}-1×10^{4} have been reported[30-33] and Koc values from 1×10^{5}-5×10^{5}, according to Langston and Burt[34]. The Koc values are an order of magnitude higher, which means that more TBT is found in sediment than in the water for a particular concentration of TBT in the sediment, expressing a higher affinity of the TBT for the sediment.

Bioaccumulation of TBT within the tissue of marine organisms appears to follow slightly different rules than simple partitioning. Meador[23] concludes that the amount of TBT accumulated in the marine organisms can only be determined by kinetic models. The amount of body lipid is proportional to the toxic response of the organism to TBT, but it is not proportional to the amount of TBT residue on the organisms' tissue.

Some extent of TBT degradation may occur when TBT is exposed to UV light [35] and bio-degradation has also been reported.[36, 37] Both procedures appear to proceed by de-butylation. Typically, the by-products are dibutyltin, monobutyltin and CO_2. Seligman *et al*[38] measured the degradation of TBT in coastal sea water and reported a half-life of ten days. The degradation was attributed mainly to biological activity, as a separate experiment showed that UV light degradation proceeded much slower.

The only significant tin-carbon bond formation reaction in the environment appears to be methylation. Methylation combinations of tributyltin and its by-products lead to a plethora of methylated compounds, some of them toxic.[39]

In general, the behaviour of TBT in natural waters can be predicted but the models require good understanding of the chemistry of TBT as well as characterisation of the properties of the water, sediment and the tissue present. Degradation may occur under some conditions but the degradation may not always result in de-contamination.

1.5 Legislative framework for the management of TBT-contaminated dredgings

1.5.1 Background legislation on TBT and contaminated soils

The International Maritime Organisation (IMO), a specialised agency of the United Nations with responsibility for safety and security of shipping and the prevention of marine pollution by ships, acknowledged the harmful effects of organotin antifouling agents in 1990. IMO adopted a resolution to eliminate the use of TBT-containing paints on non-aluminium hulled vessels < 25 m and also eliminate the use of such paints with a leaching rate of more than 4 μg TBT per day. In 2001, the IMO's "Convention on the control of antifouling systems on ships"[40] banned the application of TBT-containing paints globally. According to the convention, from 1st of January 2003 and by 1st of January 2008 all ships should either not have such paints on their surfaces and external parts or they should have a sealing layer preventing the leaching of such paints. The Convention would become effective 12 months after at least 25 countries had ratified it. After the accession on the treaty by Panama on the 27 of September 2007 the Convention will come in full effect from 27 September 2008.[41]

Dredgings from coastal, estuarine or inland port areas are typically tested for tributyltin contamination. The criteria set by the Oslo and Paris Commission on the protection of the marine environment of the North-East Atlantic made up from representatives of 15 governments and of the European Community (OSPAR Commission)[42] included TBT in the List of Chemicals for Priority Action in 1998 (amended in 2007)[43].

If TBT is found in dredgings then its concentration should be checked against legislative threshold values in order to decide whether the concentration of TBT is negligible or not. If not, then the TBT-contaminated dredgings should be treated to eliminate the harmful properties of TBT or they should safely be disposed of.

In Europe, dredged material is considered waste and it is regulated accordingly. Waste is defined in the European Waste Directive 2006/12/EC[44] as "any substance or object in the categories set out in Annex I (of the 2006/12/EC Directive) which the holder discards or intends or is required to discard". Dredgings depending on their origin may fall in the category of "Construction or demolition wastes (including excavated soil from contaminated sites)" of chapter 17 or other chapters of the European Waste Catalogue (EWC 2002)[45]. The EWC, a document referred to in various pieces of legislation in Europe and the UK, provides an index of wastes listed according to their source in 20 chapters. Each category of waste is given a code from 01 to 20 and contains sub-categories, which are given a six figure code.

An important requirement set by the Environmental Protection Act in 1990[46], for anyone dealing with waste (including TBT-contaminated waste) in the UK, is the Duty of Care. Its purpose is to ensure that all the information is provided so that the waste does not, at any stage of its management, pose a threat to human health or the environment. The Environmental Protection (Duty of Care) Regulations 1991[47] require a transfer note to accompany the waste during any transfer and the Landfill Regulations 2002[48] amend the requirement adding that the waste should be identified according to the waste codes of the EWC and any hazardous or non-hazardous properties of the wastes should be stated.

1.5.2 Disposal of TBT-contaminated sludges

A common disposal route for dredgings from ports, harbours and marinas is dumping at sea. Today, the main legislation that applies in the UK and regulates the concentration of TBT compounds for dumping dredgings at sea is: "Action levels for dredged materials"[42] by OSPAR Commission setting 0.1 mg/kg as the highest level of TBT that would not cause concern. According to the same regulations, dredged material with a TBT concentration of 0.1-1.0 mg/kg requires site specific risk assessment, whereas dredged material with TBT concentration higher than 1.0 mg/kg can not be dumped at sea.

The European Landfill Directive (1999/31/EC)[49], implemented in the UK by the Landfill Regulations 2002, uses the European Hazardous Waste Directive (91/689/EC)[50] to classify wastes as hazardous and non-hazardous according to the EWC so that the wastes can be sent to the landfill sites designed to accept hazardous or non-hazardous waste. Contaminated soil is a "mirror entry" in the EWC and not an "absolute entry", which means that it will be classified as hazardous or non-hazardous according to the concentration of any dangerous substances it contains. In order to limit the number of substances to be tested, the potentially present substances would be assessed according to the risk phrases of the Approved Supply List[51] for any hazardous properties they may have using the list of hazardous properties in the European Hazardous Waste Directive (Annex III). It should also be determined whether the waste are flammable (flash point < 55 ˚C) or corrosive (pH measurement). For the wastes that have been found to be hazardous, further tests have to be performed to establish whether the Waste Acceptance Criteria for the hazardous landfills are met, as set out in the Landfill Directive. In the UK, the analyses should be carried out by certified laboratories that meet the Environment Agency's quality criteria.

The Landfill Directive was created to regulate the classification of waste and also encourage the minimisation of waste, as well as the diversion of waste from the landfill sites by recycling, treatment and re-use. In line with this waste management policy the number of landfill sites has been dropping drastically, from 1500 sites to 450 in 2007. A landfill tax was imposed in order to make previously expensive waste treatments more economically attractive. The lower landfill tax rate for inactive waste, such as rocks and soil, is £2.5 per tonne, while the standard rate is £32 per tonne in the 2008/09 year and increasing by £8 per year from April 2009 until at least 2011.[52] Material dredged from the river beds and harbours for the interest of navigation, qualifies for an exemption. Inactive material that is used for the restoration of landfills (other than cover) and filling quarries can also qualify for an exemption under certain conditions.

Liquid wastes are banned from the landfill sites and all hazardous waste should be pre-treated according to the Landfill Directive. The pre-treatment should be a physical/thermal/chemical or biological process with the aim of changing some characteristics of the waste, such as changing its mass, reducing its hazardous nature, facilitating its handing or enhancing its recovery. Dredged sludges therefore need to be pre-treated before they can be sent to any landfill because of their water content.

1.5.3 Regulatory threshold values for TBT in water

In Europe, discharges of water likely to contain dangerous substances that go to coastal, inland and territorial surface water are regulated to avoid harm to the human health or the environment.

In the European Union members states have agreed to reduce pollution caused by the TBT compounds, since the EC Directive on the disposal of Dangerous Substances (76/464/EEC) was introduced.[53] The Dangerous Substances Directive requires elimination of its List I substances (toxic and persistent) and minimisation of its List II substances (toxic but less serious). Tin and tin compounds belong to List II substances. As a result, TBT-based paints were banned in the UK in 1987 in aquaculture and in all vessels less than 25 m long.

Pollution was defined as exceedence of the relevant Environmental Quality Standards (EQSs) set for the substances in the Directive. An EQS of 1 ng/L for TBT-compounds was set. The EQS was amended, in 1997, to 2 ng/L maximum allowed concentration for coastal and estuarine water and 20 ng/L for all freshwaters. In 2006, a new maximum allowed concentration threshold has been proposed in Water Framework Directive 2000/60[54], lowering the limit to 1.5 ng/L TBT for all waters.

A summary of the regulatory limits for both sediment and water is shown in Table 2.

	Sediment (mg/kg)	***Water (ng/L)***
Dangerous Substances Directive 76/464/EEC		20 (freshwater) 2 (coastal and estuarine)
Framework Directive 2000/60		1.5 (all waters)
OSPAR Action levels for dredged materials	0.1-1.0	0.01-0.1

Table 2. Summary of the legislative limits in the UK for TBT contamination

1.6 Treatment options for contaminated soils

After finding contamination in soils, the contaminated material is typically disposed of in a landfill or it is treated so that it stops posing a threat to human health or the environment. Treatment of contaminated soils may be necessary to de-contaminate a large area or to allow re-use of the contaminated soils as a construction material. Treatment is also necessary at times as a pre-treatment step to allow disposal at a landfill site.

In the case of sediment dredgings, the contamination is already removed from the position where it was originally found (the seabed) and the possible approaches for the remediation of the sludges would therefore be containment- based or treatment-based.

Treatment of the contaminated material in order to minimise its toxicity, a procedure which is often called remediation, can be carried out: a) by destruction of the contaminant b) by extraction (mobilisation and recapture or concentration and recovery) of the contaminant but then there is a further need for treatment or disposal c) by recycling and d) by stabilisation, which makes the contaminants less mobile or less toxic.

In order to minimise treatment costs, identification of hot-spots is some times carried out to separate material with much lower contaminated levels. This material typically requires a less expensive way of treatment or disposal to be rendered safe and is likely to be of a much higher volume compared to the volume of material with high levels of contamination.

1.7 Re-use of de-contaminated material

Before any re-use of de-contaminated material can be allowed it is necessary to demonstrate that it does not meet any of the criteria for contaminated land any longer. In the UK, contaminated land is defined in Part 2A of the Environment Protection Act 1990[46] as:

“Any land which appears to the Local Authority in whose area it is situated to be in such a condition, by reason of substances in, on or under the land, that:

a) significant harm is being caused or there is a significant possibility of such harm being caused, or

b) pollution of controlled waters is being, or is likely to be caused".

It is also required that the Local Authority is satisfied that there is a pollutant linkage in order to define a land as contaminated. According to the same Act: "A pollutant linkage requires each of the following to be identified: a) a contaminant, b) a receptor and c) a pathway capable of exposing a receptor to the contaminant".

Determining the effectiveness of a remediation technique is based on the above criteria for contaminated land. The existence of a receptor in the area necessitates the exclusion of the existence of a source and a pathway that are likely to cause significant harm. This can be determined by the concentration of TBT remaining in the dredgings (source), or the concentration of TBT in the water produced by leaching tests (pathway), after the treatment. A leaching test is a test to assess the amount of a contaminant that could be flushed out of the waste by water. The concentration of TBT in the waste or in the water produced by the leaching test after the treatment should comply with the set limits. Several such tests have been developed in order to assess the leaching of contaminants under different conditions and from different types of wastes. In general, set limits can be found in the legislation or can be site specific.

The site specific limits take into account the hydrogeology of an area, the physical-chemical properties of a contaminant, its toxicity, as well as the end use of the land. In the UK, guidance on the management of land contamination has been issued by the Department for Environment Food and Rural Affairs and the Environment Agency in Contaminated Land Report 11[55].

1.8 Aims and objectives of this project

This work has been carried out in the framework of a KTP (Knowledge Transfer Partnership) project, and it was a collaboration between the University of Southampton and Land & Water Ltd (the largest inland dredging company in the UK, at the time).

The aims of this project were to assess the present methods of remediation for TBT contamination in sediment dredgings and to develop new methods that would be commercially feasible for use by Land & Water Ltd.

The objectives were to:

- develop analytical techniques that would allow the fast determination of TBT in sediment samples at levels below the OSPAR Commission level for disposal at sea (0.1 mg/kg). Additionally, evaluate X-ray fluorescence as a fast and facile technique for the identification of hot-spots of TBT contamination

- develop analytical methods that would allow the fast determination of TBT in sediment leachates

- assess the suitability of existing methods for the remediation of TBT-contaminated sediments based on published data

- compare the ability of the most promising remediation methods, and any new ones, to reduce the level of TBT in the sediments or in the leachates of the sediments

- compare he effectiveness and suitability of materials to be used in new remediation methods

- recommend remediation methods for TBT contaminated dredgings

2 Review on the remediation of butyltin-contaminated sediments and water

Remediation of TBT contamination can be achieved by converting the TBT species (and any other butyltin species present) to less toxic compounds. Alternatively, the contamination can be removed from the soil (or water) or made unavailable to the potential receptors (aquatic organisms). Both water and sludge de-contamination techniques are presented in this Chapter. Sometimes both are necessary, as for an *ex situ* remediation both the dredged sediment and the water of its dewatering process need treatment.

A review of the technologies that have been used or tested on TBT contamination follows, along with details of any representative case studies that have been published. Pre-treatment techniques are included as they can be part of the remediation procedure. Techniques can be categorised as destruction, stabilisation or extraction. A trial of sediment containment (capping) in a sea disposal ground is also included in this chapter, as sea disposal is often presented as part of the remediation options. The outcomes of the remediation techniques vary not only because some of them are more efficient than others but also because according to the end use or disposal/discharge route of the decontaminated sludges or water the criteria regarding the acceptable concentration of TBT change. Information on the target concentration of each case study, if available, is therefore given separately.

2.1 Pre-treatment

During the remediation of contaminated sediments pre-treatment steps are necessary before a technique can be carried out or in order to reduce costs.

2.1.1 Dewatering of sludges

When dealing with contaminated sludges dewatering is often necessary and can be achieved with mechanical presses and/or with the assistance of an additive. In the case of TBT, lime and a polyelectrolyte have been evaluated as additives for dewatering by the research group of TBT Clean, an EU-sponsored research project (LIFE02 ENV/B/000341)[56]. Increased levels of TBT were observed in the filtrate water with the use of lime. This was attributed to increased solubility of TBT due the high pH (pH 12). The filtrate water therefore required further treatment for the removal of TBT before its discharge or re-use. The use of the polyelectrolyte did not increase the pH but the filtrate water still required further treatment due to other undesirable characteristics. It was found that the pressing time depended on the water content of the sediment and did not depend on the type of additive.

2.1.2 Separation of the soil fractions

Separation of the different fractions of soil is a common pre-treatment step and is usually carried out by screening of the soils with the help of water. It is based on the principle that contaminants are often associated with the finer fraction of a soil (<63 μm) and therefore isolating the finer fraction of the soil may lead to a substantial reduction in the mass of contaminated material.

Highly and moderately TBT-contaminated sediments collected from the port of Antwerp for the research project TBT Clean[56] were separated in four fractions: < 63 μm, 63-125 μm, 125-250 μm and >250 μm. No clean fraction was however found. The largest fraction by mass was the material that passed through the 63 μm sieve (~70%) and it was the one with the highest proportion of the TBT. In the highly contaminated sediment the sand fraction (>250 μm) contained 23% of the TBT, which was attributed to the presence of paint flakes. This was confirmed later by microscopic analysis. It was concluded that separation of the size fractions could not be used solely as the remediation technique for the sediments. It could, though, be one of the pre-treatment steps. Separation of the sand fraction by hydrocycloning was adopted, since it was thought that the paint flakes could be later isolated and also because the sand fraction could be re-used, due to its useful properties. For the hydrocycloning some water was added to adjust the solid content of the sediment and the cut-off point was set at ~ 80 μm. The sand fraction produced underwent some simple manual washing and the TBT levels after that for the sand fraction of the highly and moderately contaminated sediment were 9.15 mg/kg and 0.765 mg/kg respectively.

The sand fraction was further treated with pilot-scale density separation and laboratory-scale flotation. The density separation was carried out using spiral technology based on the difference of the specific gravity between the paint flakes and the sand particles. The floatation was based on dissolved air floatation (DAF). For DAF an amount of frother is added to a water cell which is under pressure (~5 bar). When the water cell is exposed to atmospheric pressure air bubbles are generated due to the difference in pressure, which create the floatation effect. Due to the rapid sedimentation of the sand particles constant mixing at 250 rpm was necessary to keep the particles into suspension. The DENVER floatation was also used (Figure 7). The DENVER device consisted of a vessel with an agitator placed in the centre, which mixed the suspension and also contributed to the aeration and generation of air bubbles. The air bubbles assisted in the formation of froth (after the addition of a frother) and also transport the hydrophobic particles to the surface. The TBT reduction efficiencies achieved were 60% and 63% for the DAF and DENVER methods respectively. The study concluded that more research was necessary in order to optimise the additives used and scale-up the tests.

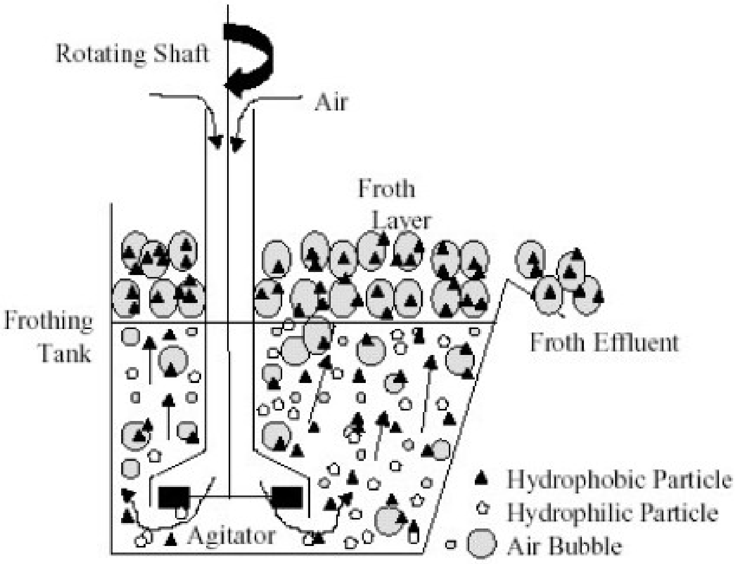


Figure 7. Principle of the DENVER floatation device (from Ref[56] with kind permission from Envisan)

2.2 Remediation by destruction techniques

For a destruction technique to be effective, TBT should be degraded to innocuous products. This could be carried out by the breakage of the Sn-C bond and conversion of TBT to, ideally, Sn(IV) and non-toxic organic compounds or CO_2 and H_2O. In practice, TBT can also be converted to many other forms, of unknown toxicity by the reaction of one or more of the carbons in the organic groups. It should be noted that analytically these may not be easy to determine, as these forms might not be detected with the analytical methods employed for the measurement of TBT.

Focusing on the cleavage of the Sn-C bond by natural processes, this could be carried out by UV irradiation from the sun, chemical cleavage, as well as by processes with negligible significance in normal environmental conditions in nature, such as gamma irradiation and thermal cleavage (at >200˚C).[57] Degradation of TBTO with UV irradiation is theoretically possible, as UV light with 290 nm wavelength has approximately 330 kJ/mol energy and the energy necessary to break the Sn-C bond is 190-220 kJ/mol.[18] TBTO absorbs light in the UV region at 300 nm and less strongly at 350 nm. Solar light is attenuated as it transmits through water and it can only affect the upper layer of the water column (the exact depth varies). Chemical cleavage is possible but generalised predictions on the reactivity of the Sn-C bond are difficult to make. Mean metal-carbon bond dissociation energies descend in the following order D(C-R)>D(Si-R)>D(Ge-R)>D(Sn-R)>D(Pb-R) according to Skinner[58] and the electronegativities of the Group IVb elements are believed to follow the order of C>Pb>Ge>Sn>Si according to Allred and Rochow[59]. These measurements show that the Sn-C bond is of medium strength and that it is not very polar. Both nucleophilic and electrophilic reagents (such as halogen, mineral acid, carboxylic acid, thiol, phenol, alcohol, metallic or non-metallic halide, alkali, alkali metal) can chemically cleave the Sn-C bond but the reaction may be sterically hindered when bulky molecules are involved.[60] Homolytic fission of the Sn-C bond is also possible[61]. Removal of TBT by biomass or biological degradation can also occur[62]. Such activity has been observed in the water and in sediments.

The methods that have been published attempting the removal of TBT can be categorised as using: a) thermal destruction b) photolysis and chemical oxidation c) electrochemical oxidation and d) biological degradation/sorption (bioremediation).

2.2.1 Thermal destruction

Thermal destruction aims to destroy the TBT molecule converting it to non-toxic or less toxic products such as tin oxide, CO_2 and water.

2.2.1.1 Combustion of TBT-containing paint waste

According to Song *et al* [63], the total combustion of TBT and DBT in paint waste from a shipyard has been achieved at 1000°C with over 1 hour of treatment or just 1 hour at >1000°C. Only a small amount of MBT was found after the treatment (0.27 mg/kg of the 22 mg/kg dry wt of total organotins in the initial sandblast waste). The combustion vessel was connected to a gas absorption system for the measurement of the combustion products.

The main compound detected in the fuel was CO_2 which indicated that TBT was oxidised to inorganic tin, CO_2 and H_2O, according to Song *et al.*

2.2.1.2 Combustion of TBT in sediments under pressure

TBT-contaminated dredged material has been thermally treated by Mostofizadeh [64] in order to degrade the TBT. It was found that the high water content of the dredged material required high energy and therefore cost to be dried off before the degradation of the TBT could begin. As TBT is thermally unstable, it was decided to heat up the sediments under pressure, to prevent the evaporation of water. According to Mostofizadeh, the decomposition of TBT proceeded with de-butylation and the products remained within the sludges and did not evaporate into the gas phase, as the experiment was carried out under pressure. A test-system was built which could treat around 15-20 kg of sediment (Figure 8). A 230°C temperature with a residence time of 2 hours at 35 bar were found to be necessary for the elimination (< 1 µg/kg) of TBT, DBT and most of the MBT contained in the sludges. Based on the test set-up in Figure 8, two full-scale systems were designed with annual capacities of 85,000 and 170,000 tonne/year in order to calculate the treatment cost. The costs calculated were 11.5-15 €/tonne dredged material.

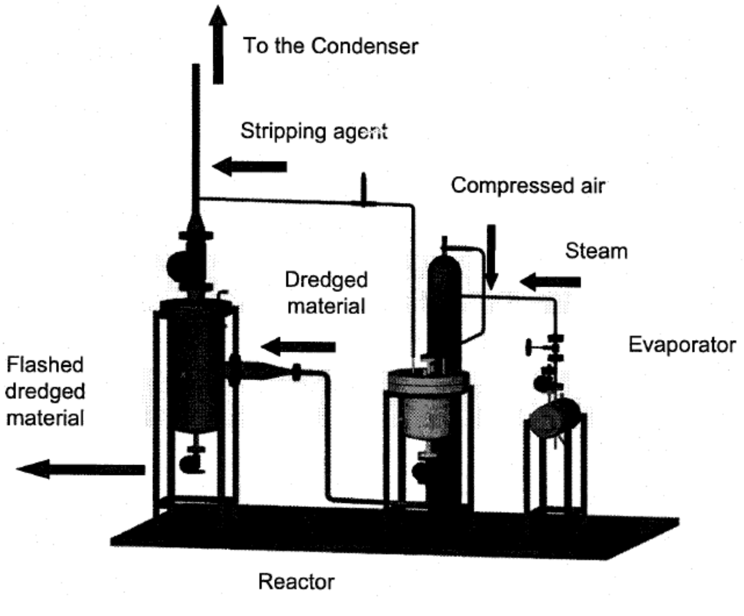


Figure 8. System for the thermal treatment of TBT-contaminated sediments under pressure (with kind permission from the author [64])

2.2.1.3 Thermal treatment of TBT-contaminated sediments

During the project TBT Clean, thermal treatment of TBT-contaminated sediments from the port of Antwerp, Belgium was evaluated[56]. A dewatering step was deemed necessary, as the moisture content of the sediments was 50-70% and it was delaying the temperature from rising above 100°C. The thermal treatment was carried out in a full-scale thermal desorption unit at 22 tonnes/ hour and at different temperatures from 300-450°C. The treatment was regarded as having been successful at 450°C with a residence time of 15 minutes, as TBT was taken down from 72.6 mg/kg to 0.29 mg/kg, DBT from 1.29 to 0.02 mg/kg and MBT from 1.97 to 0.05 mg/kg.

2.2.2 Photolysis and chemical oxidation

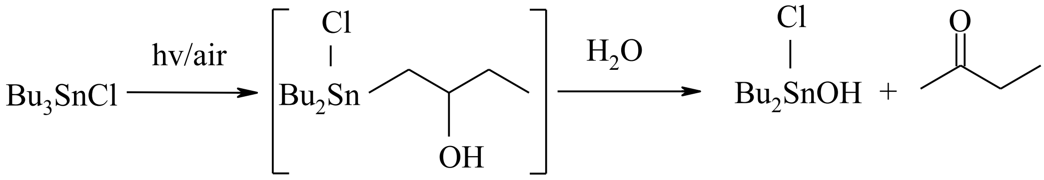
The simple photolytic degradation has been explored[35, 65], as well as the photolytic degradation involving additives to catalyse or enhance the chemical oxidation (TiO_2 [66], Fe(III) [67], H_2O_2 [68]). A study comparing the efficiency of three oxidation methods (photolysis, photolysis with the addition of H_2O_2, oxidation with Fenton's reagent) has also been published [69]. Oxidation with ozone [70] with or without the addition of H_2O_2 has also been investigated. Additionally, the use of potassium permanganate has been evaluated [71]. The efficiencies achieved in these studies and the findings are described below.

2.2.2.1 Photolysis

Duhamel *et al* [65] investigated the photolytic break-down of TBT in freshwater and in saline water. The products in the gas phase were 1-butene and 2-butene and in the liquid phase 2-butanone, 1-butanol and small amounts of ethanol and acetaldehyde. Maguire *et al* [35] confirmed that degradation of TBT proceeded with debutylation resulting in inorganic Sn. Work was carried out by Navio *et al* [72] to clarify the UV degradation of TBT and its products. In air-equilibrated aqueous solutions (at pH 5.5) the butyltins TBTCl, $DBTCl_2$ and $MBTCl_3$ were found to absorb UV light within the 190-290 nm region. The photo-degradation products detected were DBT and inorganic Sn. The fact that MBT did not appear was attributed to the very high degradation rate of MBT and the following order was given for the degradation rates MBT>>DBT>TBT. In tests carried out in de-gassed solutions it was found that TBT degradation accelerated while DBT degradation decelerated. The authors gave two possible mechanisms for the photo-degradation of TBT in air-equilibrated solutions. One was the homolytic cleavage of the Sn-C bond producing free radicals:

$Bu_3SnCl + hv \rightarrow Bu_2Sn^*(Cl) + Bu^*$

The other was the elimination of the β-hydrogen (related to Sn):



2.2.2.2 *UV/TiO₂*

The photo-assisted degradation of butyltin species in aqueous suspensions of TiO_2 was also studied [66]. TBTCl, DBTCl and MBTCl (5 μg/L) were dissolved in aqueous suspensions of powdered TiO_2 (0.25 g /L) and irradiated with a UV lamp (λ= 185-366 nm). After 46 hours of irradiation some oxidation products were detected by GC-MS (gas chromatography-mass spectroscopy). These were: 1,1,2,3,3-pentachloropropane, $Bu_2Sn(OH)_2$ and $BuSn(OH)_3$. It was noted by the authors that the existence of other products with concentrations below the limit of detection could not be excluded. Another factor that contributed to the uncertainty regarding the existence of other products was the fact that gaseous products of the treatment, such as CO_2, were not captured. Deposition of tin oxides was detected on the surface of the TiO_2 in the initial stages of the treatment (within the first 5 hours), which was a sign that the butyltins were converted to inorganic tin. The authors commented on the fact that this deposition was also poisoning the TiO_2 catalyst, preventing TBT levels from being reduced to a satisfactory level. Having established that aqueous solutions of the butyltins were stable in the dark, Navio *et al* attributed the observed degradation of the butyltins to TiO_2 photo-assisted degradation. Surface analysis confirmed adsorption of the butyltins on the surface of TiO_2. No adsorbed butyltins or organic compounds were detected after 46 hours of irradiation, which was attributed to total conversion of the adsorbed butyltins to inorganic products. The study showed that the degradation of DBT and MBT was much faster than that of TBT. This was explained by the fact that adsorption of DBT and MBT on TiO_2 was more efficient than the adsorption of TBT, because of their higher charge and fewer ligands [66].

A mechanism was put forward for the degradation of butyltins, but the authors admitted that they did not have evidence for all the steps proposed (Scheme 1). According to Navio *et al*, irradiating TiO_2 with photons of sufficient energy (≥ 3.0 eV) results in the generation of a pair of a free electron (e^-) and a hole (h^+). The electron can then be trapped by molecular oxygen, adsorbed on the TiO_2, and the generated electron hole can lead to the oxidation of the adsorbed butyltin to a butyltin radical cation. This cation would decompose producing hydroxyl or butyl radicals or butyl cations. These products are thought to initiate oxidative reactions leading to the final inorganic products of tin oxides, CO_2 and H_2O. The authors note that equation 7 of Scheme 1 may also represent a direct attack of *OH on Bu_3Sn^+, when both species are adsorbed on the surface of TiO_2.

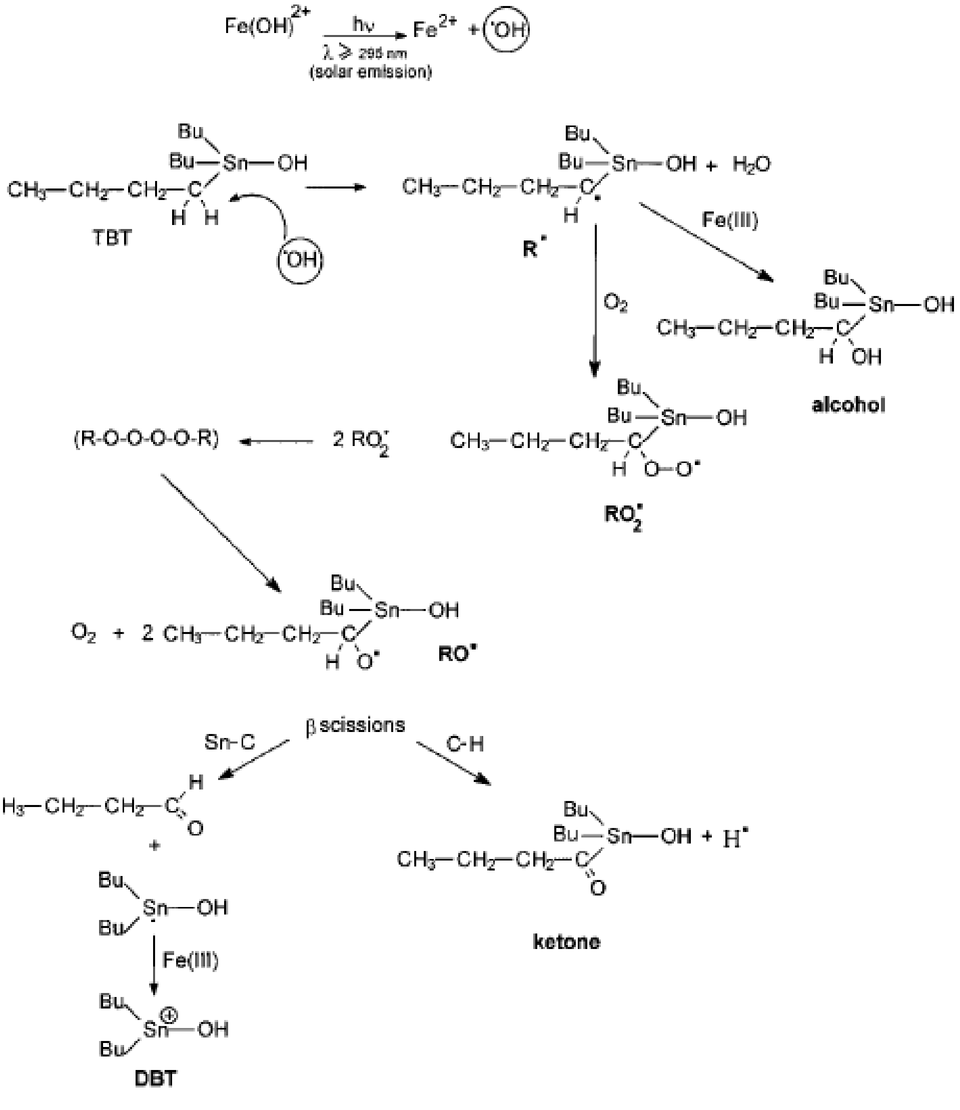
Another interesting finding of the same study was the fact that the degradation rate of TBT increased with pH in tests carried out at pH 2, 5.5, 11 and 13.5. This was attributed mainly to the adsorption characteristics of the surface of TiO_2, which allow more efficient adsorption of TBT and O_2 at pH values > 5.6 [66].

$TiO_2 + hv \rightarrow (h^+ \sim e^-)$	exciton formation	eqn. 1
$(h^+ \sim e^-) \rightarrow$ heat, proton	recombination process	eqn. 2
$(h^+ \sim e^-) \rightarrow h^+ + e^-$	exciton dissociation	eqn. 3
$O_2\,(g) \rightleftharpoons O_2\,(ads)$	oxygen adsorption equilibrium	eqn. 4
$O_2\,(ads) + e^- \rightarrow O_2{*}^-$	electron trapping	eqn. 5
$OH^-(ads) + h^+ \rightarrow OH{*}(ads)$	hole trapping by adsorbed hydroxyl group	eqn. 6
$Bu_3SnOH\,(ads) + h^+ \rightarrow Bu_3SnOH]{*}^+$		eqn. 7
$Bu_3SnOH]{*}^+ \rightarrow OH{*} + Bu_3Sn^+$		eqn. 8
$Bu_3SnOH]{*}^+ \rightarrow Bu{*} + Bu_2Sn^+OH$		eqn. 9
$Bu_3SnOH]{*}^+ \rightarrow Bu^+ + Bu_2Sn{*}OH$		eqn. 10
$Bu_2Sn{*}OH + OH{*} \rightarrow Bu_2SnOH_2$		eqn. 11
$Bu{*} + O_2(ads) \rightarrow BuO_2{*} + [O] \rightarrow \rightarrow$	oxidation	eqn. 12
$Bu{*} + O_2{*}^- \rightarrow \rightarrow \rightarrow$	oxidation	eqn. 13
$BuO_2{*} + O_2{*}^- \rightarrow \rightarrow \rightarrow$	oxidation	eqn. 14
$Bu^+ + HO_2 \rightarrow BuOH \rightarrow \rightarrow \rightarrow$	oxidation	eqn. 15
$Bu_3Sn^+(ads) + O_2(ads) \rightarrow Bu_2Sn^{2+} + [Bu{*} + O_2^-]$		eqn. 16

Scheme 1. Sequence for the TiO_2-photoassisted degradation of butyltin chlorides (adapted with permission from Ref[66]. Copyright 1996 American Chemical Society)

2.2.2.3 UV/Fe(III)

The photoinduced degradation of TBTCl in aqueous solution by Fe(III) (3×10^{-4} mol/L) and UV radiation (365 nm) has been reported.[67] More specifically, an aqueous solution containing 1.9 mg/L TBTCl, 100 µg/L $DBTCl_2$ and 0 µg/L $MBTCl_3$ (as Sn) was measured to contain 60 µg/L TBT, 80 µg/L DBT and 170 µg/L MBT after 90 min irradiation with UV light. According to the mechanism proposed by Mailhot *et al*, the Fe(III) aqueous complexes produced *OH radicals and Fe(II) when irradiated with UV light through an electron transfer mechanism (Scheme 2).



Scheme 2. Mechanism for the degradation of TBT by UV-Fe(III) (from Ref[67] with kind permission from Wiley)

The *OH then gradually debutylated the TBT in solution. The Fe(III) species were the only ones absorbing the UV light, as TBT was found to only absorb negligible amounts of energy when irradiated with λ> 290 nm light. The degradation mechanism involved an abstraction of a hydrogen from a carbon atom at an α- or β- position to the tin, resulting to a radical species R*. A partial hydrolysis of TBTCl to TBTOH was assumed to have occurred before the abstraction of hydrogen. It was thought, by Mailhot *et al*, that the electrophilic attack by the *OH would not otherwise be favoured due to the positive charge of the ionic form of TBT. The products of photo-degradation were identified with GC-MS. The major products at the early stages of the irradiation were DBT and MBT and inorganic tin. Organotin oxidation products were also detected at lower concentrations, as a family of 2 ketones and 2 alcohols (attack at the α- or the β- carbon atoms), during the irradiation of a TBT aqueous solution. Similarly, 2 ketones and 2 alcohols were detected during the irradiation of DBT and MBT solutions, meaning that the same mechanisms applied to their degradation. Mailhot *et al* noted that during the irradiation of TBT the formation of DBT was strongly favoured (8:1) compared to the formation of the ketone. Another minor family of products was detected but not identified. The production of alcohols as degradation products was found to be favoured in the absence of oxygen. According to Mailhot *et al*, in the presence of oxygen the radical species R* is oxidised to ROO* and the unstable tetroxide ROOOOR is formed, which decomposes producing O_2 and alkoxy radicals (RO*). Alkoxy radicals, according to Mailhot *et al*, typically undergo β-scissions. Depending on whether the scission takes place at the C-H or the Sn-C bond the products are a ketone or an aldehyde and DBT (when TBT is the starting compound) respectively (Scheme 2). The authors claim that after 24 h of irradiation only inorganic tin was detected. Also, that after >40 hours of irradiation, 97% yield of CO_2 was achieved, based on a calculation of 12 mol CO_2 production per mol of TBT degraded. Irradiation with solar light (higher energy) degraded the butyltins faster, according to Mailhot *et al*, as the concentration was below the detection limit (not given) of the GC-FID (gas chromatography- flame ionisation detection) after only 8 hours.

2.2.2.4 UV/H_2O_2 and comparison with TiO_2 and Fe(III) addition

Work carried out by Breedveld *et al*[68], used UV irradiation (λ=254 nm), in the presence of H_2O_2 (300 mg/L), which generates *OH when irradiated with UV. The treatment reduced the levels of TBT in real wastewater below the Norwegian maximum allowed discharge limit of 100 ng/L, within 2.5 min. When TiO_2 or Fe(III) were added instead of H_2O_2 no improvement was observed. Eco-toxicology experiments showed that despite the decrease in the concentration of TBT there was no decrease in the eco-toxicity of the wastewater.

This was attributed, by Breedveld *et al*, to intermediate products of the photolysis or other toxic compounds potentially present in the wastewater. The cost of the treatment was estimated to be 0.06-0.07 €/m^3 wastewater.

2.2.2.5 Comparison of photolysis (UV), UV/H_2O_2 and oxidation with Fenton's reagent

A study by Grievson[69] compared the efficiency of TBT removal from spiked deionised water and spiked wastewater by degradation using UV-photolysis, UV/H_2O_2 and Fenton's reagent (ferrous sulphate and hydrogen peroxide).

In deionised water, irradiation with UV light (λ=254 nm) removed only 45% TBT, as TBT was not found to absorb strongly at this wavelength. Addition of H_2O_2 (3 mM) increased the removal of TBT (0.51 μmol/L) from water to 89%. In wastewater, much higher efficiency was observed, 99% and 100% respectively. The increased efficiency of the treatment in wastewater was attributed to the presence of ferric iron and it was suggested that the mechanism of degradation would be the same as the one proposed by Mailhot *et al*[67] (Scheme 2).

Fenton's reagent generates a cycle of reactions between Fe(II) and Fe(III), which also produces *OH:

$Fe(II) + H_2O_2 \rightarrow Fe(III) + OH^- + HO*$

$Fe(III) + H_2O_2 \rightarrow Fe(II) + HO*_2 + H^+$

$HO* + H_2O_2 \rightarrow HO*_2 + H_2O$

$HO* + Fe(II) \rightarrow Fe\ (III) + OH^-$

$Fe(III) + HO*_2 \rightarrow Fe(II) + O_2H^+$

$Fe\ (II) + HO*_2 + H^+ \rightarrow Fe(III) + H_2O_2$

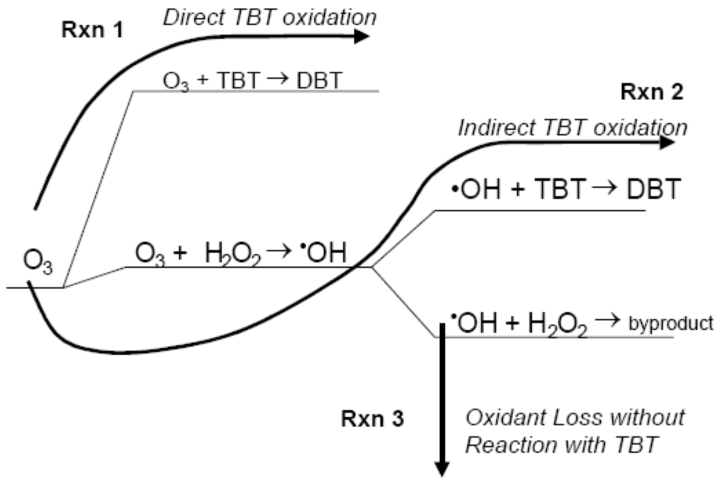
$HO*_2 + HO*_2 \rightarrow H_2O_2 + O_2$

In the study by Grievson, Fenton's reagent (0.3 mM Fe(II) and 0.3 mM H_2O_2) removed 73% of TBT at pH 3 within a treatment period of 120 min.

According to the study, the cost of the UV or UV/H_2O_2 treatment, which was considered to be more effective when compared to Fenton's reagent, was estimated to be £8.14-28.95 per m^3 of wastewater to be treated (£0.05 per KWh assumed).

2.2.2.6 Oxidation with ozone

The oxidation of TBT in water using ozone was tested with or without the addition of H_2O_2 by Schafran *et al*[70]. The performance of this method was not satisfactory as the results were not consistently lower than the 50 ng/L TBT regulatory limit of Virginia, USA against which they were compared. According to the author, the performance was affected by many parameters (temperature, dissolved organic matter, particulate matter) which resulted in a poorly controlled process. A simplified representation of the processes occurring during the oxidation of TBT with ozone (with or without addition of H_2O_2) is shown in Scheme 3.



Scheme 3. Simplified representation of reaction pathways (Rxn 1,2 and 3) during treatment with ozone and H_2O_2 (from Ref[70] with kind permission from the author)

2.2.2.7 Oxidation of TBT-contaminated sediments with $KMnO_4$ and H_2O_2

Tests of oxidation of TBT in contaminated sediments were carried out within the framework of the research project TBT Clean[71]. From the oxidants considered (permanganate, hydrogen peroxide, sodium persulfate, ozone) permanganate in the form of $KMnO_4$ and hydrogen peroxide were selected to be tested. $KMnO_4$ was found to be more efficient than H_2O_2. Efficiencies for contaminated sediments with both low (3.5 mg/kg) and high (30 mg/kg) TBT content were higher than 96%, resulting in final concentrations of about 0.1 mg/kg and 1 mg/kg TBT respectively. Some disadvantages of the method are: the high oxidant dose necessary (0.5 kg of MnO_4^- per kg dry matter) and the fact that 70%

moisture content is necessary for the reaction, which means that dewatering would be necessary after the completion of the oxidation. Most importantly there is the risk of unpredictable side reactions of the oxidant with the organic matter, which might generate toxic by-products.

2.2.3 Electrochemical degradation

Degradation of organotins by reduction or oxidation reactions has been tested in contaminated slurries and sediments.

2.2.3.1 Electrochemical treatment of TBT-contaminated slurries and sediments

The degradation of TBT in sediments by electrochemical oxidation in a suspension of sediment and water has been evaluated and optimised by Stichnothe *et al*[73-75].

According to Stichnothe *et al*, the exact mechanism of degradation in sediments is not yet known but the most important reactions are regarded to be:

$2\ (C_4H_9)_3Sn^+ + 3\ OCl^- + 2\ O_2 + 3\ H_2O \rightarrow 2\ SnO_2 + 6\ C_4H_9OH + 3\ Cl^-$ (oxidation)

$(C_4H_9)_3Sn^+ + 4\ Cl^- + H_2 \rightarrow SnCl_2 + 3\ C_4H_{10} + 2\ HCl$ (reduction)

Stichnothe *et al* believe that debutylation of the TBT was performed by reactive species, such as chlorine and hypochlorite, generated by electrolysis employing IrO_2 anodes and steel cathodes. The optimised conditions were 76 A/m^2 current density, 3.3 m^2 anodic area installed, voltage of 4.5 V and sediment residence time of 1.15 h. The concentration of TBT in real contaminated sediment (2.6 mg/kg TBT) and real sediment with lower contamination (0.194 mg/kg) was reduced below 0.100 mg/kg TBT (0.034 mg/kg and 0.016 mg/kg TBT respectively). It should be noted that the method treated co-existing PAHs (poly-aromatic hydrocarbons) but not the heavy metals or PCBs (poly-chlorinated biphenyls) present. The operation cost for a 720,000 tonnes/annum plant was expected to be 10 €/m^3 and 13 €/m^3 for the high and low contamination respectively (assuming 0.06 €/KWh).

An electrochemical destruction trial for TBT was carried out by the TBT Clean research group[71]. The TBT contaminated sediments needed to be diluted to a 5% dry content suspension for the treatment and a 0.5 M NaCl concentration was necessary for the treatment to work. The concentration of TBT appeared to rise in the first half an hour of treatment and diminished to 100 µg/kg after 24 hours. DBT appeared as a degradation product and was degraded to MBT, which was generally low but appeared to increase slowly towards the end. The formation of mineral oil compounds was observed, which was attributed to the breakdown of organic matter in the sediments. The power consumption, provided enough chloride was present, was regarded as moderate by the authors of the study. An adverse effect of the high concentration of chloride is the production of EOX (extractable halogenated organics), which may be toxic.

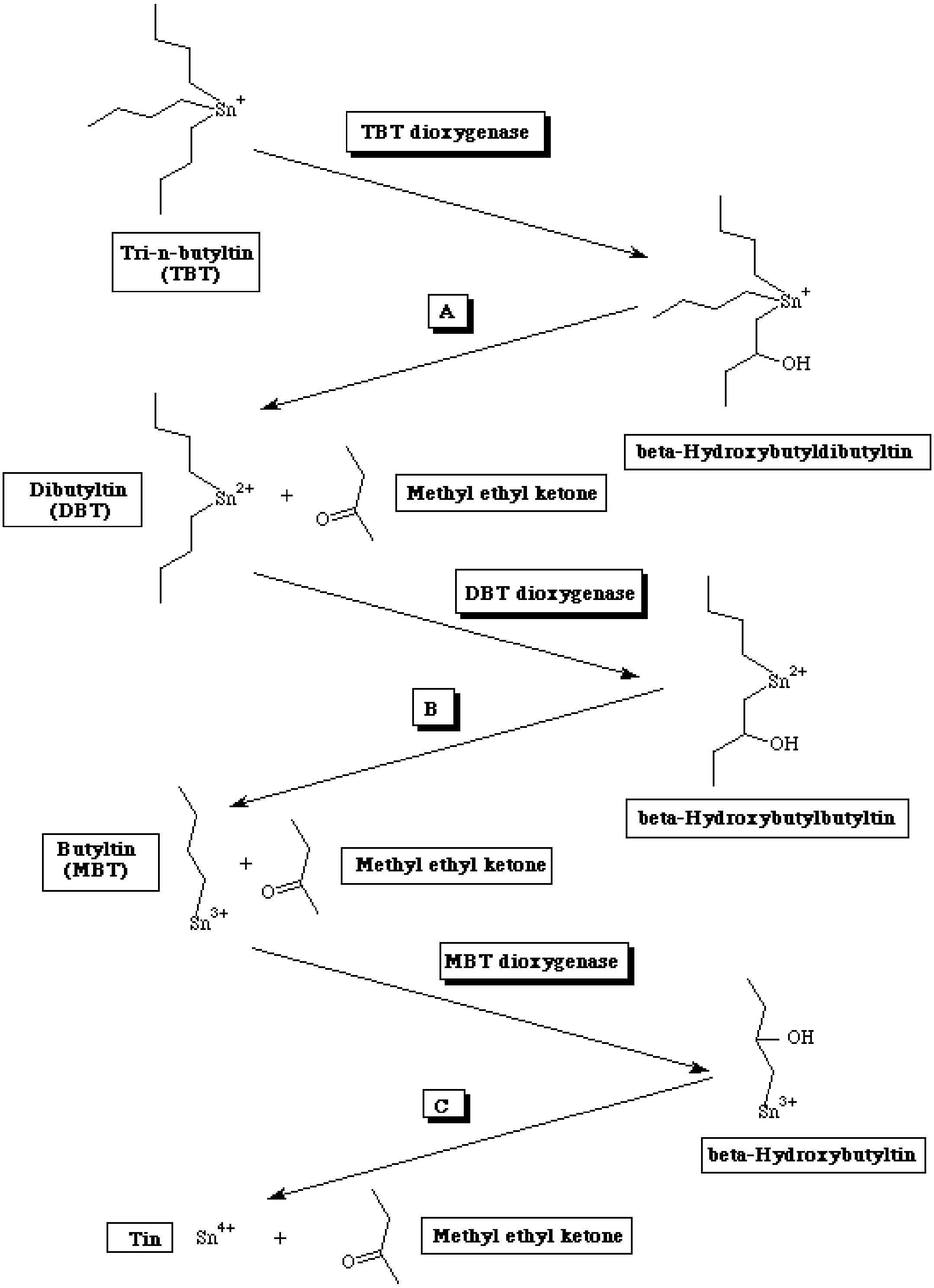
An electrokinetic treatment has been developed by Hansen[76] for the company Churngold Remediation for the treatment of the fine fraction of contaminated soils. The set-up for the technique involved an anode zone with pH 2-3, a cathode zone with pH>10.5 and an iron rich band with iron in the mineral phase located between the two. According to Hansen, the technique creates an environment that accelerates ferric iron mineralisation and the treatable compounds include TBT, heavy metals, chlorinated solvents, hydrocarbons, radionuclides and pesticides.

2.2.4 Bioremediation

Bioremediation is a general term for the removal of contaminants achieved by biological action or by adsorption on biomass. In the case of TBT, bioremediation has been studied using plants (phytoremediation[71, 77, 78]) or microorganisms[71, 79, 80]. Bioremediation is often compound-specific, as only few or only one species is usually efficient in removing a particular group of contaminants. The removal is usually attributed to biodegradation mechanisms[79, 81], when TBT is debutylated and used as carbon source by TBT-tolerant (and resistant) organisms (like bacteria, fungi[82, 83] and microalgae[84]) or on adsorption/absorption of TBT on organic matter[79].

A limitation of this technique is the fact that organotins have antibiotic properties (which was the basis of their commercial use as anti-foulants) therefore highly contaminated sites are not suitable for the growth of the microorganisms. Another limitation is that the removal requires significantly longer times than other techniques. Bioremediation could be expected to considerably progress assisted by genetic engineering, as genetically modified TBT degrading bacteria may be produced in the future.

A path has been proposed by Ellis *et al*[85] (Scheme 4) for the biological degradation of TBT.



Scheme 4. Biodegradation pathway for TBT (adapted from Ref[85] and used with permission from the University of Minnesota Biocatalysis/Biodegradation Database http://umbbd.msi.umn.edu/)

A TBT dioxygenase attacks the β-hydrogen (related to Sn) of a carbon chain of TBT producing β-hydroxybutyldibutyltin. The Sn-C bond breaks between Sn and the hydroxylated carbon chain resulting in DBT and a methyl ethyl ketone. With two similar steps, MBT and then Sn^{4+} are produced releasing a methyl ethyl ketone as well at the end of each step.

Studies of the removal of TBT by biomass are described below and show just some of the different ways biomass can contribute to the removal of TBT.

2.2.4.1 Removal of TBT from wastewater with activated sludge

The removal of TBT, DBT and MBT by activated sludge, from wastewater treatment plants, was studied in a laboratory scale experiment in batch reactors.[86] TBT (100 µg/L) dropped by 97% in the wastewater after 24 hours and was non-detectable after 18 days. The disappearance of TBT from the wastewater was attributed mostly to adsorption on the solid particles, as 84% of the TBT was found in the particulate phase. Within 24 h of the addition of TBT, the degradation product DBT, and on the third day MBT, appeared in the particulate phase, which indicated that debutylation was also taking place. On the eighteenth day of the experiment only 27.1% of the initial TBT remained and a decrease of around 50% of the degradation product DBT was observed. Mass balance calculations showed a loss of mass of the butyltin compounds after the eighth day of the experiment and the appearance of inorganic tin was confirmed by electrothermal atomic absorption spectroscopy (ETAAS), attributed to biological debutylation of MBT.

Addition of another source of carbon to the activated sludge biomass resulted in only a slight cut in the half life of the TBT in the activated sludge and no improvement for DBT or MBT.

Experiments were also carried out in acclimatised activated sludge. Activated sludge was acclimatised by remaining 15 days in the presence of 10 µg/L of butyltins and 15 more days in the presence of 50 µg/L of butyltins before samples were taken. The use of this type of sludge cut the half lives of all butyltins significantly. After 10 days the removal was 99.7% for TBT, 90.4% for DBT and 49.7% for MBT.

Similar behaviour was observed in the cases of DBT and MBT.

2.2.4.2 Removal of TBT from wastewater by dead and live algal cells

Removal of TBT from artificially TBT contaminated wastewater was demonstrated using dead and live *Chlorella* and *Scenedesmus* species.[79] Dead cells removed the TBT faster than live cells. This indicates that biosorption was more efficient as a removal mechanism than cell uptake and degradation. The biosorption was attributed to physico-chemical binding of TBT to the surface of the cell membrane. The cell surfaces have a negative overall charge, due to a multitude of functional groups (carboxyl, sulfates, phosphates and other) on the membrane walls, which would attract TBT in its cationic form. *Scenedesmus* removed 90% and *Chlorella* 85% of TBT within one day. Live cells achieved such removals only after 14 days. *Scenedesmus* was more efficient due to the larger size of its cells and biomass, despite equal numbers of cells being added (1x 10^{-7} cell/mL), according to the authors of the study. This larger cell size and biomass would provide more sorption sites for TBT binding. The specific uptake (TBT sorbed per cell biomass or per unit surface area) was higher for the *Chlorella* cells, which were smaller and of lower biomass. The degradation of TBT by *Chlorella* cells was higher and it was taking place inside the cell by debutylation of TBT to DBT and MBT.

2.2.4.3 Bioremediation of TBT-contaminated sediments on land

Brandsch *et al*[87] evaluated the bioremediation of TBT-contaminated harbour sediments during their land deposition. The study included laboratory tests under aerobic and anaerobic conditions at different temperatures, as well as field measurements. It was found that the rate of TBT degradation increases under aerobic conditions and at higher temperatures. The half-life of TBT decreased proportionally with increasing temperature between 5˚C and 55˚C. At 55˚C, TBT with initial concentration of 320 μg/kg was undetectable (<1 μg/kg) after 7 months. Another finding of the study was that the degradation in water, by biological action and not photolysis, was four times higher than in sediments. In the field a 10% per year degradation rate was observed which increased to 30% in sediment that was turned for aeration. Brandsch *et al* did not observe any impact from the released TBT in the groundwater or in the surrounding areas and very low uptake by plants was measured. The study concluded that land deposition would be a very economic option and one that would not pose a threat to the environment.

A four-month land deposition and dewatering trial was carried out within the TBT Clean research project framework in 2003 by DEC[71]. Four batches of low (~3.5 mg/kg) and high (~35 mg/kg) TBT-containing sediments were deposited on land. Two of them were turned and two were left undisturbed after the deposition. The highest removal (88%) of TBT was observed on the surface (top 10 cm) of the undisturbed sediment batch. Reductions of 40-72% were observed in other bottom and surface samples from the trial. The reduction was attributed to biological action as well as UV degradation. It should be noted that TBT concentrations much higher than the ones measured initially were found one month after the beginning of the trial and this was attributed to heterogeneity of the contamination in the sediments.

2.3 Remediation by stabilisation/solidification

The remediation of TBT-contaminated sediment can be achieved using a stabilisation/solidification procedure. This approach immobilises the contaminant but does not break it down. The exact mechanism usually depends on the immobilising material. Stabilisation/solidification is an established approach and it was selected for the treatment of 23% of the Superfund sites in the US in 2007.[88]

Stabilisation of TBT has been attempted by adsorption of TBT on solid materials (activated carbon, clays and dolomite) or by preventing leaching (encapsulation in concrete by addition of cement). Information on the materials that have been used for the immobilisation of TBT and existing data on their performance are given below.

2.3.1 Adsorption on activated carbon

Carbon, in the form of activated carbon, has a large active surface area (500-1400 m^2/g)[89] making it ideal for adsorbing many chemical compounds from liquid and gas solutions. It is also known to remove TBT from aqueous solutions[90-92].

2.3.1.1 Removal of TBT from shipyard water with activated carbon

Prasad *et al*[91] tested a full-scale system for the treatment of TBT-contaminated shipyard waters. The treatment unit was operated at 190-225 L/min and the concentrations treated ranged from 5.5-6,260 μg/L TBT. The system consisted of rapid mix and flocculation units followed by a dissolved air flotation (DAF) tank for clarification and a sand filter and two columns of granular activated carbon (GAC) connected in series (Figure 9). For the coagulation, alum was used for a limited amount of time and ferric sulfate was used for the majority of the time. In the mix tank hydrated lime was added to the coagulant. An organic polymer was added at the entrance of the flocculation unit to increase floc development. The final effluent had a concentration above the regulatory limit of 50 ng/L (Virginia, USA) for 59% of the time during the 136 days of operation. This effect was attributed to polymer-associated TBT carryover through the system.

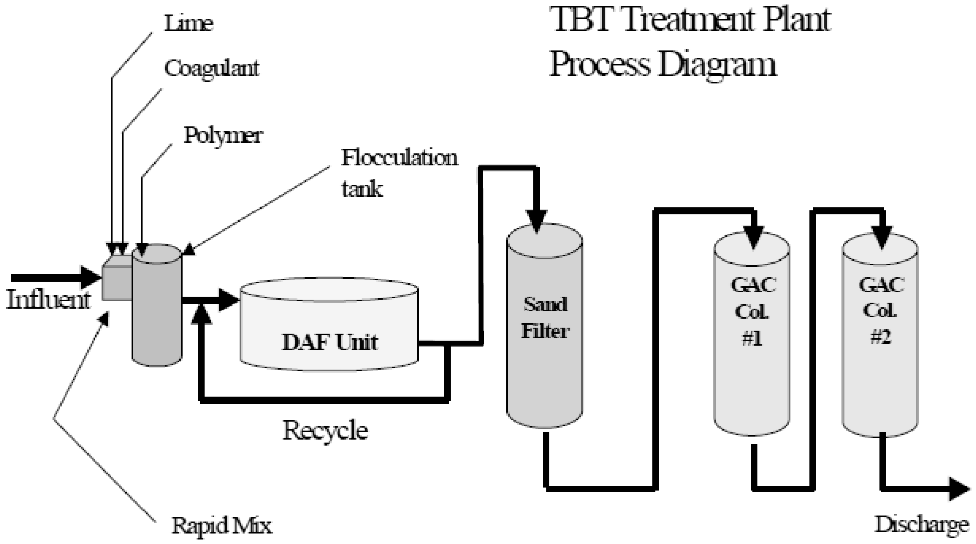


Figure 9. System for the removal of TBT from shipyard wastewater by flotation, flocculation and adsorption on activated carbon (from Ref[93] with permission from the author)

Grievson in his research[69] used 10 g/L granular activated carbon (Norit 1240 GAC) for the removal of 0.51 μmol/L TBT from water. The efficiency of the adsorption of TBT was 89% in spiked deionised water and 90% in spiked wastewater. The cost estimate was £0.02-0.07 per m^3 of wastewater (£1.2 per kg of virgin carbon and £0.6 per kg of recycled carbon assumed).

In research carried out by Vreysen *et al*[92, 94], a system was tested for the removal of TBT, DBT, Cu and Zn from dockyard wastewater. The system used sorption of the organotins and the metals on powdered activated carbon (Norit SAE Super) and on bentonite modified with an alum coagulant and an organic flocculant (Südflock P294), respectively. Coagulation and flocculation allowed removal of the sorbents and separation of the supernatant. The addition of powdered activated carbon could be replaced by the installation of a granular activated carbon column at the end of the system at medium to high organotin input levels (Figure 10). Norit SAE Super (0.6-0.7g/L) lowered the concentration of TBT in treated shipyard wastewater containing about 25 μg/L to below the discharge limit of 100 ng Sn/L TBT.

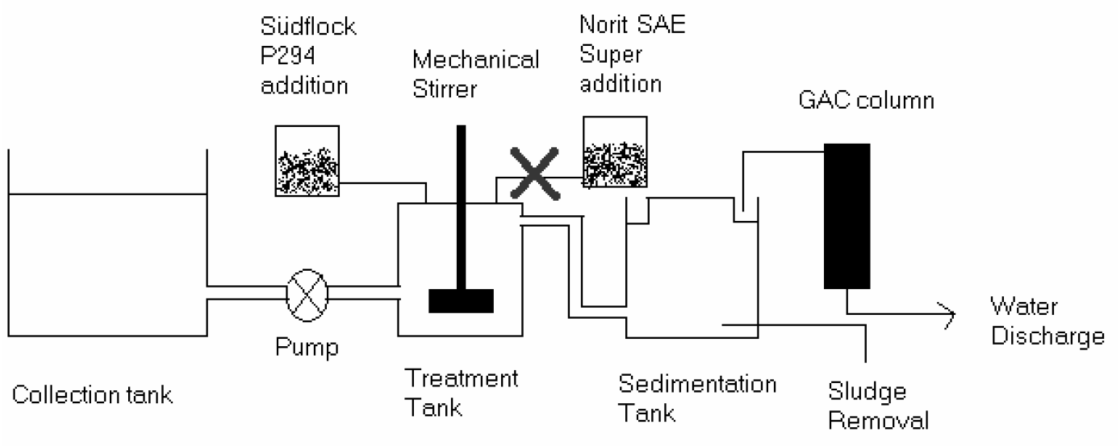


Figure 10. Diagram of the set-up for a proposed adsorption and coagulation-flocculation system for the removal of organotins, Zn and Cu (from Ref[92] with permission from the author)

2.3.2 Adsorption on soils and minerals

TBT is typically encountered at levels of one order of magnitude higher in sediments than in water in the environment. That has been attributed to the high partitioning of TBT into the organic matter contained in sediments[19, 33] and to adsorption on mineral surfaces.[29, 95]

Two main sorption mechanisms are therefore believed to be responsible for the adsorption of triorganotins on sediments. One mechanism is the coulombic forces that develop between the triorganotin cation and the negatively charged surfaces (e.g. of clays) and the other is the hydrophobic forces that lead to sorption of the triorganotins. These sorption mechanisms have been exploited in applications for the fixation of TBT that have used pure soil minerals (dolomite[96]) and clays with artificially increased organic content[97] as additives.

2.3.2.1 Removal of TBT from shipyard water with dolomite

The removal of organotins from shipyard wastewater by dolomite (sedimentary rock) has been tested by Walker *et al*[96]. The dolomite used was mined in Co. Fermanagh, Northern Ireland and it contained 44% $MgCO_3$ and 53% $CaCO_3$. The mean particle size was 91.5 μm. The dolomite was charred for a 6-12 hour period as this procedure was found to increase its specific surface area. In a pilot scale trial 8000 L of shipyard wastewater were mixed with 5 kg of adsorbent and mixed continuously for 48 hours. The efficiency of the dolomitic adsorbent was compared with the efficiency of adsorption by a commercial granular activated carbon (Filtrosorb 400). According to Walker *et al*, the dolomitic adsorbent performed slightly better than the granular carbon and reduced the concentration of Sn ions (organotins were not directly measured) by 80% to 4 μg/L.

2.3.2.2 Immobilisation of TBT in sediments with modified clay

Smectite-based clay (a group of clays, containing principally montmorillonite[98]) has been treated with organic (quaternary ammonium salt) and inorganic (hydroxyl aluminium, transition metals) compounds to produce a modified clay (E-clay, Envirotreat). The E-clay (5.5% w/v) can be mixed with contaminated sediments to chemically bond contaminants in order to immobilise them.[97] This technology was applied ex-situ for the treatment of TBT contaminated silt in Mylor Harbour, Cornwall. According to Envirotreat[99], the levels of TBT in the water recovered from the leaching tests of stabilised sediment samples taken from that site were <100 ng/L TBT, which was below the limit agreed with the regulatory authorities (50000 ng/L TBT).

2.3.3 Solidification with cement

Cement has often been used as an additive to sludge in order to reduce the water content and convert it to a more manageable material. The advantages of ordinary cement as an additive are its low price, good availability, consistent composition, stability over time and also the fact that it is not toxic or biodegradable.

2.3.3.1 Stabilisation of TBT-contaminated sediments with cement

In Vuosaari harbour (Helsinki) about 100 kg of TBT were found over 100 observation points and 80% of it within a 20 hectare area, where concentrations of TBT varied significantly and in some cases exceeded 5 mg/kg dry weight. The maximum amount measured was 15 mg/kg dry weight. 500,000 m^3 of TBT-contaminated sediment (mainly clay) were stabilised by mixing them with 130 kg/m^3 of sediment Portland-composite cement. The type of cement was CEM II/ A-M (S-LL)[100], which contains Portland cement and 6-20 % composite materials (granulated blast furnace slag, pozzolana, fly ash and limestone)[101]. The sediment/cement mix was re-used as filling material for the construction of embankments. During construction, the areas, where the contaminated sediment was going to be placed, were isolated and excavated, then filled with sea sand on which the carefully dredged contaminated material was placed as a 5 m thick layer and was mixed with cement (Figure 11). The material was covered with a geo-textile. The stabilised layer was covered with a drainage system. The required permeability (≤ 5 x 10^{-9} m/s) and shear strength (≥ 70 kPa) were obtained. According to Havukainen *et al*[102, 103] from Ramboll Finland, the company undertaking the works, the very low permeability prevented any contamination from the stabilised material leaching to the sea.

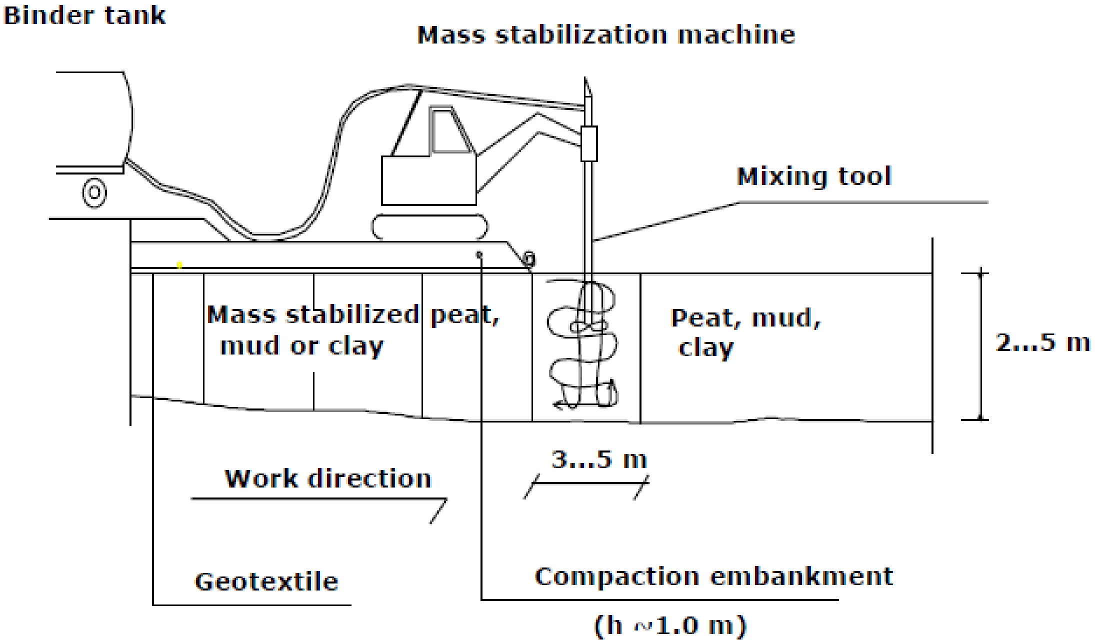


Figure 11. Set-up for the reuse of contaminated sediments with the addition of cement (from Ref[102] with permission from Ramboll Finland Oy)

2.4 Extraction

Apart from the two main remediation options (destruction and immobilisation) for TBT contamination, extraction techniques based on the partition of TBT in organic solvents and also on volatilisation of TBT have been tested.

2.4.1 Solvent extraction of TBT from shipyard wastewaters

Abbott *et al*[1, 104] developed a design for the removal of TBT from contaminated water from dockyards (Figure 12). The design was based on the fact that dockyards often have already installed a system of pumping wastewater and passing it into a sump. A treatment unit could then be installed in between, which would remove TBT by partitioning into a solvent. The steps according to the design in Figure 12 would be: collection of the wastewater (area 1) and pumping to a primary reservoir (area 2), the flow control unit (area 3) would then pump water to the core of the processor unit. The processing of the water would be carried out by adding solvent that would be carefully dosed and dispersed. Some water could be drawn (area 5) into the dosage and dispersion unit (area 6) and this water would then re-join the flow of the water in the reactor tubes (area 4). In the reactor tubes the partition of TBT would take place and the emulsion created would then pass into the oil-water separation unit (area 7). The water could then be discharged or retained for further treatment (area 8) or pumped back into the primary reservoir (area 2) for immediate re-treatment. The solvent recovered from the separation could be further treated for the removal of any remaining water in areas 7, 9 and 10. Different oils can be used as solvents, such as diesel. According to Abbott *et al,* important considerations regarding the solvent to be used are its cost, re-use and disposal options as well as flammability and volatile organic compounds (VOCs) control during the operation. Such a treatment unit operated in pilot scale treating 10 tonne/h in Wear Dockyard in Sunderland, UK in 1997.

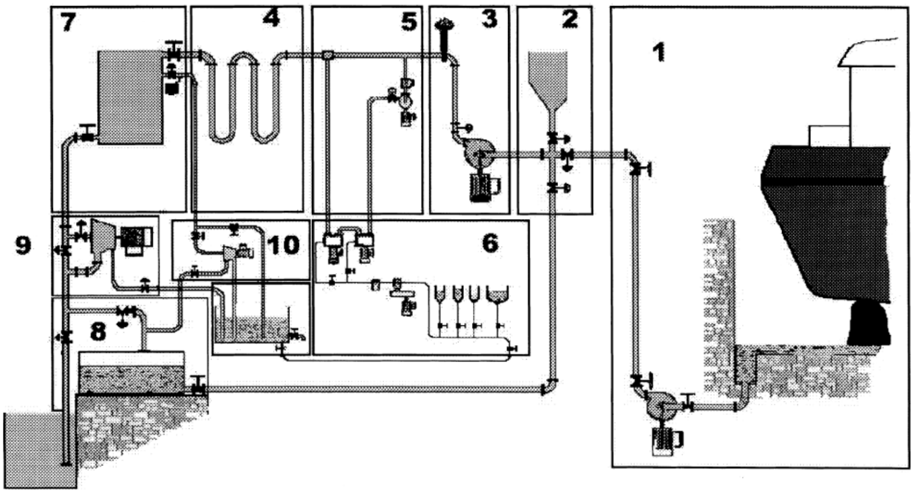


Figure 12. System for the treatment of TBT-contaminated dockyard water (from Ref[1] with kind permission from Elsevier)

In another study, the extraction of TBT from shipyard wastewater with marine diesel has been examined as a wastewater clean up method by Song *et al*[63]. 1 L of water containing 4 mg/L TBT was shaken with 10 mL of diesel. After 1 hour the remaining TBT in water was 2.8 µg/L and after 5 hours 800 ng/L.

2.4.2 Stream stripping of TBT from sediments

The stream stripping of TBT from sediments has been suggested as a technique for the treatment of contaminated sediments.[105] The method employs spontaneous vaporisation of TBT from the sediment due to change in the temperature and pressure conditions. The system would need to be connected with air and water treatment units (Figure 13). The removal of TBT from contaminated sediments containing 2.7 mg/kg TBT and 0.6 mg/kg

TBT was 99% efficient resulting in concentrations of 0.021 mg/kg TBT and 0.007 mg/kg TBT, which are below any suggested regulatory limit, according to the study.

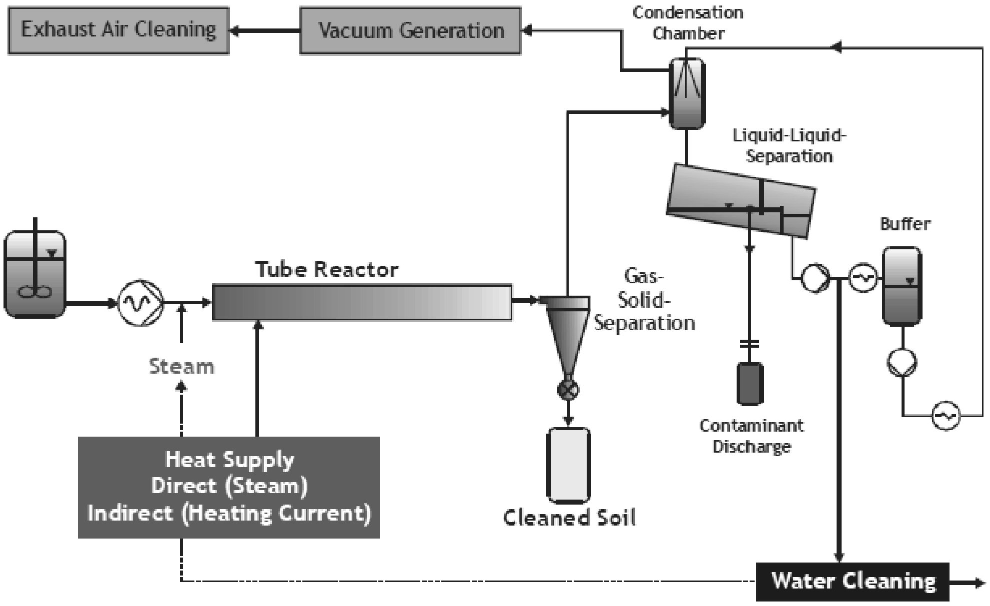


Figure 13. System for the removal of TBT from contaminated sediments proposed by Eschenbach et al[105]

2.4.2.1 Extraction of TBT from contaminated sediments with alkaline water

The release of TBT from contaminated sediments into the water by increasing the pH, was evaluated during the TBT Clean project[56], as the water was considered to be easier to clean. The pH was increased to pH 12 by the addition of lime. Only a 3% mass transfer was observed. The low mass transfer was attributed to re-immobilisation of the extracted TBT onto the sediment particles. In order to prevent it, activated carbon up to 100% dry weight was added to quickly adsorb TBT from solution. Still, only 30% mass transfer was achieved and this method was not explored further.

2.5 Sediment capping at sea

Sediment capping at sea has been used as a method for dealing with TBT-contaminated sediment. It is included here as it is often referred to as a remediation option or an alternative.

2.5.1 Capping trial of TBT-contaminated sediments

The first trial of containment at sea in the UK was carried out by the company

Envirocentre Ltd[106] in 2005. 60,000 m^3 of TBT contaminated dredgings from the Tyne Estuary were relocated to an existing sea-disposal ground and they were capped with fine sediment to ensure isolation from the environment. Sand was placed on top to avoid erosion of the capping layer. The trial was based on guidance from the US Army Corp of Engineers and extensive monitoring is expected to provide valuable data for the evaluation of the technique.

2.6 Conclusions

For the remediation of TBT contaminations several different approaches have been explored up to now. The treatment methods are based on the physical and chemical nature of TBT in order to destroy it, immobilise it or extract it in a more manageable medium and treat it later. Containment options such as confinement on the sea bed have also been considered. From the number of different approaches it is clear that no perfect solution has been found yet and different techniques are best for different types of TBT contamination.

The suitability depends on the type of medium that requires de-contamination (water or sludges), the presence of TBT-containing paint flakes, the size of these paint flakes and whether they are easily removable. Other important parameters are the equipment that is available or accessible in each case, as well as the time-scale or deadlines by which the de-contamination should take place and also the availability of space.

A summary of the technologies that have been proposed is given in Table 3.

Treatment	*Matrix*	*Efficiency of removal*	*Cost (€/m^3)*	*Pros*	*Cons*
Combustion[56, 63, 64]	Sludge	Up to 100%	High (energy)	Fast, efficient, other organic contaminants destroyed, reduction of volume	High energy consumption, residue for disposal
Oxidation[66-71]	Sludge/Water	Up to 99%	High (energy + additives)	Fast, efficient	Toxic by-products
Electrochemical Oxidation[71, 73-76]	Sludge	Up to 99%	10-13	Efficient	Toxic by-products, Difficult MBT debutylation
Bioremediation[71, 78, 79, 86, 87]	Sludge/Water	Up to 90%	Low	Simple	Slow, suitable for moderate contamination
Activated C[69, 91, 94]	Water	90-99%	High	Efficient	Treatment of de-activated carbon needed
Organophilic clays[97]	Sludge	N/A	High	Simple, fast, on site re-use of materials	Long-term reliability not proven
Cement[100, 102]	Sludge	N/A	Low	Simple, fast, on site re-use of materials	Long-term reliability not proven
Extraction[1, 63, 104, 105]	Water/Sludge	Up to 99%	High	Efficient	Disposal of solvent, flammability, VOCs
Capping at sea[106]	Sludge	N/A	Low	Simple, fast, applicable to large volumes	Long-term reliability not proven

Table 3. Comparison table for TBT treatment technologies

From the techniques examined in this Chapter, oxidation and electrochemical oxidation were not considered further due to evidence of generation of toxic by-products. Liquid-liquid extraction of TBT from contaminated water would utilise large quantities of organic solvent which would also brings about flammability control and disposal problems and costs. Bioremediation was a method restricted to moderately contaminated sediments and would require significant time and space resources to be available. Capping at sea was a technique that was beyond the scope of this work to test. The techniques that were therefore selected to be assessed were combustion and immobilisation with adsorbents.

The main focus of this project is the remediation of TBT-contaminated sludges therefore combustion could be tested to confirm whether the final sludge contains TBT below the 0.1 mg/kg OSPAR Commission[42] level for the sea disposal of dredged material. Still, the question of energy input remains as one of the greatest concerns is the very high energy consumed during the dewatering step of the combustion of sludges.

Also, adsorbents could be tested not only for water but also mixed in with contaminated sludges to reduce the amount of TBT coming out in the leachate, as it was demonstrated in the modified clay case study (Section 2.3.2.2). In that case study the limit agreed with the regulatory authorities was 50 μg/L TBT, therefore such levels could be the target concentrations for the leachates. A stricter approach would be the EQS concentration for coastal and estuarine or freshwaters which is 20 ng/L and 2 ng/L TBT respectively. Nevertheless, the target concentration should be site specific and a universal maximum acceptable leachate concentration for TBT might not be realistic.

3 Review of the analysis of butyltin-contaminated sediments and water

3.1 Introduction

Reliable TBT determination methods for sediment and water samples are necessary in order to measure the contamination and also verify and assess the efficiency of a remediation method. Over the last decades a number of different methods have been reported for the determination of organotin compounds in sediments, water and biota.[107-109] Monitoring of organotin concentrations in sediments and biota has been of great interest, as such samples can be used to assess both historical and current contamination.[110, 111] It seems, though, that the scientific community has not agreed on the best technique for the analysis of environmental samples for organotins. The purpose of this chapter is to review the main techniques used for the analyses of organotin compounds in sediment and water.

Typically, such analyses involve extraction of the organotins from the matrix and their derivatisation prior to final determination. The extraction step from sediments is often troublesome due to the strong association of the organotins with abiotic matrices. The organotins exist in many forms (as polymers, chlorides, fluorides, carbonates, sulfates, sulfides, hydroxides, oxides) and can interact with abiotic matrices with ionic or hydrophobic forces. The extraction or derivatisation step aim to cleave the organotin part from the counter ion or other part. The derivatisation step is also necessary as the organotins are not always in a suitable volatile form or have chromophore groups to allow direct measurement. A difficulty in the analysis is that derivatised organotins for use as calibrants are not readily available.

3.2 Extraction

Extraction of the organotins is necessary to transfer them into an organic solvent for the derivatisation to take place or for further clean-up or measurement. The extraction of organotins is the most controversial step of the analysis. The organotins can be found incorporated in paint flakes, adsorbed on particles or suspended in the water column. When the organotins are suspended in the water their extraction into an organic solvent is straightforward, but when they are strongly associated with sediment particles or locked in paint flakes the extraction can be problematic. Typically a solvent (apolar or polar) is employed with or without the addition of acid. Stirring, shaking, reflux, microwave irradiation or ultrasonicating is used to assist the dissociation of the organotins from the matrix. Complexing agents are often added to enhance the extraction.

3.2.1 Solvents

The extraction into apolar solvents alone, such as pure hexane[112], benzene and toluene[113] is not very common in the analysis of sediment and water samples. The potential problem with this way of extraction is the unsatisfactory recovery of MBT due to its higher ionic character in comparison with other organotin species typically found in the samples (such as TBT and DBT).

More common is the use of low to medium polarity solvents together with acid, which is used in order to convert the butyltins to forms that can be extracted more easily into the organic solvents. This seems to be particularly important for MBT, which requires high concentrations of acid to displace it from the matrix and to convert to its non-polar form. Even though medium polarity solvents are considered more efficient than apolar ones for the extraction of organotins, they have low selectivity and therefore result in interferences in the derivatisation and determination stage due to co-extraction of a large number of other compounds. Low polarity solvents with complexing acids are often used in order to combine high selectivity and extraction efficiency.[114] Hydrochloric, hydrobromic and acetic acid or a mixture has been used together with various solvents. Hydrobromic acid has been reported to increase the extraction of organotins into pentane probably through the formation of neutral ion pairs.[115] Pentane, hexane[116], isooctane, ethyl acetate (EtOAc)[117], isobutyl acetate, benzene, toluene, diethylether and DCM are reported as possible solvents. Also mixtures of solvents like hexane/ethyl acetate[118], hexane/isobutyl acetate, chloroform/ethyl acetate, toluene/isobutyl acetate and hexane/diethyl ether have been employed.

NaCl has also been added in some cases for its salting out effect, or to promote ion-pairing when HCl is used, for the extraction of organotins from the aqueous phase into the organic solvent. [116]

Polar solvents have also been used in the analytical procedures. In this category the solvents used are aqueous HCl, acetic acid or HCl in polar organic solvents (methanol (MeOH)[119], acetone[120]), acetic acid[121], pure polar organic solvents (MeOH, DCM/MeOH, butanol, MeOH/EtOAc) and polar organic solvents in alkaline conditions. The extraction is assisted by ultrasonication[122] or accelerated by a focused microwave field[121-124]. If necessary, a liquid-liquid extraction (LLE) of the organotins follows with an immiscible organic solvent (benzene, $CHCl_3$/DCM, EtOAc/MeOH, DCM, hexane, cyclohexane, toluene, hexane/EtOAc).[108, 114] This extraction is often promoted by the use of complexing agents or the salting out effect.

3.2.2 Other extraction techniques

Other extraction techniques in the literature are supercritical fluid extraction (SFE)[125, 126] and solid phase extraction (SPE)[127-129]. In SFE the organotins are extracted into CO_2 with the assistance of an organic modifier. The use of complexing agents and derivatisation in the extraction cell prior to the extraction have been evaluated to improve this technique.[125, 126] The advantages of SFE are that shorter extraction times and smaller quantities of solvents and acids are required. In the SPE techniques a silica-based solid phase is used, covalently modified with C_{18}[128, 130] or C_8 alkane groups. This extraction technique can be used as a pre-concentration step as well, especially for water samples where large volumes might need to be treated, or as a separation step. The organotins are eluted from the solid phase with a suitable solvent. When fluorimetry is the detection method the elution is carried out with acetonitrile/AcOH/water or MeOH/AcOH/water containing oxalic acid and triethylamine (TEA).[129] The combination of SPE with SFE has also been demonstrated.[131]

For the isolation of the derivatised organotins from the reaction solution solid phase microextraction (SPME) with a polydimethylsiloxane (PDMS) fibre has also been used.[119, 132, 133]

A new technique separating TBT from other organotins has been reported using a molecularly imprinted polymer[134].

3.2.3 Complexing agents

Complexing agents are often added in the extraction step to promote the extraction of organotin species with a high ionic character like MBT, into low polarity solvents or supercritical fluids. Diethyldithiocarbamate (DCC or DCCT) in the form of sodium diethyldithiocarbamate (NaDDC) or diethylammonium diethyldithiocarbamate (DEA-

DCC) as well as ammonium pyrrolidinedithiocarbamate (APDC) and tropolone have been used.[114, 126, 135-137]

One of the most common complexing agent used is tropolone (2-hydroxy-2,4,6-cycloheptatrienone) (Figure 14). The effect of tropolone has been found to be the same within the concentration range 0.01-0.5% w/v of organic solvent.[109] Some researchers dispute the role of tropolone in the extraction, as the mechanism with which tropolone is complexing the organotins is not clear.[108]

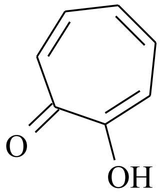


Figure 14. Structure of the complexing agent tropolone

The action of complexing agents can be inhibited by highly acidic conditions like those required for the extraction of MBT from sediments. For example tropolone, with a pKa=7[138], would be protonated in low pH conditions and its complexing ability would be diminished. Another issue is that tropolone co-extracts other compounds and therefore reduces the selectivity of the extraction for organotins. Also, large amounts of tropolone or other agents might interfere with the analysis.

3.3 Derivatisation

The most common way of determination is gas chromatography (GC), which requires conversion of the tin species to volatile forms by derivatisation. Even though there have been methods reported for GC determination without prior derivatisation, they are not robust enough due to potential decomposition of the analytes[139, 140]. The derivatisation reactions employed for organotins are alkylation or hydride generation.

3.3.1 Alkylation reaction

One option for the alkylation of the organotins is the use of Grignard reagents. Depending on the Grignard reagent used, methylation[141, 142], ethylation[131], propylation[143], pentylation[127, 135, 141, 144] and hexylation[126, 145] can be achieved. Particular attention should be paid using this method because the Grignard reagent reacts violently with water. It therefore requires dry conditions, which can lead to a relatively long analytical procedure, and an exchange of solvents has to be carried out if protic solvents are used during the extraction stage. The Grignard reagents have to be purged with nitrogen to avoid reaction with the atmospheric moisture. Also, a LLE has to follow for the isolation of the derivatised organotins. A large excess of the Grignard reagent is necessary as the reagent could otherwise be spent on the alkylation of potentially co-extracted compounds.[125] The reaction time is also important. 30 min is adequate[145] for most organotins and disproportionation reactions might occur during longer contact times[109]. Lower recoveries have been reported for the volatile species of the methyl and ethyl derivatised organotins due to losses, therefore evaporation to dryness should be avoided in these cases.[145] Also, the methylation method cannot be used if the determination of naturally occurring methylbutyltins is of interest.[146] Hexylation produces more thermally stable species resulting in the elimination of evaporation losses and better separation during gas chromatography.

Another, less lengthy option is the use of sodium tetraethylborate ($NaBEt_4$) as the ethylation reagent.[121, 147, 148] The use of tetrapropylborate as an alkylation reagent has also been reported for the determination of naturally occurring ethylated species.[149] The alkylating reagent sodium tetrakis(4-fluorophenyl)borate has been reported for the derivatisation of TBT and resulted in a 5-fold improvement of the detection limit compared to pentylation, which was attributed to the higher Sn-aryl bond dissociation energy.[150] The advantage in this type of reagent is that the reaction can take place in aqueous media and can take place simultaneously with the extraction step.[151] Therefore the analysis is simpler and faster. Buffering of the solution between pH 4 and 6 is important. In pH below 4 the reagent reacts with H^+ and decomposes, while above pH 6 the organotins convert to their hydroxide forms (TBT pKa=6.25).[152] This becomes even more important if acid has been added during the storage or the extraction of the sample prior to the derivatisation. Simultaneous extraction/derivatisation with $NaBEt_4$ is very difficult with sediment samples as strong acidic conditions are often employed for the dissociation of the organotins from the matrix. In that case continuous addition of the reagent and mixing would be necessary to ensure that every desorbed molecule is derivatised by freshly added reagent and immediately extracted into an apolar solvent, so that the desorption continues.[115]

3.3.2 Hydride generation reaction

An alternative reaction for the derivatisation of organotins is hydride generation (HG) with sodium tetrahydroborate ($NaBH_4$), an inexpensive reagent.[153, 154] The reaction can be carried out in aqueous media and simultaneous extraction/derivatisation can be performed in NaOH-MeOH[155]. Control of the pH is considered necessary for acidified samples to avoid rapid degradation of the reagent by H^+.[115] Due to the volatility and reactivity of the organotin hydrides this method is less often used for off-line determination[113, 156-158], due to reproducibility problems.[109, 115] HG is often followed by cryogenic trapping (CT)[159-161] and/or solid phase micro-extraction (SPME)[162, 163] for the extraction of the hydrides. This derivatisation reaction is not robust enough for sediment samples due to matrix effects, which inhibit the hydride generation.[164]

3.4 Clean-up

Clean-up is often required to remove co-extracted compounds in organic apolar solvents that might interfere in the subsequent analysis stages when GC is the final determination method. In the majority of the cases the clean-up comes after the derivatisation in order to remove compounds that would interfere during the determination stage. The common absorbants are Florisil (magnesium silicate)[116, 144-146, 165, 166] and alumina[108, 114, 118, 151, 167].

With sediment samples activated copper[114] is used for desulfurisation but this method only removes elemental sulfur and not the alkylated sulfides generated during the derivatisation with Grignard. For this purpose $AgNO_3$-coated silica gel has been employed, which removes elemental and organosulfur but is not suitable if phenyltins are of interest because they decompose.[168] Dimethyldioxirane (DMD) has also been used for sulfur elimination.[108]

Finally, in some analyses no clean-up is carried out because of the selectivity of the procedures for organotins.[125, 157]

3.5 Determination

3.5.1 Gas chromatography

Since capillary chromatography was developed, GC has become the most popular method for the separation and determination of the organotins. The high resolution that can be achieved allows the simultaneous determination of many organotin compounds. Samples to be analysed can be spiked with other organotins as internal standards (I.S.) and surrogate compounds can be added to check the recovery of each analytical step.

Several injection systems have been developed (split-splitless, cold on-column, temperature programmable) which allow the complete volatilisation of several μL of sample. Packed or deactivated injector tubes have been used to prevent contamination of the column.

The high efficiency of capillary columns allows the separation of organotins even by non-polar non-selective stationary phases, like dimethylpolysiloxane or 5% diphenyldimethylpolysiloxane (DB-1, HP-1, SA-1, SPB-1, DB-5, BP-5, HP-5, RTx-5, SE-54, Tr-5).[149, 169-172] It has been found that there is a correlation between the number of carbons in the alkyl substituents of the organotins and the retention time, i.e. organotins with the same number of carbons have the same retention time. Therefore higher polarity stationary phases, like 50% diphenyldimethylpolysiloxane (DB-17) are used for the separation of phenyl- and cyclohexyltins.[108]

Since the development of more selective and low cost detectors a whole range of detectors that had previously been employed for GC including flame photometric detection (FPD)[125, 173, 174], flame ionisation (FID)[175], atomic absorption spectroscopy (AAS)[176] are now rarely used. In contrast, the pulsed flame photometric detector (PFPD)[132, 143, 147, 148, 177-185], the next generation of the FPD, is popular due to its selectivity for tin and low detection limits for the determination of organotins. Mass spectrometric detectors (MS)[120, 173, 186-188] also remain popular. Inductively coupled plasma mass spectrometry (ICP-MS)[149, 189], microwave induced plasma atomic emission spectrometry (MIP-AES)[132] and ICP-AES[190] have also been used.

3.5.2 Liquid chromatography

Liquid chromatography (LC), in different modes (ion-exchange, reversed-phase, normal-phase and ion-pair) and high performance liquid chromatography (HPLC) is also used.

Ion-exchange chromatography has been applied for the separation of the mono-, di- and tributyltin with SCX columns (Zorbax[191], Partisil[192]). Normal-phase separations of organotins is usually carried out on cyanopropyl columns.[193] The mobile phase consists mainly of hexane together with a solvent of higher polarity, which is necessary to prevent the adsorption of organotins on unreacted silanol groups of the column. Reverse-phase (RPLC) approaches use octadecyl- (C_{18})[194] or octa- (C_8) bonded silica stationary phases and polar mobile phases, while cyanopropyl silica column[195] with gradient elution has also been used. The most common detectors are: ICP-MS[196], fluorimetry[129, 197] (after post-column derivatisation, as organotins lack native fluorescence), AAS, electrothermal AAS (ETAAS)[192, 198], MS, laser enhanced ionisation (LEI) and ICP-AES[199].

3.5.3 Detection limits

The detection limits of the methods discussed cannot be clearly compared. The difficulty lies in the fact that the detection limit is not always given, also in that the way the limits are calculated are not always given and the mass units are not always clear to which form (Sn, chloride, cation) they refer to. Nevertheless, general conclusions can be drawn.

Aguerre *et al*[132] has compared the performances of different detectors for the same analytical procedure. The lowest detection limit was delivered by the ICP-MS but the PFPD is only one or two orders of magnitude behind. It seems that gas chromatography can more comfortably deliver sub-pico gram detection limits[132, 136, 161] than liquid chromatography without employing the expensive ICP-MS detector and without pre-concentration steps.

Liquid chromatography systems have improved over the last decades and can be very useful in monitoring programmes as they can now achieve detection limits of pico gram order.[129, 192, 196]

3.6 Other issues

3.6.1 Sample preparation

Sampling, transportation and storage are not always reported. Usually the samples are transferred to the lab and stored until the analysis.

Water samples are usually stored in the dark at 4 °C and acidified to pH 2 to avoid degradation by sunlight or biodegradation by microorganisms in the water column. For TBT no changes have been observed in sediment samples that have been frozen wet or dry. The drying of the sediments can be done in various ways (air dried, oven dried or freeze dried). For drying at approximately 50 °C no losses have been reported for TBT but DBT and MBT might be subjected to changes.[200]

Sediment sample preparation often involves sieving of the sample, especially since organotins are associated with the fine fraction of the sediment. After sieving, the sample has to be homogenised due to the potential presence of TBT-contaminated paint flakes. Very good mixing is necessary in wet sediment, and ball-milling has been suggested as a homogenisation method for dry sediment.[115] Paint flakes are more likely to be present if the sample comes from harbours or dockyards. Samples from open marine environments tend to be more homogenous as the organotins come from the water column. Five to six replicates per analysis may be therefore necessary to give a representative value in the cases of highly contaminated sediment samples.

3.6.2 Spiking

When developing an analytical method spiking is essential to create a sample that resembles the real samples in matrix effects, volume and concentration. Spiking levels vary and the organotins are usually added as their chloride salts dissolved in polar organic solvents (MeOH[129, 196] or acetone[136]). The use of apolar solvents is not advisable as the interaction of the organotins with the environmental matrices will not be satisfactory.

3.6.3 Calibration

Calibration is necessary in all the analyses. Researchers choose a calibration method according to the characteristics of the analysis. The calibration can be done with external or internal standards (I.S.).

When determining the organotin compounds with liquid chromatography derivatisation is not necessary and commercially available organotin salts can be used for the external calibration solutions. In analyses with gas chromatography a derivatisation step is usually carried out. One difficulty when using external calibration is the lack of readily available alkylated organotins. Even though QUASIMEME[201] provides some pentylated and ethylated standards for butyltins, few researchers have used them. In most cases the alkylated organotins are prepared in-house. Another option is to use spiked solutions of organotin salts and subject them in the whole analysis (extraction, derivatisation, determination) and in this way compensate for losses in the whole process and variability in the determination stage. In order to account for potential matrix effects the spiked solutions for calibration should be in real analyte-free matrices, which are not readily available.

When analysing real samples, spiking with species similar to the analyte allows the tracing of each stage of the analysis. The I.S. calibration will compensate for losses in the analytical stages that follow the addition. If the I.S. is added at the beginning of the analysis and undergoes extraction and derivatisation then it is also called a surrogate as it will compensate for losses occurring throughout the whole procedure. If the I.S. is added just before the chromatographic determination it is usually a tetraalkylated organotin and it will compensate only for the chromatographic variations. In many cases a combination of surrogates and I.S. is used to make the calibration more robust.

Organotins used as surrogates and I.S. depend on the organotin of interest in the analysis. Most common compounds used are tripropyltin (TPrT) and tetrabutyltin (TeBT). Others have also been used including dimethylbutyltin (DMeBT), tripentyltin (TPeT)[114, 202] and tricyclohexyltin (TCyT)[108, 126]. Surrogates with different degrees of alkylation and different alkyl- groups have been shown to be necessary because the behaviour of a surrogate during the extraction or alkylation stages is not necessarily comparable with all the analytes in the sample.[203]

Another method of calibration is the standard additions method and in this case the matrix effects play a significant role. It is often employed where cryogenic trapping (CT)[160] or solid phase micro-extraction (SPME)[119, 132] of the derivatised compounds is used.

3.6.4 Accuracy

For demonstrating the accuracy of a method two approaches are employed. The first approach is measuring the recovery of organotins in a spiked sample and the second one is the analysis of a CRM (certified reference material).

One of the most important considerations when using a spiked sample is the spiking stage. During spiking a similar interaction of the organotins with the matrix as in real samples should be pursued. Otherwise, the extraction behaviour and consequently the recovery can be dissimilar between the spiked samples and the real environmental samples. In the case of the presence of TBT-contaminated paint flakes in the sediment samples the extraction recovery is very difficult to simulate in spiked samples. It is advisable to perform spiking in different matrices and at different levels, within the range of concentrations found in the environment.

CRMs are used in order to overcome the difficulty of matrix differences. The concentrations of organotins have been established by inter-laboratory exercises. For sediments PACS-1, CRM-462 and PACS-2 have been produced (Table 4). PACS-2 is the most recently produced CRM, after problems with the extraction of MBT from previous CRMs were reported.[204]

Name	***Source***	***Type***	***Units***	***Certified values***
PACS-2	National Research Council of Canada (NRCC)	Harbour sediment	µg Sn/kg	TBT=980±130 DBT=1090±150 MBT=300 (ind. value)
CRM-462	Institute for Reference Materials of the European Commission	Coastal sediment	µg Sn/kg	TBT=24±6, DBT=63±8
PACS-1	NRCC	Harbour sediment	µg Sn/kg	TBT=1270±220 DBT=1160±180 MBT=280±170

Table 4. CRMs for butyltins in sediments

3.7 Conclusions

In Table 5 a selection of representative analyses for butyltin compounds in sediments and water are summarised. The first section of the table is about methods using GC and the second section refers to LC methods.

Sample	**Extr./ Deriv.**	**Determ.**	**Recovery**	**Det. limits**	**Comments**	**Rf.**
GC						
Spiked river water	500 mL water+0.2 g DDTC+ NaCl 100g + 50 mL toluene organic phase + Na$_2$SO$_4$ column, ev. under reduced pressure to ca. 1 mL PeMgBr, 60 min at 40°C, 5 mL (1M) H$_2$SO$_4$ + 50 mL water, ex. with 10 mL hex., ev. to 0.9 mL	GC-MS-MS (DB-5)	Spiking level: 200 ng Sn/L (%) TBT=108±2.8 DBT=106±10 MBT=90.1±16	(pg as Sn) TBT=0.35 DBT=0.29 MBT=0.29	perdeuterated organotin chlorides (surrogates) TeBT-d$_{36}$ (IS)	136
Spiked seawater	Method as above		(%) TBT=105±5.2 DBT=99.5±8.8 MBT=91.0±12			
PACS-1 (µg Sn/kg dry mass) TBT=1270±220 DBT=1160±180 MBT=280±170	2 g dry sample, (10 mL toluene+4 mL conc. AcOH, 5 min sonication) x3 LLE (10 mL aq. 0.5% APDC, 1 min) x2 Rot. evap. (30°C) to few mL, PeMgBr, 10 min, Act. copper, overnight, Act. alumina/hexane to 10 mL, Ev. with N$_2$ to 1 mL	GC-FPD (DB-17, 610nm filter)	(%) TBT=92 DBT=82 MBT=280	not given	TPrTCl, TCyTCl, TPeTCl (surrogates) TeBT (IS) *n*=3	114
CRM-462 (µg Sn/kg dry mass) TBT=24±6, DBT=63±8			(%) TBT=99 DBT=70		*n*=3	
PACS-2 (µg Sn/kg dry mass) TBT=980±130 DBT=1090±150 MBT=300 ind. value	2 g dry sample, (10 mL toluene+4 mL conc. AcOH, 5 min sonication) x3 LLE (10 mL aq. 0.5% APDC) x2 Rot. evap. (35°C) to few mL, PeMgBr, 20 min, 5 mL DMD, Act. alumina/hexane to 10 mL, Ev. with N$_2$ to 1 mL	GC-PFPD (DB-17, 390nm filter)	(µg Sn/kg dry mass) TBT=971±142 DBT=1158±157 MBT=386±84	not given	TPrTCl, TCyTCl (surrogates) TeBT (IS) *n*=3	108

Sample	**Extr./ Deriv.**	**Determ.**	**Recovery**	**Det. limits**	**Comments**	**Rf.**
PACS-2 (µg Sn/kg dry mass) TBT=980±130 DBT=1090±150 MBT=300 ind. value	0.5 g sample, 3 mL 20%HCl-MeOH (1:1, v/v), 1 h sonication, 5 min centrifugation at 1990 x g 2 mL supernatant +17 mL AcNa buffer (pH 4.3, 1.5 M), 15 min at 40°C, 1 mL 2% aq. NaBEt$_4$, 2 min 1200 rpm, 15 min with 100µm PDMS fibre	SPME-GC-FID (HP-1)	(%) TBT=89 DBT=96 MBT=200	not given	Standard additions for calibration	119
PACS-1	0.5-2 g dry wt sed.+ 1 mL AcOH + 15 mL MeOH, pH 4.5 5 mL hex. + (1 mL 2% aq. NaBEt$_4$, 1 min shaking)x3, 5 min centrifugation at 3500 rpm	GC-ICP-MS	(%) TBT=101 DBT=95 MBT=168	(pg as butyltin cations) 0.03-0.04	dimethylbutyltin bromide (IS) *n*=4	161
PACS-2 (µg Sn/kg dry mass) TBT=980±130 DBT=1090±150 MBT=300 ind. value	1 g dry sed.+ 20 mL AcOH, 12 h stirring, centrifugation 0.5-2 mL extract + 100 mL AcOh/AcONa + NaOH up to pH 4.8 + 0.3-0.5 mL 2% aq. NaBEt$_4$ Extr. with PDMS fibre, 40 min	SPME-GC-MIP-AES	(µg Sn/Kg dry mass) TBT=944±64 DBT=1013±89 MBT=566±36	(pg Sn/L) TBT=9 DBT=11 MBT=42	Standard additions for calibration TPrT (IS) *n*=6	132
		SPME-GC-ICP-MS	TBT=931±153 DBT=981±73 MBT=1301±27	TBT=0.6 DBT=0.7 MBT=2		
		SPME-GC-PFPD (390 nm filter)	TBT=892±214 DBT=1158±148 MBT=2000±480	TBT=1 DBT=1 MBT=4		
		SPME-GC-FPD (610 nm filter)	*not done*	TBT=6 DBT=7 MBT=31		
CRM-462 (µg as cation /Kg dry mass) TBT=70.5±13 DBT=128±16	1 g + 20 mL AcOH, 12 h stirring, 20 min centrifugation 100 µL+50 mL water+ AcOH, 2 min He flow, 10 mL 2% NaBH$_4$ 3 min He flow, Chromosorb in liq. N$_2$	HG-CT-GC to ICP-MS	(µg as cation /Kg dry mass) 78±3 124±6	(pg as cation) TBT=4 DBT=4	Standard additions for calibration *n*=3	160

Sample	Extr./ Deriv.	Determ.	Recovery	Det. limits	Comments	Rf.
LC						
Spiked water	100-200 mL water preconc. with C18 columns (cond. with: 10 mL MeOH+10 mL water at 3.5 mL/min) 5 mL 80%MeOH(v/v)-3%AcOH(v/v) at 0.5 mL/min	HPLC-ICP-MS (Kromasil-100 with 80%MeOH 1% formic acid)	Spiking level: 50 ng/L as TBTCl TBTCl=103%	(pg as TBTCl) 2	n=3	196
PACS-2 (µg Sn/kg dry mass) TBT=980±130 DBT=1090±150 MBT=300 ind. value	0.5 g sed.+ (15 mL MeOH -0.05% tropolone-0.1M AcOH, 30 min sonication)x2 Supernatant+100 mL water + 30 mL DCM, 5 min shaking, DCM layer rot. ev. to dryness + 1.0 mL MeOH+ filtr. on 0.45 µm polycarbonate filter	HPLC-ETAAS (Partisil SCX 10, with 0.1 M AcONa in 80%MeOH-water, 0.01% (m/v) tropolone)	(µg Sn/kg dry mass) TBT=840±150 DBT=870±100 MBT=180±80	(pg as Sn) TBT=135 DBT=213 942	Calibration method not given	192
Spiked water	250-500 mL water pumped at 5 mL/min on C18 columns (cond. with: 5 mL MeOH+10 mL) 10 mL water rinse, dry with air, 2 min 2 mL of 30 mg/L oxalic acid, 0.03% TEA in MeOH-AcOH-water (57.5:2.5:40) at 0.5 mL/min	RPLC-fluorimetry (C18 Kromasil-100 with MeOH-AcOH-water, oxalic acid and TEA)	Spiking level 641 ng Sn/L and sample of 500mL TBT=80±12% Spiking level 1282 ng Sn/L and sample of 250mL TBT=84±13% Spiking level 99 ng Sn/L and sample of 500mL DBT=91±4% Spiking level 197 ng Sn/L and sample of 250mL DBT=94±6%	(pg as Sn) TBT=1000 DBT=100	Calibration according to peak heights n=7	129

Table 5. Summarised selection of methods for the measurement of butyltins in sediment and water samples

From the details shown in Table 5 it becomes evident that the analytical process for the determination of TBT involves a multitude of steps, most of which require a skilled worker due to the need for accuracy and the fact that most of the manipulations need to be carried out manually. In this work the methods applied were ones that would allow the analysis of a high number of samples daily, due to the high workload that had been predicted. Simplification of existing methods with as little loss of sensitivity as possible was investigated.

For the determination step gas chromatography was selected as it seemed to deliver better detection limits than liquid chromatography (such as HPLC). A simple but reliable determination system was the GC-PFPD, which was reported to have good detection limits for TBT. Also, its selectivity for TBT means in many cases there is no need for a sulfur (interfering species) clean-up step. The low consumption of gases (unlike GC-ICP-MS) and robustness would allow an economical operation despite the high workload.

The analytical approaches that were chosen for this work are critically evaluated in Chapters 4 and 5.

4 Determination of butyltins in sediments

4.1 Introduction

In order to be able to assess the efficiency of remediation techniques that involved the destruction of the TBT in TBT-contaminated sediments, it was required to measure its concentration before and after the application of the remediation treatment. In this Chapter the development of the method for the determination of butyltin compounds in sediments is presented.

Due to the complexity of the sediment matrices, a robust analytical method was required that could achieve detection limits better than 0.1 mg/kg TBT, which is the legislative limit set by OSPAR Commission[42], below which the TBT concentration does not cause concern for the disposal of TBT-contaminated dredgings at sea. For this purpose, extraction of the butyltins into an apolar solvent in acidic conditions was selected, followed by derivatisation (hexylation) with a Grignard reagent and measurement of the hexylated butyltin compounds by gas chromatography.

For the analysis of the TBT-contaminated sediments, the option of gas chromatography was selected because of its high selectivity and sensitivity for butyltins. The GC-PFPD was chosen because of its reported excellent performance in the determination of organotins in environmental samples[132] and it would also allow the simultaneous determination of the important TBT breakdown products DBT and MBT.

In the final Section of this Chapter (Section 4.8) a technique to be used as a screening tool during site investigations for TBT contamination in sediments was assessed. This was based on the correlation of the total tin content of sediments with their TBT content. That part of the work was carried out in collaboration with Awad Alrashdi (PhD student, School of Chemistry, University of Southampton).

4.2 Optimisation of chromatographic conditions

The GC used in this project was a Varian model 3800 gas chromatograph fitted with a fused silica capillary column (Sigma-Aldrich, SA-1 bonded poly-dimethylsiloxane, 30 m length, 0.25 mm internal diameter, and 0.25 μm film thickness). The carrier gas used was nitrogen at a flow rate of 1 mL/min.

The oven programme (Table 6) was adapted from Leermakers *et al*[148], who optimised it for organotin analysis. The final hold at 270 °C for 13 min allows time for the detector to self-clean of tin oxide deposits and also ensures that potential impurities that have remained in the column volatilise and exit the system, according to Amirav and Jing[177].

°C/min	T (°C)	Hold time (min)	Total (min)
	50	3.00	3.00
50	100	0.00	4.00
7	130	0.00	8.29
20	270	13.00	28.29

Table 6. Oven temperature programme for the determination of butyltins

A type 1079 PTV (Programmable Temperature Vaporising) injector was employed, operated initially in splitless mode, isothermally at 250 °C.

The instrument was also equipped with a CP-8400 auto-sampler and a CP-8410 auto-injector which was set to inject 1 μL with the split valve to open after 1.0 min, with a split ratio of 50:1.

Other operational parameters were: the temperature of the detector (PFPD), set at 300 °C or 350 °C, the detector gas flow rates were Air1:17, H_2:14, Air2:10 mL/min. The photomultiplier tube (PMT model R647) voltage was 510 V, the trigger level 200 mV, the sampling delay 4.0 ms, the sampling width 3.0 ms and the gain (current amplification) factor 2. A BG12 optical filter was fitted having a bandpass of 340-460 nm. The combustor chamber had an internal bore of 2.0 mm.

The gas flow rates for the detection flame and the injector temperature programme were changed, their impact on the signal was assessed and if they gave a positive impact, were adopted for the subsequent experiments.

4.2.1 Detector

The GC is fitted with a pulsed flame photometric detector (GC-PFPD), an evolution of the flame photometric detector (FPD).

The sensitivity and selectivity of the conventional FPD for heteroatoms was limited by background light emissions from combustion products such as CH*, C* and OH*. These species have a broad band chemiluminescence in hydrogen-rich air/H_2 flames with a maximum hydrocarbon emission in the blue region near 436 nm. In order to overcome the obstacle of the high background emission, narrow bandpass optical filters were used in the FPD around the emission wavelength of the elements of interest (typically S and P). Despite the use of the narrow filters, the background emissions and the interference from the hydrocarbons was not completely eliminated. In addition, the emissions from the elements of interest that reached the photomultiplier were diminished in some cases due to the filters.

The PFPD came as a solution to these issues as it uses the time dependence of emissions to discriminate between elements. Its structure allows the flame to be pulsed at a set frequency. One of the differences from the conventional FPD is that the flame gas flow rates are low so that the flame can easily be extinguished. There are three gas supplies to the detector: Air1, Air2 and hydrogen (H_2). Air1 and H_2 mix before joining the eluting gases from the chromatography column on entering the combustion chamber where Air2 enters from a separate inlet (Figure 15). The gases proceed to the ignition chamber, where a constant ignition source ignites them. The gases propagate back to a quartz tube in the combustion chamber. Emissions are measured using a photomultiplier viewing the flame through an optical filter. Due to the low gas flow rates and a restriction in the flow path, the gases extinguish and are vented through the ignition chamber. Meanwhile, new gases enter the combustion chamber and set up conditions for a new ignition.

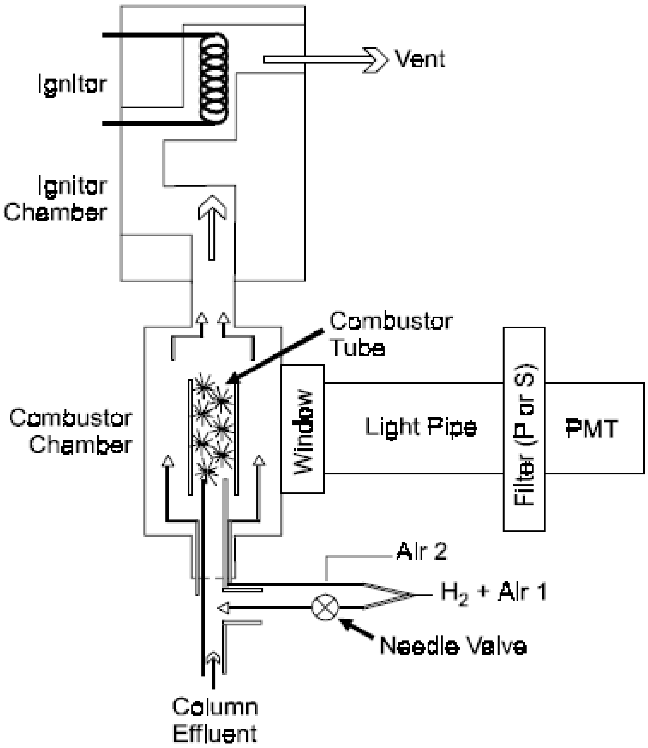


***Figure 15. Cross-section of the Pulsed Flame Photometric Detector*[205]**

Tin gives a broad emission spectrum over the range 380-540 nm, which has been attributed by Flinn and Aue[206] and Jiang *et al*[207] to its interaction with the quartz tube surface of the combustion chamber of the detector. The most useful emission is at 390 nm, which has been attributed to Sn-O species[208]. This offers 2-10 times more sensitivity than the emission from Sn-H species at 610 nm[178, 208]. The most suitable filter for the 390 nm emission is the BG12 optical filter (used in this project), which is the same one that would be used for sulfur. This means that the main potentially interfering species is sulfur, especially for the analysis of sediment samples.

The interference is eliminated by adjusting the frequency of the flame and the electronic gate delay and width settings to permit emissions from different atoms to be distinguished. This is possible because the most combustible atoms (hydrocarbons) form emitting species, such as CO*, CO_2* and H_2O*, during the hottest period of the flame pulse. The formation reaction is fast, highly exothermic and irreversible. Heteroatom emitting species, like S_2*, HNO* and HPO*, have weaker bonds with lower energies and are formed later during the cooler post-flame period with more reversible reactions. In the case of the organotins, sampling at an appropriate time delay allows the interfering sulfur emission to be excluded, as it emits later than the organotin species (Figure 16). The background hydrocarbon emission, emitting at the beginning of the flame before the tin species (Figure 16), is also eliminated in this way. The result is increased selectivity and sensitivity of the PFPD towards the tin species.

The pulsed flame propagation also allows the detector to self-clean of tin and other oxide residues that would otherwise reduce the sensitivity of the detector.[177, 178]

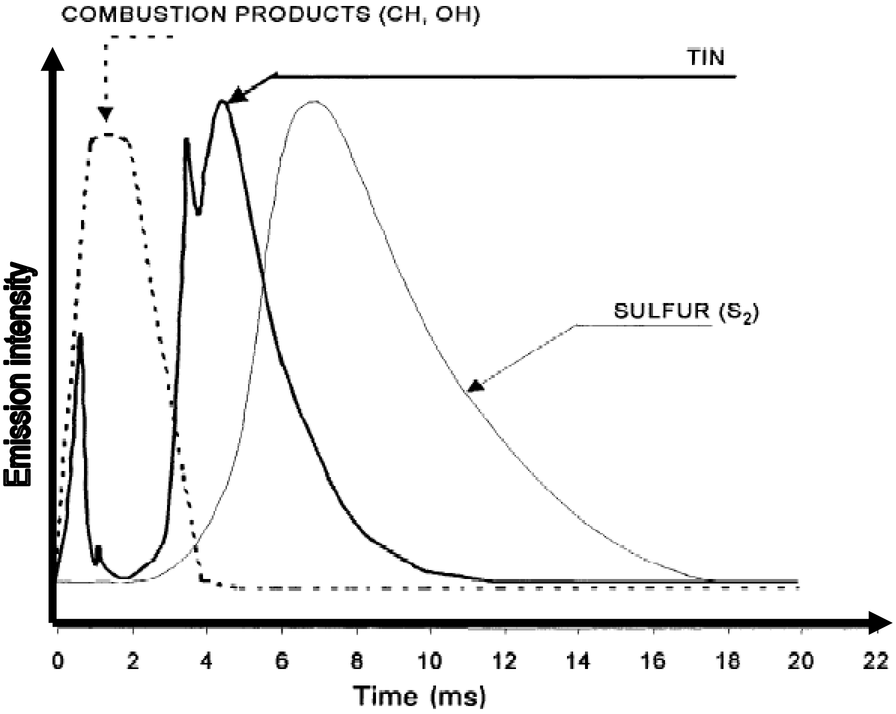


Figure 16. Emission time profile of Sn and potentially interfering species in the PFPD (adapted from Ref[209])

4.2.2 Detector optimisation

Jing and Amirav[178] found that optimum conditions for the detection of tin with the PFPD were hydrogen rich flame conditions, but then increased peak-tailing occurs. Air-rich conditions and high (350°C) detector temperatures were therefore recommended. Godoi *et al*[179] had optimised the gas flow rates for a PFPD using the 390 nm filter and the recommended values were: Air1 16.9 mL/min, H_2 12.3 mL/min and Air2 10.5 mL/min. The detector gas flow rates in this work (Air1 17 mL/min, H_2 14 mL/min, Air2 10 mL/min) were adapted from the work of Jacobsen *et al*[147] where the flow rates used were Air1 17 mL/min, H_2 13.5 mL/min, Air2 10 mL/min that give a pulse frequency of 2.6 Hz.

It was decided to use these settings initially and to carry out some injections to assess the repeatability of the signal.

4.2.2.1 Initial experiment

Accumulation of tin oxide in the detector was suspected as the reason for a decreasing signal during preliminary experiments. The self-cleaning ability of the PFPD was evaluated by carrying out injections before and after leaving the instrument to self-clean overnight.

For the injections a standard solution of hexylated butyltin compounds was used, prepared from pure compounds synthesised in-house by Dr. C. Warriner for the purpose of this project. The standard solution of 0.1 μg Sn/mL containing monohexyl-TBT (MHTBT), dihexyl-DBT (DHDBT) and trihexyl-MBT (THMBT) in hexane was injected 6 times. Then the GC was left on to self-clean overnight, and the same solution was injected 6 times the next day.

In both series of injections the signal was decreasing from injection to injection. For the first series of injections the peak height values measured for the butyltins were TBT= 47620±2861 μV, DBT= 41267±3068 μV and for MBT= 34507±2896 μV. The signal recovered overnight and then the peak height measured for the butyltins was TBT= 53303±4270 μV, DBT= 46751±5878 μV and for MBT= 38639±5280 μV. The recovery of the signal was attributed to the self-cleaning ability of the detector, claimed by several authors[147, 178].

4.2.2.2 Detector gas flows

As it seemed likely that the drop of the signal was due to tin oxide accumulation in the detector, an increase of the gas flow rates was explored. An increase of 50-100% in the gas flow rates was recommended by the instrument manufacturer (Varian) in order to reduce the tailing of the organotin peaks, which is attributed to the accumulation of tin oxides inside the detector according to many authors[210, 211].

4.2.2.2.1 Experimental

The gas flow rates were increased by 50-100% (Table 7). To assess the effects of increasing the flow rates, 3 injections (Injections 1-3) of the standard solution were followed by a 2 hour self-clean period and then 3 more injections (Injections 1’-3’) were made. The following settings were tested out with a 0.5 µg Sn/mL standard solution of each of the hexylated compounds MHTBT, DHDBT, and THMBT:

Setting	***Air1 (ml/min)***	***H_2 (ml/min)***	***Air2 (ml/min)***	***Air/H_2 ratio***	***Comments***
1	17	14	10	1.9	Tested with 0.1µg /mL
2	17	28 (+100%)	10	1.0	Non-quantifiable peaks
3	34 (+100%)	28 (+100%)	10	1.15	
4	34 (+100%)	14	10	3.1	No peaks
5	25 (+47%)	21 (+50%)	10	1.7	
6	25 (+47%)	21 (+50%)	20 (+100%)	2.1	
7	34 (+100%)	21 (+50%)	20 (+100%)	2.6	No peaks
8	34 (+100%)	28 (+100%)	20 (+100%)	1.9	

Table 7. Set of conditions for the gas flow rates of the detector

The following parameters were recorded: peak height, peak area, peak asymmetry (measured at 10% of the peak height) as an indicator of peak tailing and peak width (measured at 50% of the peak height) also as an indicator of peak tailing.

4.2.2.2.2 Results and discussion

Settings 2, 4 and 7 gave non-quantifiable peaks or no peaks at all. The disappearance of peaks may be due to two different causes. The energy of the flame may not have been sufficient to excite the molecules or the emission of the excited species was not sampled successfully by the detector due to unsuitable time gate settings or unsuitable filter. The duration of the emission depends on the flame velocity and the flame velocity depends on the air/H_2 ratio (it is slower in hydrogen-rich conditions) and the viewing opening diameter near the window and light guide of the detector[212].

For Setting 2 the fact that the peaks were not quantifiable was attributed to the increased proportion of hydrogen in the flame (100% increased). This is believed to have led to the creation of a Sn-H species in the flame, emitting mainly at 610 nm which is outside the bandpass of the BG12 (340-460 nm), the filter used in the current study.

For Settings 4 and 7, with air/H_2 ratios of 3.1 and 2.6, the fact that no peaks appeared was attributed to the fact that the air/H_2 ratio was not suitable to sustain a strong enough flame that would allow the creation of the Sn emitting species, at least not within the detection capabilities of the PMT of the PFPD.

In the following tables (Tables 8-11) the signal obtained for the injections carried out for flow rate settings 3, 5, 6 and 8 are shown.

Injections	*1*	*2*	*3*	*1'*	*2'*	*3'*
			TBT (μV)			
Setting 3	13856	12186	11704	14947	11341	11101
Setting 5	14725	13953	13189	18500	15605	14899
Setting 6	16313	15708	16060	29249	26238	24066
Setting 8	22961	20275	19549	24781	21769	21849
			DBT (μV)			
Setting 3	10034	9216	8835	10769	8411	8311
Setting 5	11228	10903	10402	14403	12312	11740
Setting 6	10404	9977	10326	24622	21609	20017
Setting 8	16782	12858	11899	16452	13228	13284
			MBT (μV)			
Setting 3	7206	6773	6417	7608	6115	6257
Setting 5	8218	8337	7943	10694	9118	8789
Setting 6	7904	7605	7827	19502	16789	15498
Setting 8	11754	9851	9182	12067	10208	10702

Table 8. Peak height of butyltins for injections 1-3 and 1'-3'

For the three butyltin compounds Setting 6 gave high sensitivity after the 2 hour detector recovery period and Setting 8 appeared to combine high sensitivity and quick stabilisation of the signal (Table 8). Settings 3 and 5 gave lower sensitivity. It was observed that the two settings with air/H_2 ratio close to 2.0 had produced the highest signal, whereas Setting 3 and 5 had had lower ratios.

Injections	***1***	***2***	***3***	***1'***	***2'***	***3'***
			TBT (µV.min)			
Setting 3	907	780	750	962	718	703
Setting 5	1199	1116	1050	1447	1217	1137
Setting 6	1162	1111	1123	1999	1748	1589
Setting 8	1393	1227	1165	1498	1306	1315
			DBT (µV.min)			
Setting 3	643	577	552	680	520	519
Setting 5	917	864	805	1110	947	900
Setting 6	740	710	720	1618	1427	1301
Setting 8	977	747	686	967	765	768
			MBT (µV.min)			
Setting 3	458	427	401	471	378	389
Setting 5	663	650	622	816	696	664
Setting 6	563	538	548	1291	1098	1009
Setting 8	678	571	529	696	589	616

Table 9. Peak area of butyltins for injections 1-3 and 1'-3'

For the peak area (Table 9) the same observations as for the peak height were made.

Injections	***1***	***2***	***3***	***1'***	***2'***	***3'***
			TBT			
Setting 3	4.0	3.8	4.1	3.7	4.0	3.9
Setting 5	4.9	4.8	5.0	4.8	4.8	4.8
Setting 6	4.5	4.6	4.3	3.9	3.7	3.8
Setting 8	3.4	3.6	3.6	3.3	3.3	3.5
			DBT			
Setting 3	4.1	3.8	3.9	3.8	4.0	3.9
Setting 5	5.2	5.0	5.0	4.9	4.9	4.9
Setting 6	4.5	4.5	4.5	3.7	3.9	4.1
Setting 8	3.6	3.5	3.4	3.5	3.6	3.4
			MBT			
Setting 3	4.1	4.1	4.0	4.0	3.8	3.8
Setting 5	5.2	4.9	5.1	4.7	4.8	4.9
Setting 6	4.6	4.6	4.6	4.0	4.1	3.9
Setting 8	3.5	3.7	3.6	3.5	3.3	3.6

Table 10. Peak asymmetry (10%) of butyltins from injections 1-3 and 1'-3'

For all three butyltin compounds Setting 8 gave the lowest peak asymmetry. (Table 10)

Injections	*1*	*2*	*3*	*1′*	*2′*	*3′*
			TBT (min)			
Setting 3	0.05	0.05	0.05	0.05	0.05	0.05
Setting 5	0.06	0.06	0.06	0.06	0.06	0.06
Setting 6	0.05	0.05	0.05	0.05	0.05	0.05
Setting 8	0.05	0.05	0.05	0.05	0.05	0.05
			DBT (min)			
Setting 3	0.05	0.05	0.05	0.05	0.05	0.05
Setting 5	0.06	0.06	0.06	0.06	0.06	0.06
Setting 6	0.05	0.05	0.05	0.05	0.05	0.05
Setting 8	0.05	0.05	0.05	0.05	0.05	0.05
			MBT (min)			
Setting 3	0.05	0.05	0.05	0.05	0.05	0.05
Setting 5	0.06	0.06	0.06	0.06	0.06	0.06
Setting 6	0.05	0.05	0.05	0.05	0.05	0.05
Setting 8	0.05	0.05	0.05	0.05	0.05	0.05

Table 11. Peak width (50 %) of butyltins from injections 1-3 and 1’-3’

For all three butyltin compounds Setting 5 gave the highest values for the peak width (Table 11). The higher peak width observed may be attributed to the low total gas flow rate compared with the rest of the Settings. Higher residence time of the flame products in the combustor may have increased the deposition of dirt and oxides on the detector window.

4.2.2.2.3 Conclusion

Setting 8 was therefore chosen as the most suitable. The criteria were the low peak asymmetry, high peak height sensitivity and rapid re-stabilisation. This was attributed to the significant increase in all three gas flow rates which resulted in reduced residence time of the butyltins in the detector. This was believed to reduce the accumulation of tin oxide deposits, and therefore tailing and low repeatability of the signal. The suitability of Setting 8 was tested further to assess its advantages.

4.2.2.3 Repeatability of new gas flow rates

In order to test the repeatability of Setting 8 (Air1 34 mL/min, H_2 28 mL/min, Air2 20 mL/min) further, a standard solution of 0.05 μg Sn/mL was injected 9 consecutive times.

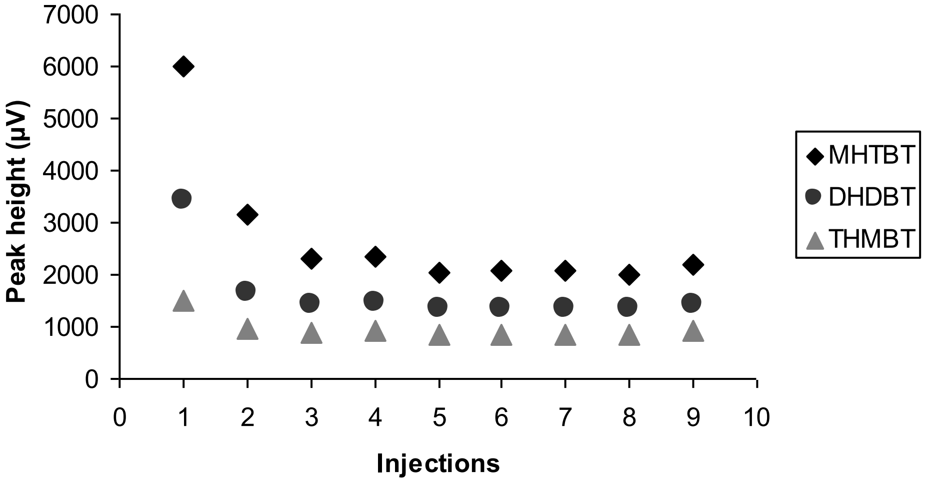


Figure 17. Peak height from consecutive injections of 0.05 µg Sn/mL standard solution at Setting 8

The new gas flow rate settings (+100%) showed that at least two or three consecutive injections (Figure 17) were still needed before the signal stabilises and it was therefore decided to explore the effect of solvent (hexane) injections without increase in the gas flow rates.

4.2.2.4 Effect of hexane injections on the detector signal

It was believed that the reason for the signal instability was the deposit of tin oxides and dirt in the detector, therefore hexane injections between the sample injections would accelerate the self-cleaning of the instrument and they would also allow presence of the "ghosting" effect (peak appearing due to compounds remaining in the system from previous injections) to be assessed.

A 0.05 µg Sn/mL standard solution of each of the hexylated TBT, DBT and MBT was injected 5 times followed by 2 injections of hexane and 4 more injections of the standard solution.

For the first 5 injections the peak height and their respective %RSD (Relative Standard Deviation) was TBT=2609±573 µV (22% RSD), DBT=1638±210 µV (13% RSD) and MBT=1053±128 µV (12% RSD). The peak height was increased and the repeatability was improved after the hexane injections: TBT=3348±174 µV (5% RSD), DBT=2184±69 µV (3% RSD), MBT=1423±44 µV (3% RSD). No ghosting effect was observed.

The signal recovered after the injections and this could be attributed to either the hexane injections or the long time interval during which no butyltin was injected. The signal increase, after the hexane injections, revealed that despite the reported ability of the detector to self-clean within 10 min[147] the deposition of tin oxide on the detector was probably still affecting the signal. It was then decided to explore ways to clean the detector.

4.2.2.5 Assessment of the effect of alternating standard solution and hexane injections

In order to examine more systematically the effect of the injections of hexane on the detector, after each injection of a standard solution (0.1 μg Sn/mL) an injection of hexane was carried out. Six injections of standard and five injections of hexane were carried out in total.

In this experiment the signal was stable after the second injection, as the first injection appeared to be necessary to condition the system. The peak heights measured for the butyltins were TBT=6956±221 μV (3% RSD), DBT=4178±242 μV (6% RSD) and MBT=2553±199 μV (8% RSD). The variability of the values measured was regarded as being satisfactory.

4.2.2.6 Effect of increasing of the self-clean time on the detector signal

The effect of the self–clean time of the instrument was examined by repeating the same experiment after increasing the run time. In the oven programme 9 more minutes were added at the end of the programme extending the run time from 29 to 38 minutes. The standard solution used was 0.1 μg Sn/mL. Six injections of standard and five injections of hexane were carried out in total.

Again, the first injection conditioned the system and the signal stabilised from the second injection of the standard solution onwards. The peak heights measured for the butyltins were TBT=5324±428 μV (8% RSD), DBT=3173±75 μV (2% RSD) and MBT=1993±51 μV (3% RSD). The results obtained with the longer run programme were very similar to those with the shorter programme.

4.2.2.7 Effect of dichloromethane injections on the signal of the detector

The effect of injections of dichlomethane was examined. Dichloromethane was chosen as it might be more effective in cleaning the detector. It was believed that DCM would be combusted by the flame in the detector ignition chamber producing Cl^* free radicals, which would then attack the dirt deposited on the detector producing volatile species.

Six injections of a 0.01 µg Sn/mL standard solution in hexane were alternated with injections of dichloromethane.

The peak heights obtained from this technique were: TBT=694±34 µV (5% RSD), DBT=396±31 µV (9% RSD) and MBT=196±25 µV (13% RSD). As there was no improvement observed this technique was not applied.

4.2.2.8 Combustor replacement

It was then decided to replace the 2.0 mm combustor chamber with a 3.0 mm one, which has been shown by Jing and Amirav[178] to slightly improve the peak tailing for tin compounds, which is caused by tin oxides deposits. The larger combustor would have a larger surface area and also the flame would be further away from the quartz surface, which would therefore be less sensitive to tin oxide deposits.

4.2.3 Injector optimisation

Attention was then directed to the injector as it was considered possible that the drop in sensitivity was coming from the decomposition of the butyltin compounds in the injector.

4.2.3.1 Programming the temperature of the injector

As the GC is equipped with a PTV injector, it was decided to lower the initial temperature of the injector from 250 °C to 170 °C and then increase it at 40 °C/ min to 250 °C final temperature to volatilise the butyltin compounds. 0.1 µL injections of a 1 µg Sn/mL standard solution of butyltins was used.

With the use of PTV the peak height measured was TBT=64720±1468 µV (2% RSD), DBT=49627±910 µV (2% RSD) and MBT=36122±2133 µV (6% RSD). It appeared to double the signal, on average, compared with a 250 °C constant temperature for which the signal was TBT=33199±3382 µV (10% RSD), DBT=21933±2758 µV (13% RSD) and MBT=14232±1810 µV (13% RSD).

4.2.3.2 Initial temperature of the PTV

The initial temperature of the PTV was optimised. Injections with different initial temperatures for the injector ranging from 140 to 260 °C were tested, in random order, using a 0.1 µg Sn/mL standard solution of butyltins. The initial temperature was maintained for 1 min (except for the experiment with initial temperature of 260ºC) and then the temperature was ramped up by 40ºC/min until it reached 260ºC as the final temperature. The final temperature was maintained until the end of the run.

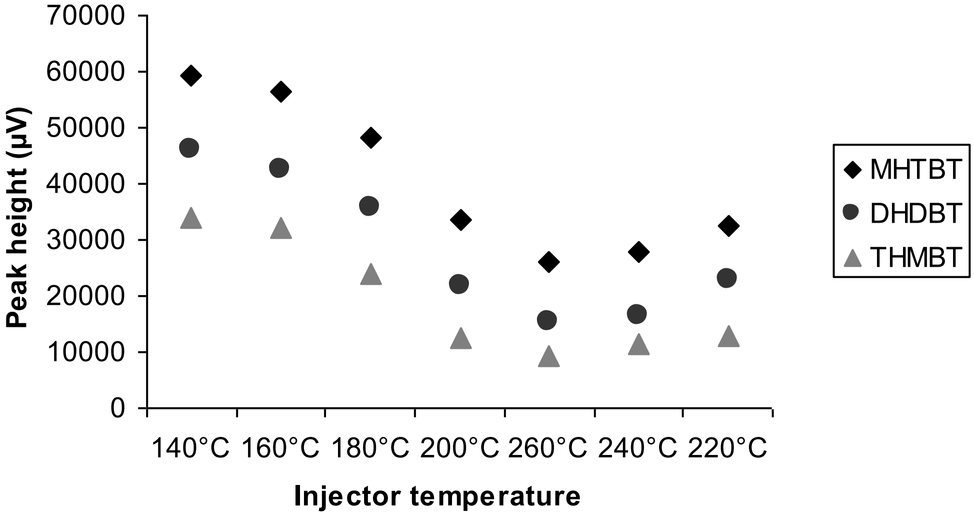


Figure 18. Signal for the same standard solution (0.1 µg Sn/mL) but with different starting PTV temperatures

The programmes with initial temperatures of 140 ºC and 160 ºC gave the highest signal (Figure 18). The repeatability of the signal from injections carried out using that temperature programme had then to be assessed.

4.2.3.3 Signal repeatability

The repeatability of the signal was tested for the two temperatures that gave the highest signal (140 °C and 160 °C) using a standard solution of 0.1 µg Sn/mL of butyltins. Six sequential injections were carried out for each temperature programme.

The peak heights from the butyltins at 140 °C were: TBT=80819±8249 µV (10% RSD), DBT=65604±4882 µV (7% RSD) and MBT=46491±1133 µV (2% RSD). For the programme using 160 °C initial PTV temperature, the peak heights were TBT=71991±3832 µV (5% RSD), DBT=57615±4978 µV (9% RSD) and

MBT=43296±2627 μV (6% RSD).

4.2.3.4 Initial PTV temperature of 150°C

The temperature of 150 °C was tested as an intermediate temperature to be used as the initial temperature of the PTV programme, as it was thought that it may combine high signal with low variability.

Six injections of a 0.1 μg Sn/mL standard solution were followed by two injections of a 1 μg Sn/mL standard solution, three further injections of the 0.1 μg Sn/mL standard, two hexane injections and three injections of the 0.1 μg Sn/ mL standard. This was done to test not only the stability of the signal of consecutive injections but also the recovery of the signal after injections of a high concentration standard and the injection of hexane.

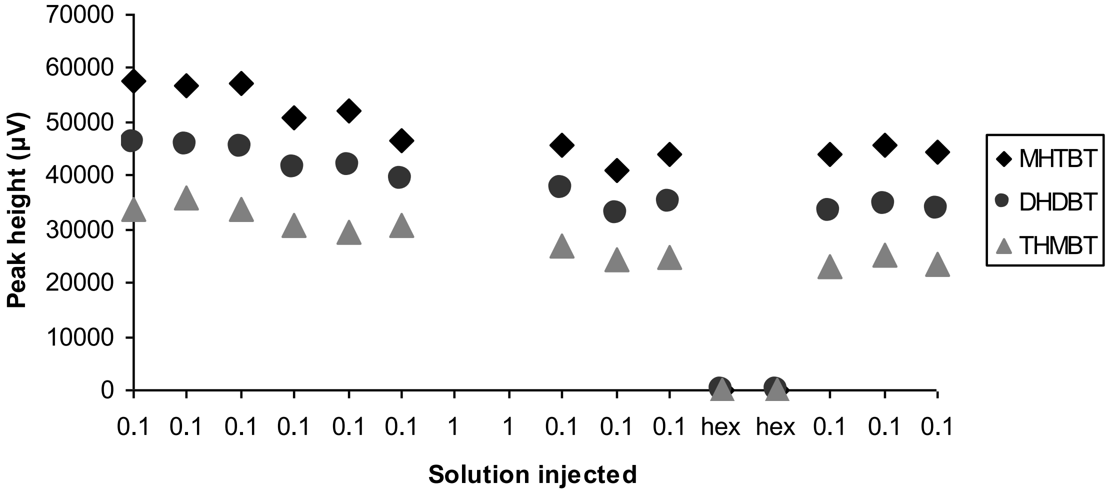


Figure 19. Repeatability and recovery of the signal after injection of high amounts of tin or pure hexane

The signal seemed to stabilise after the sixth injection (Figure 19) despite the injections of a 10 times higher standard solution or the injections of hexane. For the six first injections the values measured were: TBT=53410±4367μV (8% RSD), DBT=43241±2868 μV (7% RSD) and MBT=32420±2370 μV (7% RSD). The variability slightly improved and therefore the new PTV programme (Table 12) using a starting temperature of 150 °C was considered satisfactory.

°C/min	T (°C)	Time (min)	Total (min)
	150	1.00	1.00
40	250	24.69	28.19

Table 12. Final injector temperature programme

4.2.4 Calibration

A calibration using external standards was carried out over the range 0 to 0.25 µg Sn/mL using the newly optimised conditions (Figure 20).

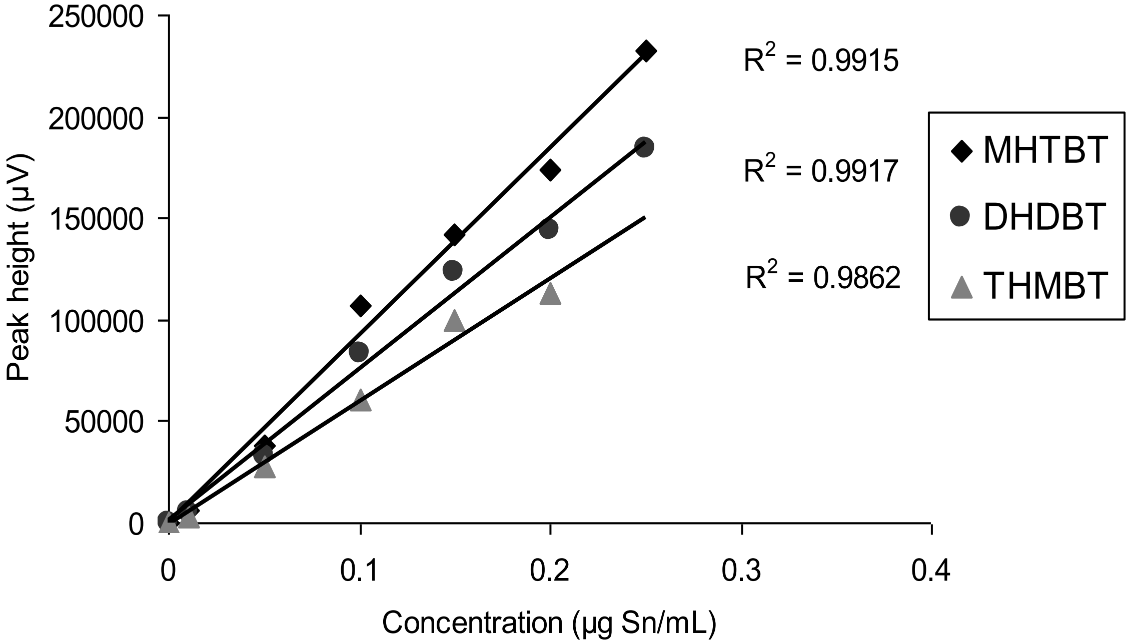


Figure 20. Calibration with 0-0.25 µg Sn/mL standard solutions

The peaks of the 0.002 µg Sn/mL standard solution were not quantifiable.

An example of the chromatography achieved after the optimisation of the detector and injector is shown below (Figure 21).

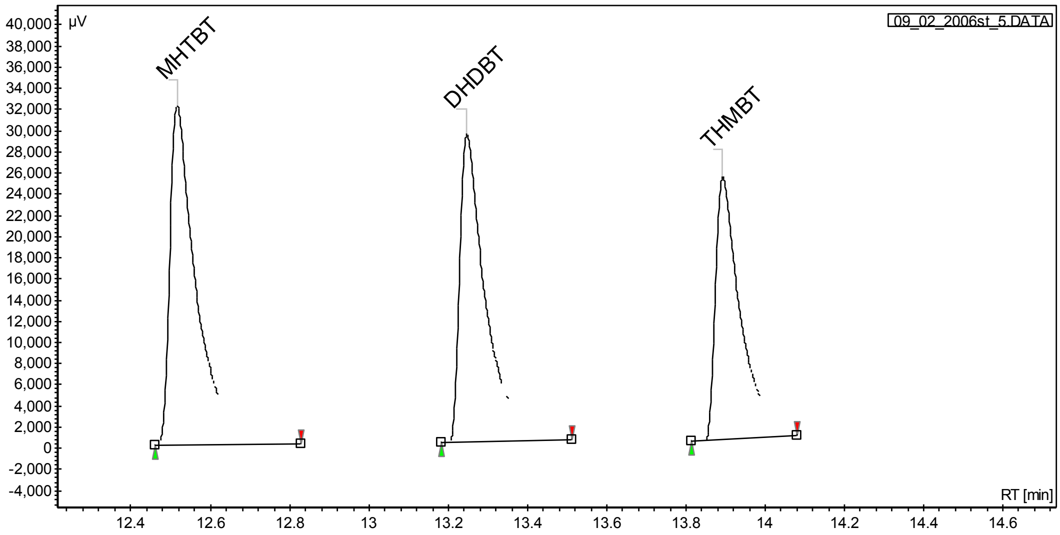


Figure 21. Chromatogram of a 0.04 µg Sn/mL standard solution of hexylated butyltins

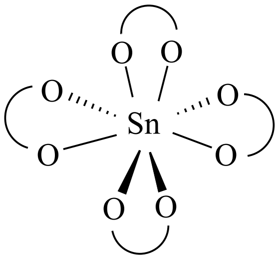
From the calibration in Figure 20, the detection limits (according to a peak equal to 3xbackgound noise) for the injected butyltins were approximately TBT=900 ng/L, DBT=1200 ng/L and MBT=1800 ng/L (as Sn) in hexane. These values were considered satisfactory as they were achieved without employing any pre-concentration. The absolute limits are TBT=0.9 pg, DBT=1.2 pg and MBT=1.8 pg (as Sn), which are lower than those achieved by HPLC-ETAAS[192] (TBT=135 pg, DBT= 213 pg, MBT= 942 pg) and higher than those achieved by ICP-MS[161] (0.03-0.04 pg, as butyltin cations).

4.3 Method description

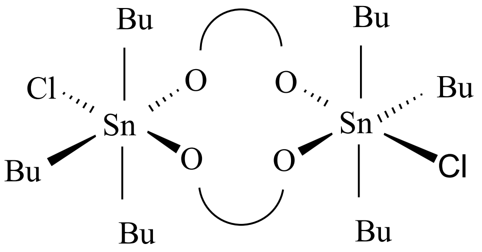
4.3.1 General method principles

The procedure would be as follows: an extraction step with an acid and a hexane/tropolone solution is carried out first. It is believed that the acid at first protonates the negatively charged binding sites of the sediments promoting desorption of the butyltin species. The excess of acid reacts further by converting the butyltins into species that have higher solubility in hexane due to their non-ionic character.

In crystals the complex of tropolone with Sn(IV) is of octa-coordinate structure[213] in which four tropolone anions are bonded with a tin atom forming eight Sn-O bonds:



As tin in the TBT species is trialkylated the same complex cannot be formed. Other types of complexes would have to be formed, such as:



For the next step (derivatisation), a Grignard reagent (hexylmagnesium bromide) is used in order to hexylate the butyltins. This derivatisation approach was chosen because of the lower volatility of the hexylated butyltins compared with other derivatisation products such as methylated butyltins.[145] This is of particular importance because the hexylated butyltins are less prone to losses during derivatisation and also during a potentially necessary evaporative pre-concentration step.

$$\text{xHexylMgBr} + \text{Bu}_{4-x}\text{SnCl}_x \xrightarrow{\text{dry hexane}} \text{Bu}_{4-x}\text{SnHexyl}_x + \text{xMgBrCl}$$

Finally, conc. HCl is added to quench the reaction and the hexane layer is separated and analysed by GC-PFPD.

4.3.2 Materials

Deionised water (>5 MΩ-cm at 25°C) was produced using an ELGA (M4) water purifier, hexane (95% HPLC grade), anhydrous sodium sulphate (dried at 400°C overnight, laboratory reagent grade) was from Fisher (UK). DCM (analytical reagent) was purchased from Rathburn Chemicals (UK). Tri(n-butyl)tin chloride (TBTCl) was purchased from BDH (UK). Di(n-butyl)tin dichloride ($DBTCl_2$, 96%), mono(n-butyl)tin trichloride ($MBTCl_3$, 95%), tetra(n-butyl)tin (TeBT, 98%), tropolone (98%), hexylmagnesium bromide (2.0 M solution in diethylether) were purchased from Aldrich (UK). Tri(n-propyl)tin chloride (TPrTCl, 95%) from Alfa Aesar (UK) and tri(n-pentyl) tin chloride (TPeT, 95%) from ABCR (Germany). Tributylmonohexyltin, dibutyldihexyltin and monobutyltrihexyltin used as external calibrants were synthesised in-house by Dr C. Warriner for the purposes of this project. Polypropylene copolymer (PPCO) centrifuge tubes with polypropylene screw closure and Teflon FEP (fluorinated ethylene propylene) centrifuge tubes with Tefzel ETFE (ethylene-tetrafluoroethylene) screw closure (both Oak ridge, capacity 50 mL) were purchased from Nalgene (UK). All glassware and the detergents Teepol and Decon 90 were purchased from Fisher (UK).

4.3.3 Preparation of standards

Standard solutions for calibration were prepared from in-house hexylated butyltin compounds assuming 100% purity. A stock solution of 1,000 μg Sn/mL in hexane was prepared every six months and was kept in the dark, refrigerated at 4 ºC.

Standard solutions of lower concentrations were prepared weekly or daily by dilution of the stock solution in hexane.

4.3.4 Method

The method is adapted from work described elsewhere.[109, 145, 202, 214] It is the core method used, but some parameters were changed after optimisation experiments described later in this chapter.

For the analysis of butyltin contaminated sediments, *ca.* 1 g (dry weight) sediment is accurately weighed in polypropylene centrifuge tubes. 2 mL of water and 2 mL of conc. HCl are added dropwise. 5 mL of 0.1% (w/v) tropolone in hexane are added and the mixture is shaken using a Griffin wrist action shaker at its highest speed for 1 hour. The mixture is centrifuged at 4000 xg for 10 min, the supernatant hexane layer is placed in a glass sample vial. Na_2SO_4 (anhyd.) is added to remove any water and the supernatant is transferred to a dry glass vial. 1 mL of 2.0 M hexylmagnesium bromide solution in diethylether is added to the hexane solution and it is left to react. After 20 min, 2 mL of conc. HCl are added to de-activate the excess hexylmagnesium bromide and the PTFE-lined cap is screwed on the glass vial. The glass vial is shaken well to ensure complete deactivation of the reagent. After the separation of the layers the aqueous layer is discarded and the hexane layer is dried with Na_2SO_4 (anhyd.) and transferred to a 10 mL volumetric flask. The reaction glass vial is rinsed with 2.5 mL of hexane which are then added to the 10 mL volumetric flask. The solution volume is made up to 10 mL with hexane.

4.4 Method development for the measurement of butyltins in sediments

In order to be able to use the method as described in Section 4.3 it was necessary to prove it was providing accurate and repeatable results. For most of the analytical steps more than one methodology was tested and the most suitable was adopted thereafter. In the following Sections these are presented. For all the experiments butyltin solutions with concentrations within the linear range of the calibration in 4.2.4 were used.

4.4.1 Effect of the drying method

4.4.1.1 Comparison of air- and oven drying

Sediment was collected on the 19/9/05 from a small boatyard on the River Itchen and large particles were removed using a 2 mm sieve. Half of the sediment was dried in an oven at 60°C. One fourth was refrigerated at 4°C and the rest was stored in a deep freezer.

Seven sub-samples were analysed from the oven dried and seven from air dried sediment. The extraction/derivatisation procedure described in Section 4.3.4 was followed.

The air dried sediment gave slightly lower yields for TBT (TBT=0.59±0.70 mg Sn/kg, DBT=0.27±0.41 mg Sn/kg, MBT<0.018 mg Sn/kg) than the oven-dried sediment (TBT=0.68±0.72 mg Sn/kg, DBT=0.23±0.31 mg Sn/kg, MBT=0.75±1.92 mg Sn/kg) but not for DBT. According to a t test (95% confidence level), the differences are not significant, so the two ways of drying do not produce different results. The high standard deviation in the analyses was attributed to the presence of paint flakes.

4.4.1.2 Comparison of wet and oven dried samples

Another sampling took place from the same location on the 5/10/05. Three sub-samples from the wet sediment (kept refrigerated) were compared with three sub-samples from the oven dried sediment. The water content of the wet sediment was calculated after an aliquot of known weight was left in the oven to dry overnight until constant weight. The determination of the content of butyltins according to the procedure described at the beginning of the chapter was carried out.

The wet sediment gave higher yields for TBT (TBT=0.21±0.09 mg Sn/kg, DBT=0.07±0.03 mg Sn/kg) than the oven-dried sediment (TBT=0.08±0.02 mg Sn/kg, DBT=0.09±0.04 mg Sn/kg), while not for DBT. The differences in the two types of samples (wet and dry) were within the experimental error so the analysis of wet and the analysis of dried sediment did not produce convincing evidence that one method is more reliable than the other.

4.4.1.3 Conclusion

According to Smedes *et al*[115] the suitability of the any drying procedure should always be assessed but butyltins are strongly adsorbed to the sediment and there is no danger of losses by evaporation during air- or freeze-drying. Drying the sediment before analysis allows easier homogenisation whereas analysing wet samples saves laborious drying procedures. It was decided that the particular sediment could be analysed even in wet form. It should be noted that other types of sediments may not behave the same.

4.4.2 Cross-contamination

Polypropylene centrifuge tubes, in which extraction had been carried out, were found to be contaminated with alkyltin compounds. This was attributed to adsorption of the butyltins on the tube walls by hydrophobic forces.

To eliminate the contamination, 50 mL Teflon FEP centrifuge tubes (Nalgene), which are generally more inert under the extraction conditions, replaced the polypropylene tubes. A new more laborious washing up procedure was also adopted for all vessels, spatulas etc. The new procedure involved rinsing with acetone, washing with Teepol, soaking in a strong alkaline detergent (5% v/v, Decon 90 solution) overnight, rinsing under running water, subsequent rinsing with 30% HCl, deionised water, acetone and oven drying.

Blank analyses in subsequent experiments did not show signs of contamination, so the action taken was considered adequate.

4.4.3 Sample mass used for analysis

In initial analyses of 1.0 g dry wt sediment samples the hexane layer was not easy to isolate and significant hexane losses often occurred during the centrifugation stage, resulting in poor repeatability. The typical repeatability achieved during the analysis of six sub-samples was for TBT=0.23±0.07 mg Sn/kg, (32% RSD) and for DBT=0.19±0.08 mg

Sn/kg, (43% RSD).

The problem was overcome by reducing the sample weight to 0.50 g dry wt. This way the separation was easier to achieve and less losses were observed. Typical repeatability achieved in this way with five sub-samples was: for TBT=0.36±0.06 mg Sn/kg (18% RSD) and for DBT=0.25±0.03 mg Sn/kg (12% RSD).

The analyses were then carried out according to the core procedure described at the beginning of the chapter and changing only the amount of dry wt sediment from 1.00 g to 0.50 g.

Direct consequence of this change was the doubling of the detection limits of butyltins in sediments. The new detection limits were: TBT=0.019 mg Sn/kg, DBT=0.024 mg Sn/kg and MBT=0.036 mg Sn/kg dry wt in sediments.

4.4.4 Efficiency of extraction

For the determination of TBT in sediment %RSD values of 2%-20% have been reported[185, 215]. It was thought that the repeatability (18% for TBT) could be improved. Work was therefore carried out to enhance the extraction of butyltins which was thought to be causing the relatively high deviation of the results.

In order to test the efficiency of the extraction three sequential extractions were carried out on each of the six sub-samples of dried sediment. Each extract was analysed separately for butyltins according to the previously described procedure.

	1st extraction		*2nd extraction*		*3rd extraction*		*Total*	
	TBT	**DBT**	**TBT**	**DBT**	**TBT**	**DBT**	**TBT**	**DBT**
Average (mg Sn/kg)	0.32	0.28	0.10	0.05	0.06	<0.024	0.48	0.33
St. Dev.	0.05	0.03	0.03	0.02	0.01	<0.024	0.05	0.04
%RSD	17	11	26	45	22	<0.024	21	13
% extracted	64%	85%	23%	15%	13%			

Table 13. TBT and DBT amounts measured after the 1st, 2nd and 3rd extraction of the dried sediment

There was a significant amount of TBT-compounds remaining in the sediment after the first extraction (Table 13). The incomplete extraction was attributed to the presence of slow-release TBT paint flakes in the sediment, leading to poor sub-sampling and poor extraction of the TBT compounds from the sediment. The extraction was more efficient for DBT and this can be explained by the fact that DBT is not contained in the paints, so it is more easily extractable.

In order to physically break the paint flakes to allow better homogenisation of the sediment, ball-milling of the sample was then assessed.

4.4.5 Effect of ball-milling on the extraction efficiency

Heterogeneity of highly TBT-contaminated samples is a well-known phenomenon attributed to the presence of paint flakes. Ball-milling of the sample is recommended by Smedes *et al*[115] as an intensive mixing technique to address this issue.

A batch of the dried sediment used in the previous experiment (Section 4.4.4) was ball-milled and then sub-sampled. Each of the six sub-samples was extracted sequentially three times with hexane and each extract was analysed separately for butyltins according to the procedure described in Section 4.3.4.

	1st extraction		***2nd extraction***		***3rd extraction***		***Total***	
	TBT	**DBT**	**TBT**	**DBT**	**TBT**	**DBT**	**TBT**	**DBT**
Average (mg Sn/kg)	0.25	0.19	0.16	0.06	0.07	<0.024	0.48	0.25
St. Dev.	0.10	0.06	0.06	0.02	0.04	<0.024	0.14	0.06
%RSD	41	31	35	26	56	<0.024	29	24
% extracted	51%	74%	33%	26%	16%			

Table 14. Amounts of butyltins measured after the 1st, 2nd and 3rd extraction of the ball-milled sediment

The average total amount of butyltins extracted did not increase after the milling, to the contrary the %RSD was slightly increased (Table 14).

Based on the above, ball-milling was not considered as a suitable pre-treatment for the sediment samples and it was not employed further.

4.5 Assessment of the extraction with dichloromethane

4.5.1 Introduction

An alternative approach for the analysis of butyltin-contaminated sediments was assessed. In the new approach DCM (dichloromethane) was the extraction solvent. The choice of DCM was made as it is known to be a “swelling solvent” which causes the polymer structures to open up. In studies on the effect of swelling solvents on paints, DCM was identified as a solvent causing high swelling.[216] During swelling, solvents diffuse into the paint structure and at the same time compounds in the paint leach out[217]. This would be the desirable effect for interaction between DCM and the TBT-containing paint flakes.

DCM with 0.04% w/v tropolone has been used by Gomez-Ariza *et al*[144] as the extraction solvent for butyl- and phenyl tins in sediments after acid treatment of the samples and followed by Grignard derivatisation, with up to 100% recoveries in spiked sediment samples. Tolosa and Readman[218] also reported >70% recoveries using DCM for the extraction of butyltins from water samples followed by derivatisation with sodium tetraethyl borate.

4.5.2 Method

In the new approach the extraction procedure was altered. DCM (5 mL) was left to swell and leach the potential paint flakes of the sediment overnight. Then, 2 mL of conc. HCl were added and the sediment was extracted by shaking for 45 min. The DCM layer was then isolated by centrifuging and transferred to a glass sample vial as described in Section 4.3.4.

4.5.3 Direct derivatisation

As stated before, some solvents can react with the Grignard reagent used in the derivatisation step. In such cases the extraction solvent has to be exchanged for a more suitable solvent.

In order to assess the suitability of DCM for the derivatisation step six sub-samples (0.5 g) of dry ball-milled sediment were extracted according to the new approach. After centrifugation the sediment remaining in the centrifuge tubes was stored for further analysis.

Three (samples 1-3) of the six sub-samples were derivatised directly in DCM and the rest of them (samples 4-6) were evaporated to dryness, using a dry nitrogen gas stream and re-dissolved in 5 mL hexane, before the derivatisation with the Grignard reagent. After addition of the Grignard reagent the rest of the core procedure, described in Section 4.3.4, was followed for all the sub-samples.

	Concentration (mg Sn/kg)		
	TBT	**DBT**	**MBT**
1-3 (DCM)	0.39±0.18	0.20±0.11	0.21±0.08
4-6 (Exchange with hexane)	0.47±0.19	0.29±0.07	0.27±0.08

Table 15. Yields for the direct derivatisation in DCM (samples 1-3) and for the derivatisation after the exchange for hexane (samples 4-6)

The peaks of the butyltins directly derivatised in DCM solutions (samples 1-3) had “shoulders”, making the quantification difficult. Also, exchange of the DCM for hexane before the derivatisation resulted in higher yields for the butyltins (Table 15), which was attributed to more efficient derivatisation.

It was therefore decided to use a solvent exchange step in analyses thereafter, after extraction with DCM.

4.5.4 Extraction efficiency

To compare the extraction efficiency of the new approach, with the hexane extraction efficiency of the previous experiments, two subsequent extractions were carried out on the sub-samples after the initial extraction with DCM. For each extraction 5 mL of DCM were added in the centrifuge tubes containing the sediment and the acid layer from the first extraction. After 1 hour in the wrist action shaker the sediment was centrifuged and the DCM layer was transferred to a sample vial and exchanged with hexane, after evaporation to dryness with nitrogen.

		Average (mg Sn/kg)	***St. Dev.***	***%RSD***	***% extracted***
1st	TBT	0.39	0.18	46	65%
	DBT	0.20	0.11	53	66%
	MBT	0.21	0.08	40	63%
2nd	TBT	0.16	0.07	44	27%
	DBT	0.08	0.03	36	29%
	MBT	0.10	0.02	22	32%
3rd	TBT	0.04	0.02	61	7%
	DBT	0.01	0.01	118	5%
	MBT	0.01	0.01	80	5%
Total	TBT	0.58	0.22	38	
	DBT	0.29	0.10	34	
	MBT	0.32	0.07	22	

Table 16. Amounts of butyltins measured after the 1st, 2nd and 3rd extraction with DCM

The DCM extraction resulted in 0.58±0.22 mg Sn/kg TBT, 0.29±0.10 mg Sn/kg DBT and 0.32±0.07 mg Sn/kg MBT measured (Table 16), after carrying out 3 extractions. The TBT amount slightly increased compared to the hexane extraction method (Tables 13-14). It should also be noted that by using this method MBT peaks appeared. MBT is considered to be of higher polarity than the TBT and DBT species. Its extraction by the DCM method was attributed to the higher polarity of DCM, when compared with the hexane.

The increase observed was within the analytical error and a conclusion regarding the extraction efficiency could not be drawn at that point. Further experiments were carried out in order to improve the experimental variability of the technique.

4.5.5 Evaporative TBT losses during DCM removal

The evaporation to dryness step was suspected of contributing significantly to the higher %RSD in the DCM extraction method. Up to 50% losses have been reported during such evaporation procedures.[214] For the evaporation step two solvents (DCM and hexane) were compared to assess the solvent-dependency of the recovery variability. The experiments were carried out using artificially spiked DCM or hexane solutions of butyltin chlorides. The analysis, after the addition of the Grignard reagent, was carried out as described in Section 4.3.4.

DCM

Eight TBTCl solutions (5 mL in DCM) spiked at two different concentrations (0.04 and 0.08 μg Sn/mL in DCM) were left to evaporate to dryness overnight in a fume cupboard.

The 5 mL spiked solutions in DCM were prepared from 4.8 mL of DCM and 0.2 mL of a 1 or 2 μg Sn/mL TBTCl solution in hexane. The natural evaporation to dryness was chosen in order to remove the uncertainty of the operation of the N_2 flow. It was suspected that the N_2 flow used for the evaporation during previous experiments was not well-controlled and might have been causing spillages of solution and therefore increased the variability of the results. After the evaporation 5 mL of hexane were added to each solution and then the derivatisation was carried out.

The recovery of TBT in the 0.04 μg Sn/mL solutions was essentially the same (52%±25%) as in the higher concentration solutions (53%±18%). This method of evaporation did not reduce the variability (48 %RSD and 35 %RSD respectively) to a satisfactory level. Part of the losses appeared to be due to degradation of TBT to DBT, as DBT peaks appeared despite the fact that no DBT had been added, possibly due to the fact that the glass vials were not refrigerated or protected from the sunlight during the evaporation.

Hexane

Hexane was also used to assess the evaporation recovery and variability. The experiment was carried out using spiked hexane solutions (5 mL) of 0.04 μg Sn/mL of TBTCl in hexane (prepared using 4.8 mL of hexane spiked with 0.2 μg Sn/mL of TBTCl in hexane). Five solutions were evaporated to dryness under N_2 flow (Samples 1-5) and five more were directly derivatised (Samples 6-10) to allow comparison.

The average recovery of the directly derivatised TBT was 96% with good repeatability (4% RSD), while for the solutions that had undergone evaporation, losses and poor repeatability were observed. The recovery for TBT in the samples 2-5 (sample 1 was discarded as an outlier) was 61%±4%, effectively the same as for solutions in DCM assessed in the previous experiment (53%±20% recovery for TBT). The solvent did not therefore appear to affect the recovery. The difference in the %RSD between the two solvents is attributed to the use of N_2 flow in the hexane solutions. The use of the constant flow instead of natural evaporation overnight had probably improved the repeatability and reduced the degradation of TBT to DBT. This was due to the significantly less time required for the completion of the evaporation and also the cooling effect of the nitrogen flow on the solution.

4.5.6 Effect of tropolone and glassware silanisation

The possibility of losses due to adsorption of the butyltin chlorides on the glassware surface was tested by carrying out the evaporation and analysis in silanised and in untreated glass sample vials. Tropolone was also added to all the solutions to reduce potential losses during evaporation, by converting the butyltins to less volatile forms. Complexing with ammonium pyrrolidine-dithiocarbamate (APDC) was also attempted, but quantification was impossible due to interfering peaks, attributed to sulfur species related to the APDC.

4.5.6.1 Experimental

The experiment involved eight 0.2% w/v tropolone in hexane solutions (4.8 mL) spiked with 0.02 mL of a 1 μg Sn/mL of butyltin chloride solution in hexane, four of which (Samples 5-8) were in silanised glass vials. The silanisation of the glassware (12 mL capacity sample vials) was carried out by immersing them into a 5% (v/v) chlorotrimethylsilane (Me_3SiCl) solution in hexane. The solutions were evaporated to dryness under N_2 flow and then 5 mL of 0.2% w/v tropolone in hexane was added to the vials to re-dissolve the butyltin chlorides prior to derivatisation.

4.5.6.2 Results and discussion

The recovery achieved for samples evaporated and analysed in the silanised vials was 82%±9% for TBT, 110%±6% for DBT and 114%±8% for MBT. For samples in the non-silanised vials the recovery was 69%±11% for TBT, 99%±11% for DBT and 105%±15% for MBT.

The >100% recovery yields for DBT and MBT were attributed to degradation (TBT→DBT→MBT). Carrying out the analysis in an iced water bath and protecting the glass vessels with aluminium foil on the outside to prevent sunlight are measures that could be evaluated for the minimisation of TBT losses.

The <100% yields for TBT can be attributed mainly to losses by evaporation, by adsorption on the glassware and by degradation to DBT. Tsunoi *et al*[136] found that treatment of the glassware with 1,1,1,3,3,3-hexamethyldisilazane increased the recovery for butyltins slightly. The increase was attributed by Tsunoi *et al*[136] to suppression of the adsorption of butyltins on the glass surface. Even though it is considered beneficial to silanise the glassware of the analysis and to carry out the extraction in a solvent-tropolone mixture, the increase in the recovery was within the analytical error. The silanisation was therefore not used.

4.5.7 Conclusions on the variability of the DCM extraction method

Carrying out the extraction step with DCM brought about the need for a solvent exchange step. The change of DCM with hexane was proven necessary in order to avoid reaction of the derivatising agent (Grignard reagent) with the solvent. As DCM and hexane are partly miscible it was decided to evaporate the solvent and re-dissolve the butyltins in hexane before further analysis. It was then found that the variability between sub-samples increased which was attributed to losses during evaporation. The experiments carried out to alleviate the problem showed that the DCM method would not improve the overall yield (Table 17), due to evaporative losses and degradation of butyltins during the evaporation step.

	% TBT recovery	**% RSD of TBT recovery**
Overnight evaporation (DCM)	53±20	32 (n=10)
N_2 evaporation (hexane)	61±4	14 (n=4)
N_2 evaporation, tropolone (hexane)	69±11	16 (n=4)
N_2 evaporation, tropolone and silanised (hexane)	82±9	11 (n=4)
Without evaporation (hexane)	96±4	4 (n=4)

Table 17. Summarised results of the evaporation experiments for TBTCl

It was therefore decided to proceed to subsequent measurements adopting the acidic extraction with hexane/tropolone and direct derivatisation.

4.6 Accuracy of the measurements of butyltins in sediments

The accuracy of the method for measuring butyltins in sediments was assessed using the marine sediment reference material PACS-2 from the National Research Council of Canada (NRCC).

It was certified in 2000 for TBT (0.98±0.13 mg Sn/kg) and DBT (1.09±0.15 mg Sn/kg) and with an indicative value only given for MBT (0.45±0.05 mg Sn/kg). The certified values for butyltins were updated by NRCC in 2004. The new values were 0.890±0.105 mg Sn/kg for TBT, 1.047±0.064 mg Sn/kg for DBT and only an information value of 0.6 mg Sn/kg was given for MBT. The certified values are based on the results of determinations by at least two independent methods of analysis. The uncertainties represent 95% confidence limits for an individual sub-sample of 250 mg or greater[219]. The expiry date of the reference material was set at December 2008 for butyltins. According to NRCC[219], PACS-2 was collected from the harbour of Esquimalt in British Columbia, it was freeze dried and screened with a sieve of 125 μm mesh. It was then blended, bottled and radiation sterilised with at least 2.5 Mrad to minimise any effects from biological activity. As the sediment contains sea salt, it is believed to have picked up moisture after the freeze drying and it is recommended to be dried until constant weight at 105 °C before analysis.

Sub-samples of PACS-2 were measured to assess the accuracy of the determination method used for butyltins in sediments in this work.

4.6.1 Experimental

Three 0.5 g sub-samples of PACS-2 were analysed according to the procedure as it had evolved from Section 4.3.4. Analysis of deionised water was used as blank analysis. The sediment sub-samples were extracted in Teflon centrifuge tubes, initially for 1 hour in a Griffin wrist action shaker with 2 mL of deionised water, 2 mL conc. HCl and 5 mL of a 0.1% w/v tropolone in hexane solution. After the first extraction the hexane layer was isolated by centrifugation at 4000 xg for 10 min and then it was removed from the centrifuge tubes and placed in glass sample vials. Fresh hexane/tropolone solution of the same concentration as before was added (5 mL) and this extraction step was repeated one more time, to a total of three extractions. The 15 mL of hexane layer containing the butyltins was dried with Na_2SO_4 (anhyd.) and then transferred to a new glass vial with PTFE lined screw cap, where 1 mL of hexylmagnesium bromide was added to each sample. The solutions were shaken and left to react for 20 min with periodical shaking of the vials. At the end of the 20 min the reaction was quenched with 2 mL conc. HCl, 2 mL of deionised water were also added and the solutions were shaken. The two phases were left to separate and the aqueous layer was discarded. The hexane layer containing the hexylated butyltins was dried with Na_2SO_4 (anhyd.) and placed in 20 mL volumetric flasks and then made up to 20.0 mL volume with pure hexane. A small volume of each sample was transferred to suitable vials and measured with GC-PFPD.

4.6.2 Results and discussion

The amount of TBT measured was 1.019±0.263 mg Sn/kg and the amount of DBT was 0.774±0.307 mg Sn/kg. No MBT was detected. The values for TBT and DBT fell within the experimental error of the values given for PACS-2, therefore for these butyltins the analysis was considered accurate. But regarding MBT, the procedure used in this experiment might result in underestimation of the amount of MBT present in the sediment. The underestimation of MBT may be attributed to incomplete extraction or derivatisation. Perhaps a longer time should be allowed for the derivatisation reaction.

4.7 Conclusions on the determination method for butyltins in sediments

The method for the determination of butyltins in sediments used in this work was adapted mainly from the work of Unger[202]. It was developed to match the requirements and resources available for this project. Several experiments were carried out to explore alternative steps to improve the recovery and repeatability in the analysis of sediment samples. Two drying techniques (air- and oven-drying) were compared and found to be equivalent. Ball-milling of the dry sediment was evaluated as a mixing technique but it was not found to be advantageous. Three sequential extractions were found to be necessary to efficiently extract the TBT contained in the particular sediment analysed (collected from a boatyard on the River Itchen in Southampton, UK). Extraction with DCM followed by solvent exchange with hexane before derivatisation was assessed using the boatyard sediment and spiked solutions but it was not found to improve the overall recovery and repeatability.

According to the external calibration based on hexylated butyltin compounds (Section 4.2.4) and taking into account the changes made to the procedure (Section 4.4) the projected detection limits (3 x noise) for the analysis of 0.5 g dry wt sediment and a final extract volume of 20 mL were: TBT=0.037 mg/kg, DBT=0.047 mg/kg and MBT=0.073 mg/kg dry wt (as Sn) in sediments. The detection limits achieved by Unger[202] in sediment samples are not given and no published detection limits were found from work employing acidic hexane/tropolone extraction of butyltins from sediments followed by hexylation or other Grignard derivatisation and measurement with GC-PFPD. Gomez-Ariza *et al*[144] reported detection limits of 0.00061 mg/kg for TBT, 0.00075 mg/kg for DBT and 0.00076 mg/kg for MBT as Sn, after acid leaching of 20 g of wet sediment, DCM/tropolone extraction, pentylation, concentration of the extract to 0.2 or 0.5 mL and measurement with GC-FPD with injection of 5-10 μL. Konieczka *et al*[220] reported detection limit of 0.0015 mg Sn/kg for TBT using hexane/tropolone extraction under pressure for 1 g of dry sediment, Grignard derivatisation, concentration to 0.3 mL and measurement with isotope dilution GC-MS with injection of 2 μL. Felizzola *et al*[221] reported detection limits of 0.0054 mg/kg TBT, 0.0002 mg/kg DBT and 0.0021 mg/kg MBT as Sn, when analysing 2 g dry sediment extracted with toluene/AcOH/sonication and APDC, pentylation, concentration to 1 mL and GC-PFPD measurement. These detection limits are lower than those achieved in the current study because of the pre-concentration achieved by analysing a larger portion of sediment, then concentrating the extract down to only 0.2-1 mL and injecting up to 10 μL.

The detection levels achieved in the present study were below the OSPAR Commission[42] action levels for dredged materials, which are set to 1.0-0.1 mg/kg for TBT. Using this method it would be therefore possible to establish if the OSPAR Commission criteria are met or not, after a clean up treatment has been applied to TBT-contaminated sediments. The benefits, therefore, of using this technique is that a satisfactory detection limit is achieved (more than six times below 0.1 mg/kg) without overnight extraction or time-consuming concentration steps, so that many samples can be quickly analysed.

The accuracy of the technique was tested by the measurement of PACS-2 harbour sediment certified for TBT and DBT. The method developed during this project gave values for TBT and DBT within the margins given for PACS-2. MBT was not detected, while the indicative value given for PACS-2 was 0.6 mg Sn/kg. More work may be therefore necessary for the efficient recovery of MBT.

Overall, the method developed for the determination of butyltins in sediments was considered satisfactory and it was used for any such experiments thereafter in this work.

4.8 Assessment of a screening technique for TBT contamination[◊]

X-Ray Fluorescence (XRF) analysis for Sn was carried out on sediment samples in order to assess this technique as a preliminary site investigation tool for TBT contamination. It was considered to be suitable as it requires only a fast, facile and non-destructive preparation of the sample to be analysed. It could be useful for the identification of TBT hot spots, especially in highly contaminated areas (boatyards, harbours) of low background Sn levels in sediments. As the detection limit for Sn using the XRF instrument available was around 1 mg/kg, which is also the maximum allowed limit for TBT in dredged materials according to OSPAR Commission[42], it would be possible to differentiate between the contaminated and non-contaminated areas. This could be done within a very short period of time as part of the initial site investigation resulting in better understanding of the site and potential savings.

4.8.1 Experimental

Twenty-nine sediment samples were collected on April 2008 at low tide, from a boatyard on the River Itchen in Southampton, UK. Twenty-six were collected around the boatyard as shown in Figure 22 and three were collected further upstream from the area of St Deny's Road bridge.

The sediment samples were collected from the surface (top 5-10 cm) of the riverbed and were placed in glass jars. They were then transferred to the lab and were immediately refrigerated and then freeze dried and sieved to remove any stones.

[◊] work carried out with A. Alrashdi (PhD student) at the University of Southampton

Figure 22. Location of sampling points 1-26. Samples 27-29 were collected upstream (location not shown on the map)

For the measurement of the TBT content sub-samples (0.5 g) of the freeze-dried sediment samples were analysed according to the procedure described in Section 4.6.1.

For the measurement of the Sn content the preparation of the sample involved ball-milling and pelletising the dried samples using 40 mm diameter aluminium cups. After the preparation, the pellets were placed in the XRF. Calibration employed the tin-certified reference material PACS-2. The 2σ detection limit for Sn was approximately 1-1.5 mg/kg. The instrument was a Philips MagiXPro fully automatic, sequential, wavelength dispersive X-Ray fluorescence spectrometer with a 4 KW maximum output operating with a Rh target tube at a maximum of 60 KV maximum accelerating voltage with a collimator (LiF, 150 μm) at a 19.8510° angle. For the analysis the Ka line of Sn was used. Measurements were taken for 100s on the peak and 80s on the background.

4.8.2 Results and discussion

The results of the analysis for total Sn and TBT are shown in Table 18.

Sample	**Concentration (mg Sn/kg dry weight)**	
	Sn	**TBT**
1	78	6.7
2	190	4.5
3	208	5.2
4	29	0.42
5	38	2.4
6	105	5.0
7	62	3.5
8	33	0.88
9	32	0.65
10	32	0.73
11	39	0.29
12	30	0.53
13	28	0.88
14	28	1.0
15	57	3.2
16	29	1.4
17	29	0.74
18	26	0.71
19	28	0.78
20	28	0.52
21	27	0.84
22	35	0.76
23	27	0.65
24	43	0.52
25	28	0.59
26	41	0.29
27	67	0.63
28	71	0.47
29	94	0.53

Table 18. Concentration of total Sn in the 29 different boatyard samples (values >40 mg/kg for Sn and >1 mg/kg for TBT are highlighted)

The typical levels of Sn in sediments are 2-3 mg/kg[9] up to 8 mg/kg[222]. Levels up to 1000 mg/kg[9] have been observed in Cornwall, due to tin mineralisation, but this is a very uncommon phenomenon and such locations are well-known. It appears that the samples tested here all had Sn concentrations of >27 mg/kg dry weight so no uncontaminated area (<8 mg/kg) was found.

From the 29 samples tested, only 11 had a Sn concentration > 40 mg/kg. Six of those samples also had a high TBT content (>1.0 mg Sn/kg). The locations of high Sn concentration appear to be random and are not proportional to the distance from the slipway, the boats or the land. Another difficulty is to establish if high Sn levels indicate TBT contamination. From the nine highly TBT-contaminated samples (concentration >1.0

mg Sn/kg), six are on areas that are Sn-contaminated as well. In five other highly Sn-contaminated areas (Samples 24, 25, 27, 28 and 29) the TBT contamination is below the 1 mg/kg threshold and in three cases of highly TBT-contaminated samples (Samples 5, 14 and 16) the Sn contamination is low. It is therefore believed that Sn hot spots are created due to a combination of random sources. Contamination from other materials (bronze where Sn is used) that accumulate in estuaries, ports and harbours could be causing localised high tin levels.

4.8.3 Conclusion

XRF analysis, of Sn alone, does not appear to accurately determine the areas where highly TBT-contaminated sediment is found. Further work is necessary to determine whether a correlation can be found when the values other metals present (given in the XRF analysis without any added cost or time) are considered.

5 Determination of butyltin compounds in water

5.1 Introduction

The success of a remediation approach applied to a contaminated waste is usually judged by equilibrating the treated waste with water, under fixed conditions and measuring the butyltins in the resulting leachate.

For the measurement of butyltins in the water recovered from the leaching tests (leachates), it is necessary to use a method that will be quick, inexpensive and also with a high throughput as many samples to be measured would be generated during screening of different methods/additives. Another important requirement was the need for a low detection limit. Even though there is not a legislative limit for the concentration of TBT in leachates at this time, it was thought that for the purpose of this work a clean leachate should have a TBT concentration within one order of magnitude compared to the EQS for waters which is 2-20 ng/L[53] for coastal and estuarine and freshwater respectively.

Three different approaches to the determination of butyltin compounds in water were therefore evaluated: 1) hydride generation with hexane extraction, 2) a new procedure that involved solid phase extraction followed by *in situ* ethylation with $NaBEt_4$ and 3) ethylation with $NaBEt_4$ and liquid-liquid extraction into hexane. In all cases the amount of organotins in the extract was detected using GC-PFPD as in Chapter 4.

5.1.1 Materials

Deionised water (>5 MΩ-cm at 25°C) was produced using an ELGA water purifier (model Option 4). Tri(n-butyl)tin chloride (TBTCl) was purchased from BDH (UK). Di(n-butyl)tin dichloride ($DBTCl_2$, 96%), mono(n-butyl)tin trichloride ($MBTCl_3$, 95%), TeBT (98%) and tri(n-butyl)tin hydride (TBTH, 97%) were purchased from Aldrich (UK). Tri(n-propyl)tin chloride (TPrTCl, 95%) was purchased from Alfa Aesar (UK) and tri(n-pentyl)tin chloride (TPeTCl, 95%) from ABCR (Germany). $NaBH_4$ (98%) was purchased from Avocado (UK). Ethyl acetate (Super purity grade) from Romil (UK) or from Fisher (UK), hydrochloric acid (analytical reagent grade), hexane (HPLC grade), methanol (HPLC grade), acetic acid (analytical reagent grade) and sodium acetate anhydrous were purchased from Fisher (UK). Non-end capped 500mg/10mL Isolute C_{18} silica cartridges (61 μm particle diameter, 54 Å pore size) were purchased from Kinesis (UK). $NaBEt_4$ (97%) was purchased from Acros Organics (UK) and was kept in a desiccator initially and in a glove box under nitrogen later to prevent its degradation by atmospheric moisture. The 0.1 M pH 3.3 buffer was prepared with 0.51 g AcOH in 100 mL of water and addition of AcONa until pH 3.3. The 1 M pH5 buffer solution was prepared by mixing 21.4 g AcONa with pure acetic acid until pH 5 in 250 mL deionised water. Teflon FEP centrifuge tubes with Tefzel ETFE screw closures were described in Section 4.3.2. The seawater used was collected on May 2007 from Southampton Water, its salinity was 33.8‰ and it was filtered using a glass fibre filter (MF300, Fisher).

5.1.2 Preparation of standards

Standard solutions of TBTH, TBTCl, DBTCl, MBTCl, TPrTCl and TeBT were prepared from the commercially available organotin compounds (assuming 100% purity). Stock solutions containing 1000 or 650 µg Sn/mL were prepared in hexane or MeOH and they were kept in the dark, refrigerated at 4 ºC.

Standard solutions of lower concentrations were prepared weekly or daily (concentrations <1 µg Sn/mL) by dilution of the stock solutions. If the solutions were to be used for spiking into water, they were diluted in MeOH.

5.2 Hydride generation

Tributyltin reacts in aqueous solution with $NaBH_4$ to produce its corresponding hydride that can be extracted into hexane.

$$Bu_3\,SnCl + BH_4^- + 3H_2O \xrightarrow{\text{pH 3.3}} Bu_3SnH + B(OH)_3 + 3H_2 + Cl^-$$

Unlike Grignard derivatisation methods, $NaBH_4$ can be used in aqueous media and therefore requires fewer steps.

5.2.1 Method

The method initially used in this work has been described elsewhere[158]. 25 mL of water was placed in FEP centrifuge tubes and was spiked with TBTCl (the amount varied) and TeBT (internal standard). 5 mL of acetic acid-sodium acetate buffer (pH 3.3, 0.1 M) were added, followed by 2 mL of hexane and 1 mL of a 3 % (w/v) aqueous solution of $NaBH_4$.

The solution was then shaken vigorously using a Griffin wrist action shaker for 15 min. The layers were left to separate and the top (hexane) layer was removed using a Pasteur pipette and analysed by GC-PFPD.

5.2.2 Chromatography of tributyltin hydride

5.2.2.1 Introduction

During initial experiments in the current study, employing the chromatographic conditions described in Section 4.2, it was suspected that TBT, as its hydride, was degrading over time whilst in aqueous solution or condensing or degrading in the injector due to an unsuitable initial PTV temperature. These possibilities were explored further.

5.2.2.2 Hydride stability

5.2.2.2.1 Experimental

Standard solutions of TBTH (0.125 µg Sn/mL) were prepared by diluting a stock TBTH solution (625 µg Sn/mL) in hexane immediately before each injection (to minimise any degradation of TBTH). One of the standard solutions (0.125 µg as Sn/mL) was re-measured after 5 hours, to test the stability of the TBTH in solution over time.

5.2.2.2.2 Results and discussion

It appeared that the first two injections conditioned the system (Figure 23) and then the GC signal stabilised for the subsequent injections (solutions 3-6).

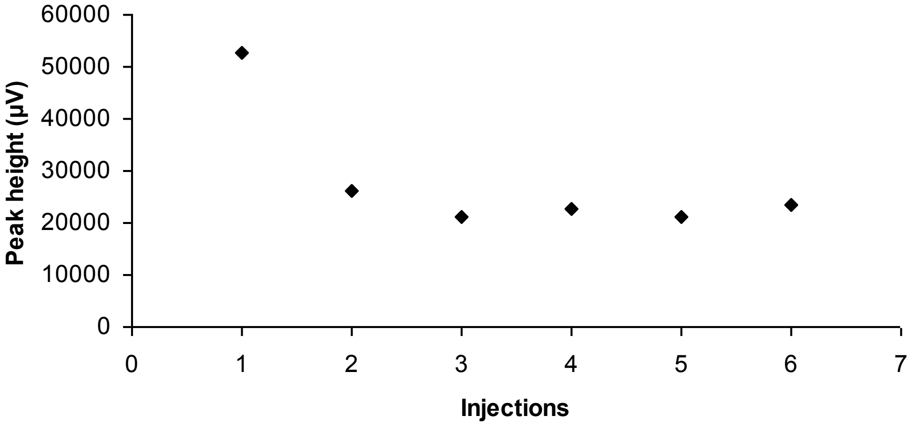


Figure 23. TBTH peak height from freshly prepared 0.125 µg/mL solutions

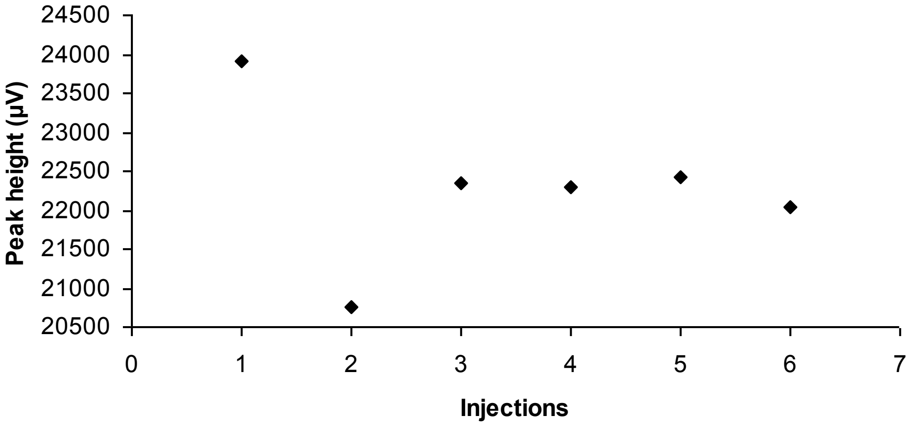


Figure 24. Six injections of a 0.125 µg/mL solution of TBTH re-measured 5 hours after its preparation

The first two injections of the standard solution again conditioned the system (Figure 24) and were discarded for the subsequent calculations.

Statistical comparison (t-test, 95% confidence level) of the means of the peak heights of TBTH standard solutions 3-6, 22094±1081 µV shown in Figure 23, and injections 3-6, 22299±1007 µV shown in Figure 24, showed that there is no significant difference.

The TBTH was therefore considered to be stable in hexane solution at a concentration of 0.125 µg Sn/mL in hexane. The role of the injector temperature was explored next.

5.2.2.3 Injector temperature

5.2.2.3.1 Experimental

To test for decomposition or condensation in the injector a 0.3125 µg Sn/mL TBTH and TeBT solution in hexane was measured at 7 different initial PTV temperatures; 100, 130, 150, 170, 190, 220 and 250°C.

After maintaining the initial temperature for 1 min, the temperature was increased at 40°C/min to 250°C. The 250°C temperature was maintained for 4-5 minutes and then dropped to 150°C at 40°C/min. This temperature was maintained until the end of the run. In the case of initial temperature 250°C the programme was isothermal. Four injections in total were carried out in a random temperature order.

5.2.2.3.2 Results and discussion

The highest signal was achieved using 130-160 °C as the starting PTV temperature (Figure 25).

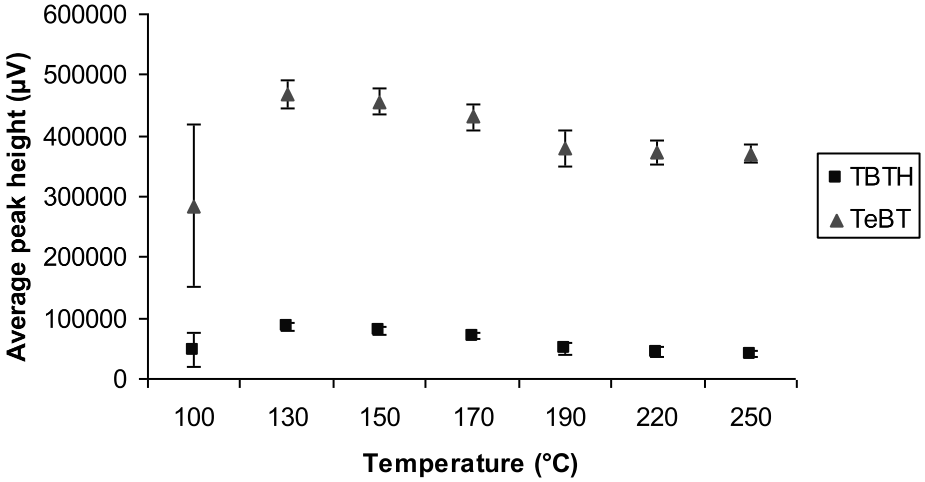


Figure 25. TBTH and TeBT peak height from standard solutions measured with 7 different starting PTV temperatures

During this experiment it was observed that the response to TBTH was approximately four to five times less sensitive than to TeBT. An example of the chromatography achieved can be seen in Figure 26. The difference of peak heights of TBTH and TeBT in a standard hexane solution containing 0.125 μg Sn/mL TBTH and TeBT is visible. An unknown compound also appeared which had the characteristic peak tailing of tin compounds. It could therefore be an impurity of the either TeBT or TBTH with a higher boiling point than TeBT.

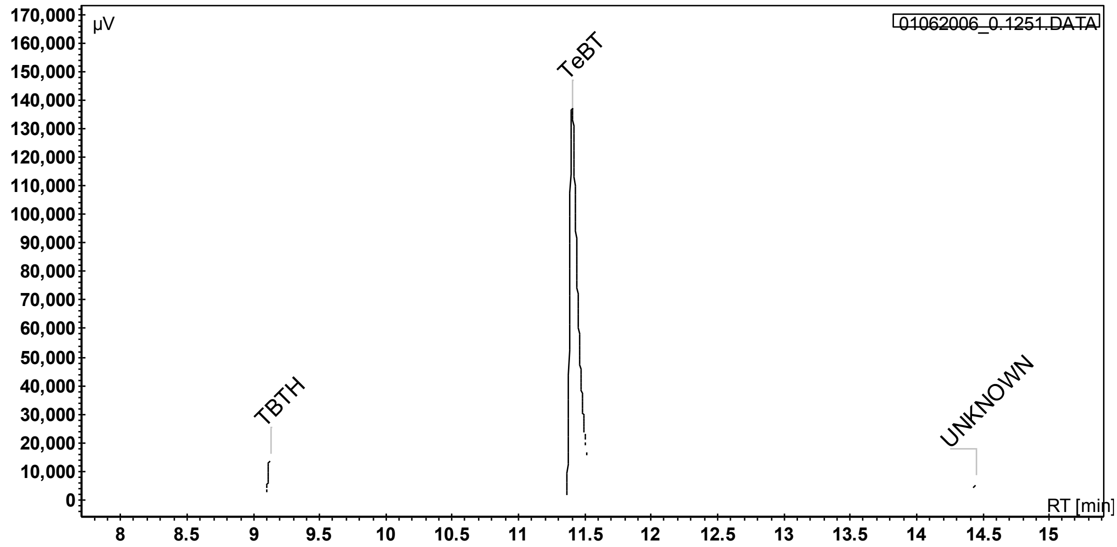


Figure 26. Partial chromatogram from the TBTH and TeBT standard in hexane (0.125 µg Sn/mL)

5.2.2.3.3 Conclusion

The starting temperature of the PTV was left at 150 °C as the highest signal was detected when temperatures of 130-160 °C were used. Further experiments were carried out to explore the difference between the response for TBTH and TeBT.

5.2.2.4 Detector response for TBT hydride

5.2.2.4.1 Experimental

In order to investigate the response-to-concentration relationship further injections of standard solutions of TBTH and TeBT over the range of 0.025-0.625 µg Sn/mL in hexane were carried out.

5.2.2.4.2 Results and discussion

The calibration curves produced showed that response from TBTH was non-linear but fitted very well (R^2= 0.9996) to the power equation $y=502688x^{1.6661}$ (Figure 27).

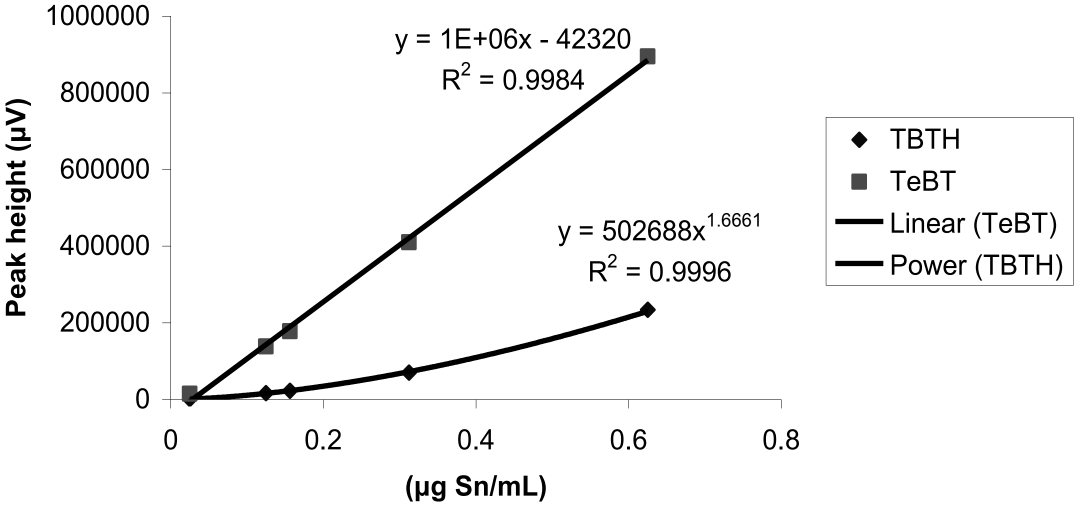


Figure 27. Calibration curves for TBTH and TeBT (0.025-0.625 µg Sn/mL)

The response of the detector (R) to TBTH followed the equation $R=a[Sn]^{1.666}$. A slight deviation from linearity has been reported by Aue and Flinn[223] for some organotin compounds using a filterless FPD system (Figure 28).

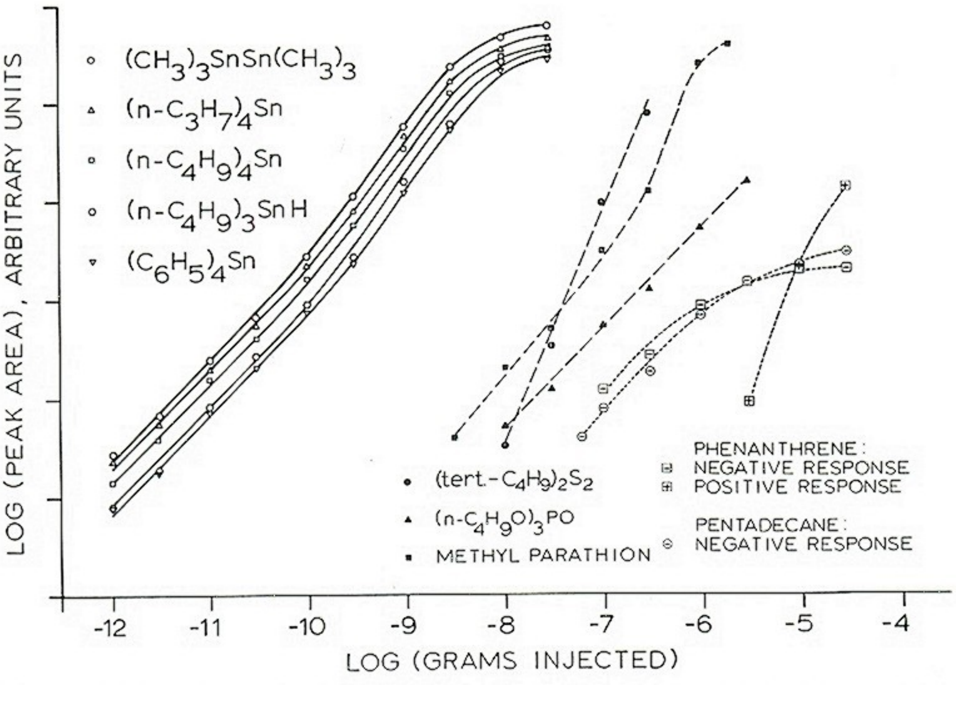


Figure 28. Calibration curve of standard solutions of several organotin compounds, sulphur and phosphorus compounds, phenanthrene and pentacene measured by a filterless FPD system (from Ref[223] with kind permission from Elsevier)

Aue and Flinn reported a linear range followed by a slightly non-linear behaviour of the organotins before the saturation of the detector. Compared to the graph by Aue and Flinn

(Figure 28), the log-log graph produced from the measurements in the current work (Figure 29) shows a narrower mass range of material injected, which is probably the area where the response is reported by Aue and Flinn to change from linear to slightly non-linear.

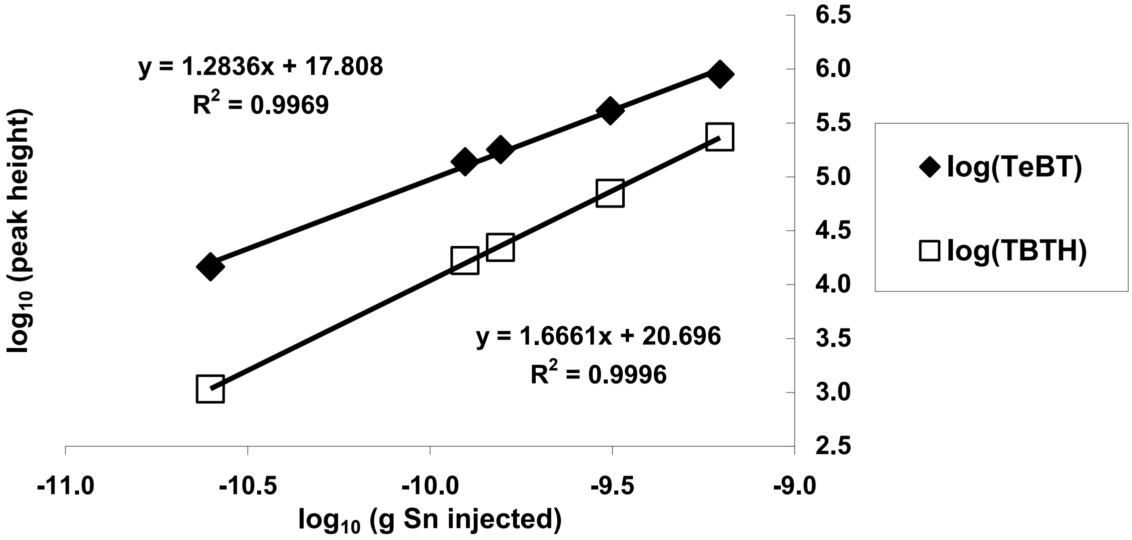


Figure 29. Log-log calibration graph of TeBT and TBTH obtained from standard solutions (0.025-0.625 μg Sn/mL with 1 μL injections)

In the current work, TBTH has a clearly non-linear behaviour, as the slope of the equation in the log-log graph is 1.6661. TeBT also exhibits a slight deviation from linearity, as the slope of the equation in the same graph is 1.2836. In the study by Aue and Flinn, where a filterless system with a bandpass of 300-650 nm was used, the non-linear behaviour appears milder. It is possible that the exponential behaviour of the emission of the tin species, observed within the bandpass of the BG12 filter (340-460 nm) used in the current study, was counteracted by another tin species emitting at a higher wavelength, for which the detector has a linear response, and reduced the overall effect observed in the study by Aue and Flinn.

An explanation for the exponential behaviour could be found when the reasons for the known exponential behaviour of other compounds are examined. The response to sulfur (an element for which the GC-PFPD has been commonly used) is widely known to be quadratic[178] ($R=a[S]^2$) or almost quadratic[224] for FPD systems and pure quadratic[212] for PFPD, when the BG12 filter is used. This exponential response is attributed to an excited state of dimeric species of sulphur (S_2*) emitting. Some of the mechanisms suggested for the creation of S_2* involve the recombination of sulphur atoms or the recombination activation of S_2 by the recombination of hydrogen atoms[225, 226]:

$S + S \rightarrow S_2^*$

$H + H + S_2 \rightarrow S_2^* + H_2$

The injection of TBTH may promote the creation of Sn_2 species that are then excited and emit within the bandpass of the BG12 filter (340-460 nm), used in the current study, similarly to the S_2^* species.

The most common species produced during combustion, other than those containing carbon, are widely regarded to be oxygen, hydrogen, HOO* and HO* free radicals.[227, 228] The Bu_3SnH is likely to be attacked by a radical in the flame. A possible mechanism for the creation of a dimeric tin species, when Bu_3SnH is injected, would be the conversion of Bu_3SnH to R_3SnH (oxidized form) and to R_3SnOH in the oxidative flame and then to species related to $R_3Sn\text{-}SnR_3$. Such reactions can occur when a triorganotin reacts with an oxide[60]. The first step of the mechanism of such a reaction is believed to be an electrophilic attack of the hydride hydrogen to the oxygen atom of the oxide. In the case of R_3SnH a possible reaction of that type would be:

$R_3SnH + R_3SnOH \rightarrow R_3Sn\text{-}SnR_3 + H_2O$

Also, a base-catalysed elimination of hydrogen from monohydrides has been known to assist the formation of tin-tin bonds[60]:

$$2R_3SnH \xrightarrow{\text{base}} R_3SnSnR_3 + H_2$$

In the flame, the HO* radicals could be the necessary catalyst for the above reaction.

The degradation of the organo di-tin compounds in the flame may proceed with two different mechanisms. One is the degradation of the alkyl groups attached to tin by HO* attack on the carbon atoms according to the reactions proposed in the Chapter 2 (Schemes 1-3) for the UV/Fe(III), the TiO_2-photoassisted and the ozone degradation of TBT by Mailhot *et al*[67], Navio *et al*[66] and Schafran *et al*[70] respectively. The source of HO* is different here (flame reactions) but the same TBT-degrading reactions may apply. Another mechanism is the supply of energy by the flame to cause homolytic fission of the Sn-C, or potentially the Sn-Sn bond, resulting eventually in de-alkylated tin:

$$R_3SnSnR_3 \longrightarrow \;....\; \longrightarrow \text{Sn-Sn}$$

$Bu_3SnQ \longrightarrow Bu_2SnQ_2 \longrightarrow BuSnQ_3 \longrightarrow SnQ_4$

The bond energy for the bonds in $Bu_3SnSnBu_3$ is not known but similar organotins involving other alkyl groups could be examined to determine whether cleavage of the Sn-Sn bond would be favoured over the Sn-C bond. In Ph_3Sn-$SnPh_3$ the Sn-Sn bond dissociation energy is 30±15 kcal/mol and the mean bond dissociation energy for Sn-Ph is similar (54 kcal/mol).[60] In Me_3Sn-$SnMe_3$ the Sn-Sn bond dissociation energy is 63-76 kcal/mol while the mean bond dissociation energy for Sn-Me is 50-52 kcal/mol.[60] Whether the Sn-Sn bond will be cleaved before the debutylation or not could be the factor that determines if the final product is in the form of Sn or Sn-Sn and eventually the linear or not response of the detector. If, under the flame conditions, the Sn-Bu bond is cleaved at a slightly higher rate than the Sn-Sn bond then the debutylation reactions would result in a Sn_2 species which could then be excited to a Sn_2^* species with a quadratic detector response. The quadratic response might then be converted to the $R=a[Sn]^{1.666}$ response, observed in this work, by combining the emission of Sn-C or Sn-O species with that of the Sn_2.

A clearly exponential response has not been reported, as yet. That might be attributed to the fact that from the studies measuring TBTH very few studies have used an FPD[156, 158, 229] and none was found to have used a PFPD. One study[229] among them used a 394 nm interference filter but a hydrogen-rich, reducing flame was used and not an oxygen-rich flame as in the present work. In the other studies the filter used was for emissions above 600 nm in order to measure the emission at 610 nm attributed to the emission of SnH[208], favoured in reducing conditions in the flame. The use of the 610 nm emission of organotin compounds was preferred with the older type of photometric detector (FPD) where the interferences from sulphur co-emitting with the organotins within the BG12 bandwidth could not be isolated, a problem that the PFPD appears to solve in most cases. Perhaps, in hydrogen-rich flames the dimerisation of Bu_3Sn^* is not favoured and a different tin species is emitting (SnH) for which the detector has a linear response.

Another reason for the lack of reference to the exponential response of the photometric detectors with organotins might be that the exponential behaviour could only be observed if a large enough range of concentrations was plotted. Otherwise, the effect might be missed or misinterpreted as linear at very low concentrations and over a short concentration range (1-100 pg Sn injected).

As mentioned in Section 5.2.2.3, the sensitivity observed in the current study for TBTH was always much poorer than that achieved from the TeBT, which indicates that the emission from the dimeric tin species is weaker than the Sn-C bond emission typically emitting within the BG12 bandpass.

Taking into account the above, if the method were to be found to be suitable for routine use, calibration of the TBTH response would need to be through a log-log calibration.

5.2.3 Optimisation of the analytical procedure

5.2.3.1 Investigation on the role of buffering

Jiang and Liu reported that buffering with pH 3.3 was the optimum[229] for the extraction of TBT from water followed by a hydride generation derivatisation reaction and headspace SPME on a fused silica fibre pre-treated with HF acid. An experiment to confirm the need for buffering in the present study was carried out.

5.2.3.1.1 Experimental

Three spiked water samples were prepared from 25 mL deionised water (pH~7) and 20 µL from a 62.5 µg Sn/mL TBTCl solution in hexane. The samples were extracted in glass separating funnels with the addition of 2 mL of 0.125 µg Sn/mL TeBT (IS) in hexane and 1 mL of 3% (w/v) $NaBH_4$ solution in water. The previously described analytical procedure (Section 5.2.1) was followed for Samples 2 and 3 but without any addition of buffer solution for Sample 1. Due to leakage problems with the FEP centrifuge tubes, they were replaced by glass separating funnels that were shaken violently by hand for 60 seconds for the derivatisation/extraction step.

5.2.3.1.2 Results and discussion

The yields of the analysed solution without buffering (87% recovery) was much higher than with buffering (38% recovery on average). It should be noted that samples 2 and 3 (with buffering) were analysed after the completion of the analysis of the previous sample. The aqueous solution of the $NaBH_4$ was prepared at the beginning of the analysis and remained in solution for 1-2 hours before being used for the final sample. Even though the difference in the yield was initially attributed to unsuitable buffering it was later discovered that it was the effect of the degradation of reagent while in solution.

There is not much data in the literature regarding TBT hydride generation carried out without buffering. In one study, comparison of the results from analyses of seawater samples where the pH was adjusted to pH 6.3 or pH 9.4 did not appear significantly different than when the seawater samples were left without any pH adjustment.[158] The pH buffering to pH 3.3 was probably important in water samples that have been acidified to pH 2 for preservation, as fast decomposition of the derivatising reagent ($NaBH_4$) is predicted to occur under such conditions. In the present work, the samples were prepared by spiking deionised water (pH 7). It was concluded that the need for buffering was not as great when spiked deionised water samples were analysed since at pH 7 a large proportion of the TBT is in its ionic (hydrophilic) form (TBT pKa=6.3[29]).

5.2.3.2 Decomposition of the $NaBH_4$

Six spiked water samples were analysed and measured sequentially, as described in 5.2.1. The spiked water samples were prepared from deionised water (pH~7) to which was added 20 µL of a 62.5 µg Sn/mL TBTCl solution in MeOH. The samples were extracted in glass separating funnels after the addition of 2 mL of 0.625 µg Sn/mL TeBT (IS) in hexane. 1 mL of an aqueous 3% (w/v) $NaBH_4$ solution was added to samples 1-5 over a time period of approximately 120 min. 0.03 g of $NaBH_4$ was added to sample 6 in solid form.

The TBT yield increased from 52% to 74% by the addition of the reagent in solid form, instead of aqueous solution (Figure 30).

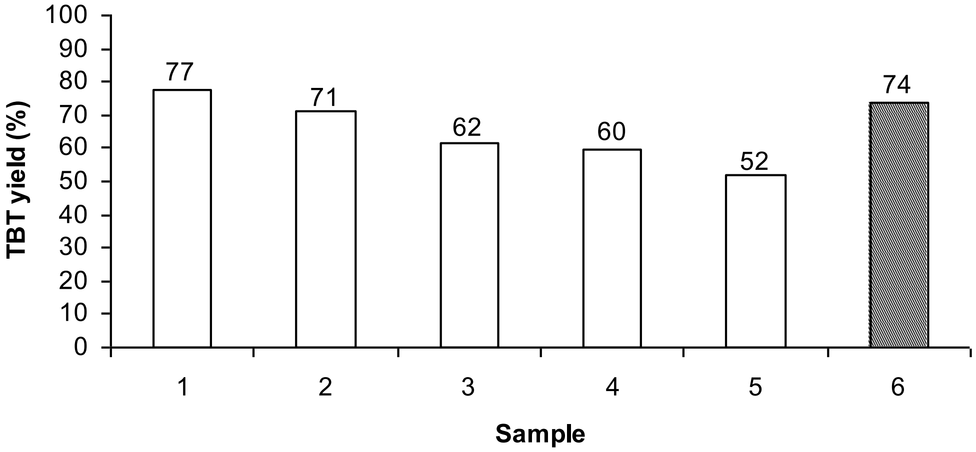


Figure 30. TBTH spiked water samples extracted sequentially without pH buffering. Solid $NaBH_4$ instead of aqueous solution was added to Sample 6

It appeared that the reagent was degrading in aqueous solution and it should therefore either be added as a solid or within a few minutes of the preparation of its solution.

5.2.3.3 Repeatability and accuracy

5.2.3.3.1 Experimental

To test the repeatability of the hydride generation procedure incorporating all the new changes (glass separating funnels instead of Teflon centrifuge tubes, without pH buffering and adding solid $NaBH_4$) six spiked 25 mL water samples containing 0.125 µg Sn/mL TBTCl were derivatised with 0.03 g $NaBH_4$ each and extracted with 2 mL of 0.125 µg/mL TeBT solution (IS) in hexane according to the procedure described in Section 5.2.1. Quantification was carried out using standard solutions of 0.125 µg Sn/mL TBTH and TeBT as external calibrants.

5.2.3.3.2 Results and discussion

The TBTH yield was 119±13%, after the correction with the IS, with a %RSD of 12%. The repeatability was considered satisfactory and was similar to that which had been previously reported for TBT (11%), when replicate extractions of the same sample containing 1.0 µg/L TBT were carried out with this method[158].

The estimated limit of detection (based on 3 x noise) for TBT was 1.5 pg injected (as Sn) or approximately 300 ng/L for a 25 mL water sample (as Sn). This limit of detection was achieved with the sample volume used in the method development experiments and would improve if a larger volume was used. Takahashi[156] reported 10 ng/L, which was achieved when 1000 mL of seawater sample was analysed and the extract concentrated down to 1 mL and measured by GC-FPD. That detection limit would be worse than the 4 ng /L that could be achieved in the current study if Takahashi's concentration techniques were applied. Similarly, Matthias *et al*[158] reported 7 ng/L , which was achieved when 100 mL of water sample were analysed, the extract concentrated down to 0.05 mL and measured by GC-FPD. That would be worse than the 2 ng/L that could be employing Matthias' concentration techniques.

5.2.4 Conclusions on the HG method

The hydride generation method was not used further, due to issues that appeared. The non linearity of TBTH had not been previously reported, so further investigation and confirmation of this behaviour would be necessary that would be beyond the scope of this project.

Secondly, the detection limit was not satisfactory, more development work therefore would be necessary to improve it. This could be accomplished by analysis of a larger volume of the sample and/or by evaporation of the extract after the derivatisation. These were means that had been employed by others, using off-line systems, for the enhancement of the detection limit of the hydride method[119, 121]. That would mean that the hydride generation method could lose its advantages of a fast and facile method compared to the method of ethylation by $NaBEt_4$, a method commonly used in the analysis of water samples (see also Section 3.3.1).

5.3 Solid phase extraction with in situ ethylation

A new approach was developed to overcome the problems encountered with the hydride generation method and to increase the level of pre-concentration.

The conventional ethylation of TBT using $NaBEt_4$ has been described elsewhere [147, 148]. The $NaBEt_4$ ethylates the tributyltin in an aqueous solution buffered at pH 5.

$Bu_3SnQ + NaBEt_4 \rightarrow Bu_3SnEt + BEt_3 + Na^+ + Q^-$

In this study it was combined with solid phase extraction (SPE) to pre-concentrate the TBT. Like hydride generation, this method was fast and simple, but the ethylating agent $NaBEt_4$ is more expensive than $NaBH_4$ and supply can be unreliable. On the other hand, this method is popular, better documented for off-line systems and has been shown to produce more reproducible results for organotins[230] than the hydride generation.

5.3.1 Solid phase extraction

SPE cartridges have been used for the pre-concentration and/or extraction of butyltins[127, 128, 130, 131, 231] and a pre-concentration factor of 250 has been reported with a 500 mL sample[197]. Many materials have been evaluated as sorbents including the conventional hydrophobic C_{18} bonded silica in discs or cartridges such as Lichrolut RP-18[127] and Bond Elut C_{18}[197], a macroporous copolymer containing lipophilic divinylbenzene and hydrophilic N-vinylpyrrolidone (Oasis HLB[127]), styrene-divinylbenzene (Amberlite XAD-2[232]), and the more polar Superclean Cyano[197] and Superclean Diol[197]. The last two more polar sorbents were not efficient for organotins[197] and Oasis HLB was more efficient[127] for di-organotins (especially for diphenyltin) than conventional C_{18} bonded silica.

Apart from the sorbent material, the effects of other parameters on the extraction efficiency of the SPE, such as the sample pH and the presence of complexing agents, like tropolone, had been documented in the literature. For the extraction of organotins from water, when sample pH values of 2, 3, 5 and 8 were tested, pH 2 was found to be optimum for Oasis HLB.[127] To assess the use of tropolone, the sorbent material (Oasis HLB) was conditioned with tropolone (0.01%) in one experiment and tropolone was added in the sample (0.01%) in another experiment. In both cases the recovery of organotins was higher when no tropolone was used, with the exception of MBT for which the addition of tropolone to the sorbent was beneficial.[127]

For the extraction/pre-concentration step C_{18} (octadecyl) bonded silica SPE cartridges were chosen for the development of the new analytical approach that was based on *in-situ* derivatisation of extracted butyltins within the SPE cartridge. The compounds of interest are retained by the non-polar modified sorbent by hydrophobic interactions and then eluted from the cartridges using a low-medium polarity solvent, such as ethyl acetate. Tetrabutyltin (TeBT) was incorporated as internal standard to check the elution of the ethylated derivatives from the cartridge.

5.3.2 Method

The SPE cartridges outlets were connected by their Luer tips through 2.05 mm bore PVC tubing to a peristaltic pump. A flow rate of 1.9 mL/min was maintained up until the derivatisation step. The procedure began with the conditioning of the SPE cartridges with 10 mL of methanol and then rinsing with 10 mL of deionised water. The water sample was then pumped through the cartridge.

Then 4 mL AcOH-AcONa buffer (0.1-1 M, pH 5) was passed through the cartridge. 2 mL of 0.1-1% w/v aqueous solution of the $NaBEt_4$ reagent was added and the peristaltic pump was stopped after the reagent first reached the end of the SPE cartridge, leaving the $NaBEt_4$ in contact with the cartridge packing.

After 30 min the peristaltic pump was restarted and once the whole amount of the reagent had passed through the cartridge, the cartridge was rinsed with 10 mL of deionised water.

The cartridge was then fitted to the vacuum system shown in Figure 31 to initiate the elution for the first 10-15 seconds. Then the vacuum system was disconnected and the organotins were slowly eluted by gravity (flow rate *ca.* 0.2 mL/min) with 2 mL of ethyl acetate containing the IS (TeBT). The TeBT added varied according to the expected level of butyltins and also the linear range of TeBT, as established by calibration experiments previously carried out (Section 5.2.2.4).

The eluate was dried with anhydrous Na_2SO_4.

Finally, the TBT content in the eluate was determined by GC-PFPD.

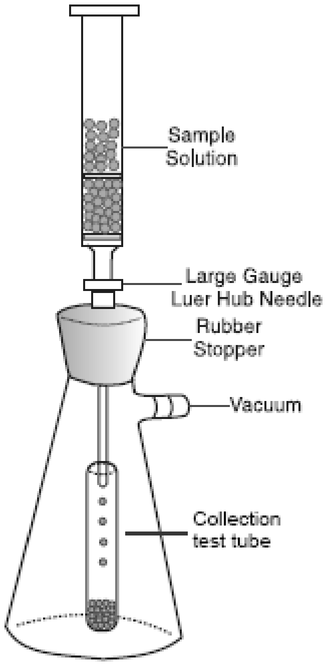


Figure 31. Vacuum system (from Ref[233] with kind permission from Supelco, a division of Sigma-Aldrich)

5.3.3 Chromatography

All of the chromatographic operation conditions were as specified in Section 4.2.

5.3.3.1 Injection volume increase

To test whether a lower detection limit could be achieved by increasing the volume of extract sample injected into the gas chromatograph, 1 µL to 5 µL injections were carried out with a standard solution (0.01µg Sn/mL TeBT).

5.3.3.2 Results and discussion

Peak height was found not to be linearly related to injection volume (Figure 32) due to the development of peak splitting with larger volume injections (Figure 33).

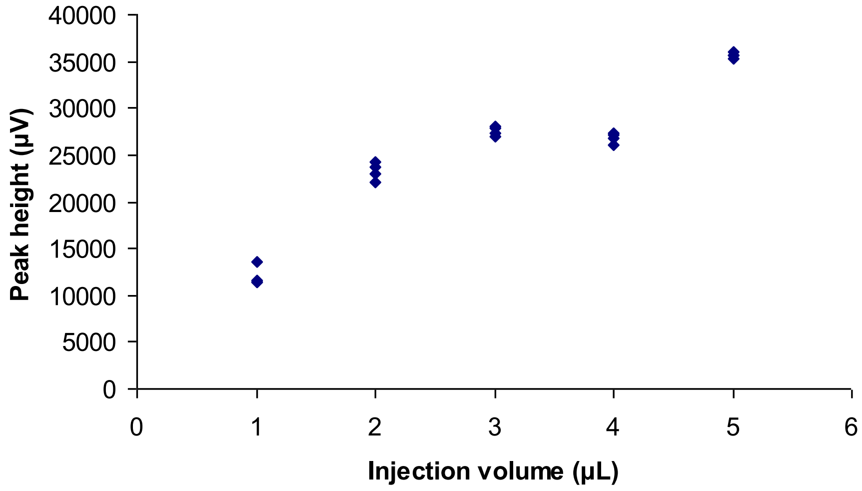


Figure 32. Comparison of peak heights for injections of different volumes from the same solution (0.01 µg/mL TeBT)

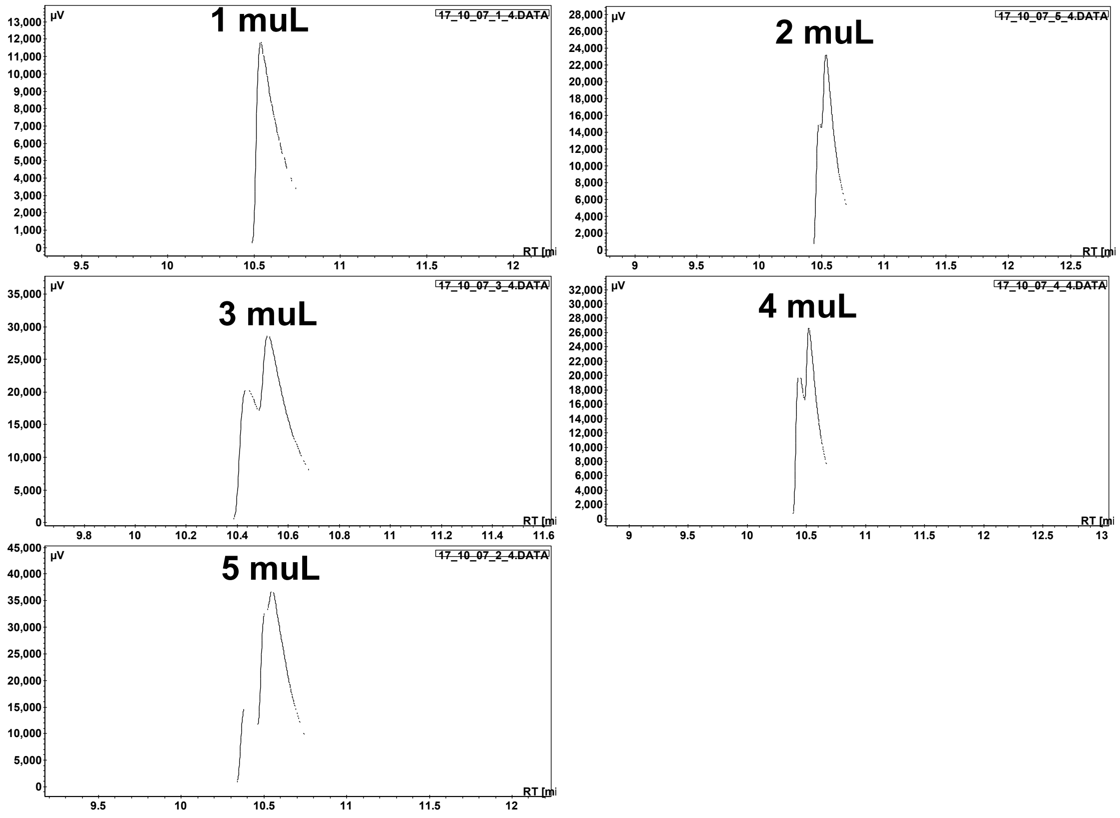


Figure 33. Partial chromatograms of 1 µL- 5 µL injections of a 0.01 µg/mL TeBT solution

In the splitless injection, employed in this work, using the PTV injector, there are two re-concentration mechanisms occurring. The first one is cold trapping, where the sample enters the hot injector then the components with high boiling points condense at the beginning of the column, which is set at a much colder temperature. The second mechanism is a solvent effect. The oven temperature is below the solvent's boiling point and the volatile compounds condense at the beginning of the column together with the solvent forming a thin liquid layer. The layer diminishes in length, as the solvent volatilises, resulting in peak focusing. When a large amount is injected there may be several droplets of solvent resulting in peak splitting in the chromatogram. To overcome this obstacle a retention gap could be fitted.[234-236] The retention gap is a short deactivated non-bonded fused silica capillary column connected to the front of the analytical column. This retention gap traps any impurities from the sample and provides the extra volume necessary for the extra amount of solvent to focus. It helps the re-concentration of the sample components at the beginning of the analytical column, as it has lower affinity for the components compared to the analytical column.

Other options to avoid peak splitting involve the control of the injector temperature, using the PTV[172]. One option is to use cold splitless injection with solvent venting, where the initial temperature of the injector is 10-20 ˚C below the boiling point of the solvent. This can help to concentrate the components in the injector and slowly volatilise them as the injector temperature increases, after most of the solvent has been vented. Another option, available in specialised systems, is solvent venting with flow stopping by reducing the pressure in the column to prevent the flow of analytes and solvent onto the column.[235]

5.3.4 Initial calibration

Pure ethylated butyl tetraalkyltin compounds were not commercially available and indirect calibration was therefore carried out with water samples of known analyte concentration.

Aliquots of deionised water (25 mL) were spiked with 10, 20, 30 and 40 μL of a 6.25 μg Sn/mL solution of butyltin chlorides and TPrTCl in MeOH. The analytical procedure previously described was followed (Section 5.3.2).

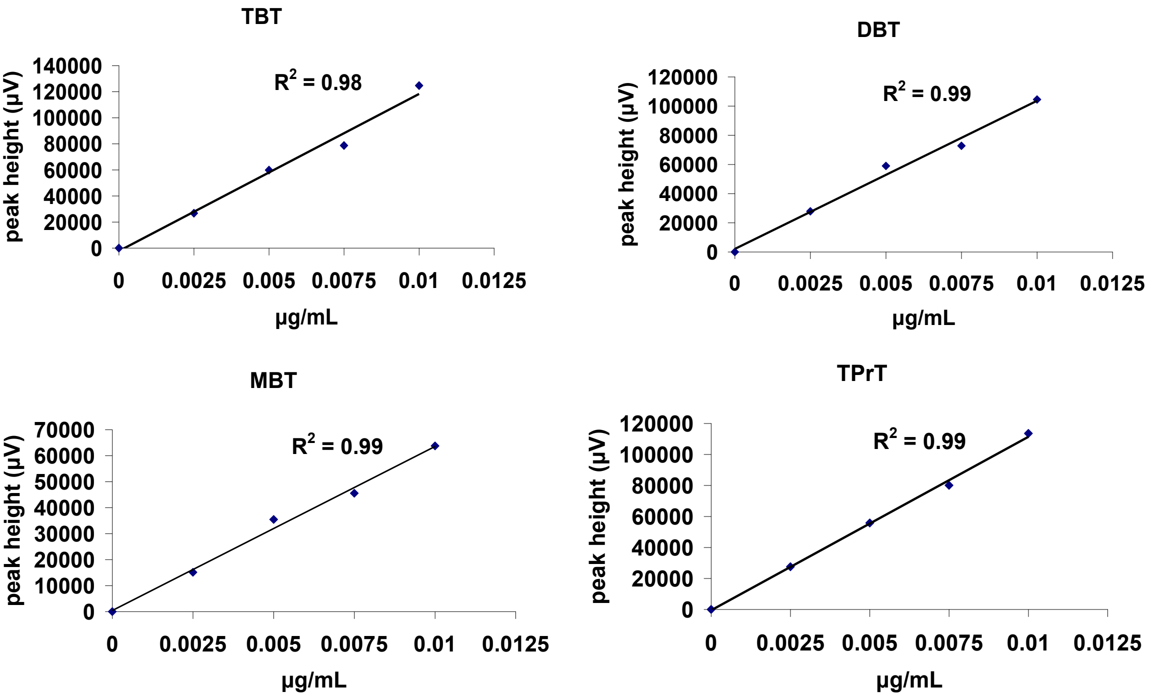


Figure 34. Organotin solutions of 0-0.01 µg Sn/mL in water

Good linearity was achieved for all organotins tested (Figure 34).

The detection limits (when a 600 µV peak = 3 x noise signal) for the ethylated derivatives were 0.7 pg for TBT, DBT and TPrT and 1.2 pg for MBT (as Sn) for 1 µL injections.

5.3.5 Effect of eluent polarity

Change of eluting solvent was considered to increase the elution of the ethylated butyltins without increasing the solvent volume to avoid deterioration of the detection limits.

5.3.5.1 Experimental

The elution with ethyl acetate was compared to elution with 50:50 ethyl acetate:hexane, which was used to reduce the polarity of the eluting solvent, and to elution with DCM, which is a higher polarity eluting solvent.

Deionised water aliquots (25 mL) were spiked with 20 µL of a 6.25 µg/mL butyltin chlorides solution. The analytical procedure described in Section 5.3.2 was followed until the elution step.

For Samples 1 and 2 an elution with 2 mL of ethyl acetate containing 0.0625 µg/mL of TeBT (IS) was carried out. A second elution with 2 mL pure ethyl acetate followed to check for incomplete elution of organotins. For Samples 3 and 4 the eluting solvent was 50:50 ethyl acetate:hexane (or DCM) containing 0.0625 μg/mL TeBT. A second elution with 2 mL pure ethyl acetate (or DCM) followed to check for incomplete elution of organotins. The extract of the 1st and the 2nd elution was measured separately.

5.3.5.2 Results and discussion

The elution with 50:50 ethyl acetate:hexane gave poor resolution of peaks in the gas chromatography, therefore this combination of eluting solvents was rejected.

In the first elution with DCM, the peak heights of TBT and DBT appeared to be higher on average compared to the peak heights using ethyl acetate. This was attributed to the higher volatility of DCM, which caused extracts 3 and 4 to concentrate during the vacuum-assisted elution. Because of the concentration of the samples the quantification of the butyltins was not possible since it was already known from previous experiments that the IS (TeBT) was retained by the cartridges and was therefore not suitable to use it to correct the peak heights. In the second elution some butyltins were detected but their quantification was not possible due to the concentration of the extracts by the vacuum used to assist the elution.

From the eluting solvents/mixes used in the previous experiments none appeared to eliminate the problem of the incomplete elution of organotins. Information regarding the best eluting solvent for tetra-alkylated organotins was not available as alkylation of organotins prior to extraction from SPE cartridges had not been reported before. Ethyl acetate was therefore chosen as the eluting solvent, as it was compatible with the chromatographic system subsequently used and it had intermediate polarity which would allow the elution of the ethylated butyltins from the C_{18}-bonded silica cartridges.

5.3.6 Elution volume

In order to check whether all the alkylated tins were eluted into a 3 mL aliquot of ethyl acetate, a second elution was carried out and the eluate was measured separately.

5.3.6.1 Experimental

Deionised water samples (25 mL) were spiked with 20 μL of a 6.25 μg/mL solution of each of the three butyltin chlorides.

For Samples 1-3, two aliquots (2+1 mL) of ethyl acetate were used. This was decided as two separate extractions/partitions of the ethylated butyltins into ethyl acetate were expected to deliver a slightly higher overall extraction yield than one extraction/partitioning. The first aliquot was 2 mL of ethyl acetate, containing 0.15625 μg/mL TeBT (IS) and the second aliquot was 1 mL of pure ethyl acetate. The two eluates were combined for measurement. A second elution with 1 mL of pure ethyl acetate (extracts 1'-3') was carried out. The eluate was analysed separately to test for any derivatives remaining in the SPE cartridges.

5.3.6.2 Results and discussion

3 mL of ethyl acetate was found to be sufficient to elute the organotins, as no TBT was found in the subsequent elution (extracts 1'-3'). It was decided to adopt a 4 mL elution volume. The final extract was made up to 5 mL prior to its analysis, in order to avoid concentration changes resulting from solvent loss during the vacuum assisted elution.

In studies where SPE was used to pre-concentrate waster samples different volumes were used for the elution of the organotins (in the chloride form). Gonzalez-Toledo *et al*[129, 197] reported that after pumping 250 or 500 mL of water sample through the cartridge the elution was carried out with 2 mL of oxalic acid and triethylamine in methanolic-acetic acid water. Different elution volumes (2, 4 and 8 mL of acetonitrile) necessary to quantitatively elute the organotins loaded on Oasis HLB were examined by Diez *et al*[127] and 4 mL were found adequate.

5.3.7 Sample flow rate

In order to analyse larger volume samples using SPE cartridges, it was necessary to reduce the time the samples take to pass through the cartridges.

5.3.7.1 Experimental

Six water samples (50 mL) were spiked with 10 μL of a 0.1 μg/mL (as Sn) TBTCl solution in MeOH. Three (Samples 1, 2 and 3) of the six samples were pumped through SPE cartridges using a peristaltic pump at a rate of 4.2 mL/min and the rest (4, 5 and 6) were pumped through at the previously employed slower rate of 1.9 mL/min.

5.3.7.2 Results and discussion

The peak height when employing the fast flow rate was 33334±1374 μV and 30523±4265 μV with the slow flow rate. No significant difference was observed by using a t-test (95% confidence level) for the results of the two different speeds. Both sample speeds are therefore considered suitable for the extraction step. The highest speed was then adopted as it saved time and would allow samples to be analysed 45% faster. Sample loading rates of 5 mL/min have been reported as suitable[127, 197].

5.3.8 Effect of pH and salinity on extraction efficiency

The effect of pH and salinity on the extraction efficiency of the SPE cartridges was investigated. This was necessary as many water samples need acidification for preservation at pH 2 or have high salinity (seawater samples), which could affect the extraction by the solid phase extraction cartridges.

5.3.8.1 Experimental

The effect of pH was tested by analysing deionised water samples (10 mL), three of which were spiked acidified water and three were spiked non-acidified water.

The effect of salinity was examined by comparing 10 mL replicate samples of spiked seawater and of spiked deionised water.

A combination of increased salinity and acidification at pH 2 was tested by comparing 10 mL samples of spiked acidified seawater and spiked non-acidified deionised water.

The spiking was done using 10 μL of a 10 μg Sn/mL methanolic TBTCl solution. The acidification was carried out with conc. HCl until pH 2 that had been found to be optimum for another sorbent material (Oasis HLB)[127]. A blank solution was also analysed and no TBT was detected. The samples were pumped through the cartridges using a peristaltic pump at 4.2 mL/min.

5.3.8.2 Results and discussion

The acidification could have an effect on the non end-capped silica contained in the cartridges. The optimum pH for adsorption of the organotins on the surface of the uncapped silica is the pH area where the silica surface has a negative charge and TBT is in its cationic form, pH=5.5-7.5.[29]

$>SiOH \rightleftharpoons >SiO^- + H^+$ pKa = 6.56[29]

$TBT^+ + H_2O \rightleftharpoons TBTOH + H^+$ pKa= 6.3[29]

$>SiOH + TBT^+ \rightleftharpoons >(SiO^-)(TBT^+) + H^+$ - log K= 2.47 ± 0.6[29]

On the other hand, acidification in real samples may promote the conversion of the butyltin compounds in less water-soluble forms[232] and increase therefore their affinity for the hydrophobic sites on the C_{18} cartridges.[127] The acidification might not have the same impact on spiked samples, as the TBT is introduced in the chloride form which is hydrophobic.

Indeed, in the current work the acidification of the samples did not affect the yield of the analysis. The acidified solutions produced approximately the same signal (19197±1253 μV) as the non-acidified (17741±3168 μV), which was also confirmed by t-test analysis (95% confidence).

The salinity could be expected to increase the extraction yield of TBT from water by reducing its solubility in water, because of the salting out effect of NaCl, but it did not appear to influence the extraction yield in the current experiment. The peak height of the seawater samples was 13364±4496μV and was not significantly different (t-test, 95% confidence level) from the control (deionised water) samples with peak height of 19458±1314 μV.

As expected from the two previous experiments, the results from the acidified seawater samples with a peak height of 16508±2646 μV were not significantly different (t-test, 95% confidence level) from the control samples of 14991±6343 μV peak height. The SPE/ethylation procedure was therefore considered suitable for the analysis of acidified or non-acidified saline water samples.

5.3.9 Concentration of the extract

Concentration of the extract was considered, to lower the detection limit of the method. This is a technique very widely used and it is commonly carried out with a rotary evaporator[237] or with an Ar[172] or N_2 flow[127, 237].

5.3.9.1 Experimental

A solution of 50 mL containing 0.0125 µg Sn/mL TBTEt in ethyl acetate was divided into 10 sub-samples of 5 mL each. Three of the sub-samples were evaporated to dryness with a N_2 flow and three were evaporated until the last few drops. All these six sub-samples were then made back up to 5 mL volume with ethyl acetate. The concentration of the six sub-samples that had undergone evaporation was compared with that of three other sub-samples measured directly (with no evaporation).

5.3.9.2 Results and discussion

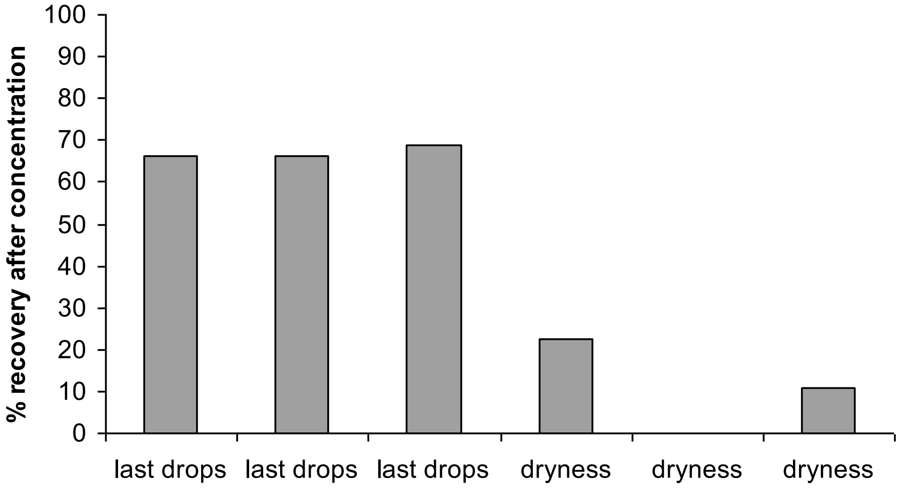


Figure 35. Recovery (%) of samples undergone evaporation

Losses were observed during the evaporation of the solvent. Losses of up to 50% have been previously reported[214] and more than 60% losses were previously observed in this work during the evaporation of DCM in solutions containing TBTCl (Section 4.5.5). It appeared that evaporation to dryness can cause up to 100% losses (Figure 35) and would therefore be unsuitable as a concentration step. The evaporation to the last few drops still causes some losses but this could be corrected using an internal standard, which should behave very similarly to the TBT under these evaporation conditions.

5.3.10 Finalised procedure

The changes made in the analytical procedure appear in bold italics letters in Figure 36.

Wash: 10 mL methanol ***(5-10 mL/min flow rate)***

⇩

Pre-condition: 10 mL deionised water ***(5-10 mL/min)***

⇩

Extraction: acidified water sample (250 mL) ***(5-10 mL/min)***

⇩

Buffering: 10 mL pH 5 AcOH-AcONa 1M buffer ***(5-10 mL/min)***

⇩

Derivatisation: 2 mL of 1% w/v $NaBEt_4$ solution in pH 5 buffered water

⇩

Elution: with ***2+ 2 +1mL*** of ethyl acetate

⇩

Make up solvent to 5.0 mL volume + Na_2SO_4 anhydrous

⇩

Analysis: GC-PFPD

Figure 36. Finalised analytical procedure for the SPE/ethylation method

5.3.11 Repeatability

The finalised SPE/ethylation procedure (Section 5.3.10) was applied to four 250 mL filtered seawater samples acidified until pH 2 with conc. HCl. The water samples were spiked with 10 µL from a 10 µg Sn/mL methanolic solution of TBTCl resulting in a concentration of 400 ng Sn/L. This theoretically yields, after derivatisation, a solution of 0.02 µg Sn/mL TBTEt in the 5 mL ethyl acetate eluate. A vacuum pump was used instead of a peristaltic one and the flow rate was at least 5 mL/min, which had been reported as suitable[127, 197], and not exceeding 10 mL/min. A procedural blank was also analysed.

The peak heights of the four spiked solutions had an average of 27746 µV ± 2024 µV and 7 %RSD. The repeatability of the method was very satisfactory. Extraction of butyltins on C_{18} disks followed by *in situ* Grignard derivatisation, supercritical fluid extraction of the derivatised disks and determination with GC-FPD had a repeatability of 8.2 %RSD for TBT.[131] Spiked seawater extracted with liquid-liquid extraction, followed by Grignard derivatisation and determination with GC-MS-MS had a 5 %RDS for TBT.[136]

5.3.12 Accuracy

External calibrant solutions of ethylated TBT in hexane, purchased from QUASIMEME[201], were used to calculate the yield of TBT from the SPE/ethylation procedure.

The calibrant solution was 10,200 µg/mL of TBTEt (molecular weight) in 1.2 mL of hexane. From this stock solution a 0.046 µg Sn/mL TBTEt solution in hexane was prepared and injected together with the derivatised samples of seawater of the previous experiment (Section 5.3.11).

The yield of SPE/ethylated TBT calculated from the QUASIMEME external calibrant solution was on average 93%±7%. The accuracy was very satisfactory. Recoveries reported in the literature have varied, from 84%±12% for TBT for a 250 mL spiked water sample extracted on C_{18} SPE cartridges and determined by RPLC-fluorimetry[129] to 105%± 5% for TBT in a 500 mL spiked seawater sample extracted by liquid-liquid extraction, followed by Grignard pentylation and GC-MS-MS determination[136].

5.3.13 Calibration curves for the SPE/ethylation method

A new calibration curve was necessary for the ethylated butyltins, derivatised according to the final procedure (Section 5.3.10).

Aliquots of deionised water (25 mL) were spiked at three concentration levels with 10, 20 and 30 µL of a 6.25 µg/mL solution of MBTCl, DBTCl, TBTCl and TPrTCl (as Sn) in MeOH. For each concentration level two spiked water samples were derivatised. The concentrations of the derivatised organotins in the final solution were 0.0025, 0.005 and 0.0075 µg Sn/mL. A low range of concentrations was selected because of the low concentration range for the butyltins found in water samples.

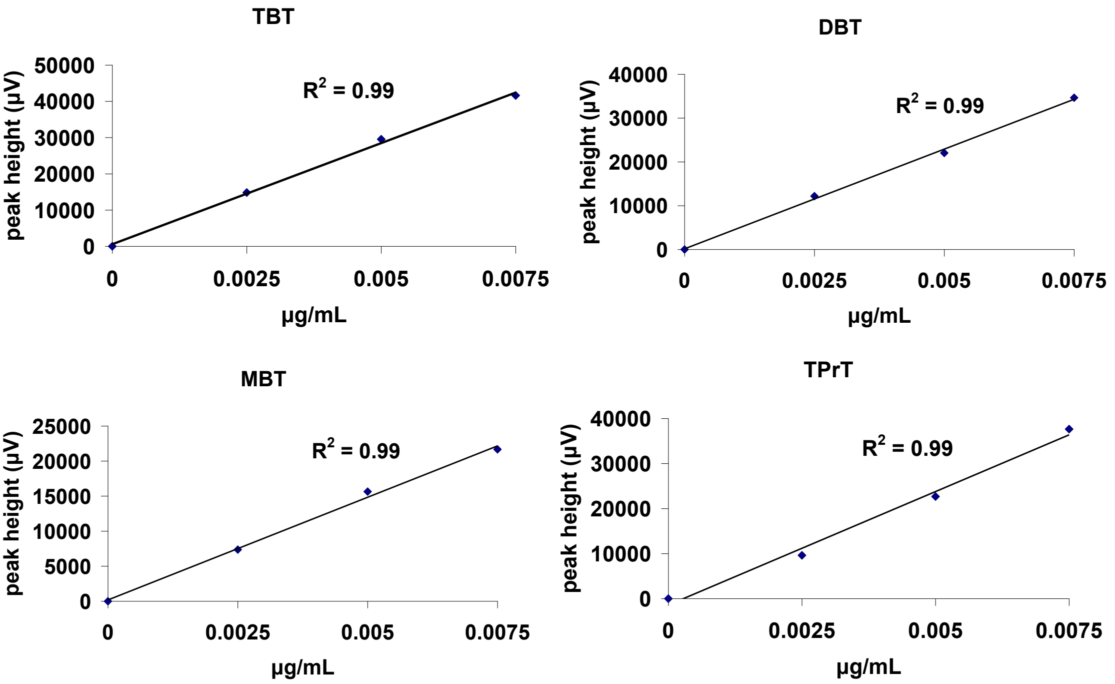


Figure 37. Calibration in the range of 0-0.0075 µg Sn/mL for the SPE method

Very good linearities were achieved for all three butyltins and for the surrogate TPrT (Figure 37).

The detection limits of the method (3 x noise signal peak=600 µV) are 10 ng/L for TBT, 12 ng/L for DBT and 20 ng/L for MBT as Sn in water for a 250 mL sample. The instrument's detection limits are 0.5 pg for TBT, 0.6 pg for DBT and 1 pg for MBT as Sn. In this study, the volume of sample could be increased achieving even better detection limits. Detection limits from 40 ng/L[197] (250 mL of sample treated) to 10 ng/L[127] (volume of sample not stated) for TBT have been reported for methods employing SPE just for the pre-concentration/extraction step. Combining *in situ* derivatisation and supercritical fluid extraction (CO_2) of the derivatised C_{18} silica disks achieved a 6-9 ng/L[131] limit of detection for TBT when treating 1 L of seawater. A scale-up of the procedure in the current work from 250 mL to 1 L could give a 2.5 ng/L detection limit for TBT.

An example of the chromatography of the organotin compounds in ethyl acetate is shown in Figure 38. The sample injected contained 0.0075 µg Sn/mL ethylated TBT, DBT, MBT, TPrT and 0.005 µg Sn/mL TeBT.

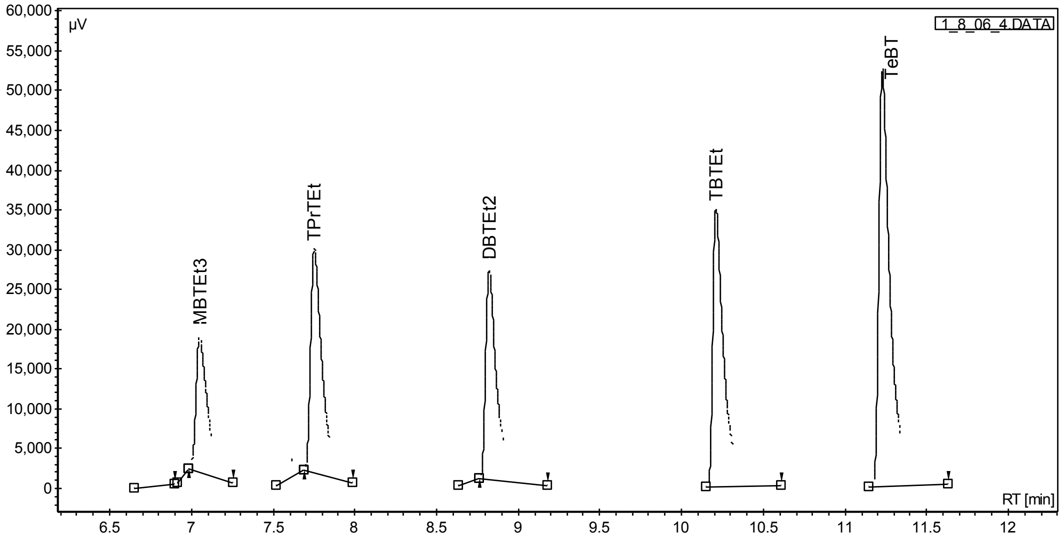


Figure 38. Partial chromatogram of the ethylated TBT, DBT, MBT, TPrT (0.0075 µg Sn/mL) and TeBT (0.005 µg Sn/mL) solution

5.3.14 Conclusions on the SPE with in situ ethylation procedure

The solid phase extraction followed by *in situ* derivatisation was considered to be promising, offering the possibility of automation and reducing organic solvent consumption, glassware, losses of analytes during handling and personnel effort. One limiting parameter could be the presence of particles in the water sample, which may block the cartridge packing preventing the sample and then the reagents flowing through. As this analytical method was developed to measure TBT in leachates obtained by shaking contaminated dredgings with water, the particulates in theses leachates may cause difficulties. The leachates often contained some suspended particles (e.g. clay particles), still remaining despite centrifuging, which caused blockages of the cartridge, delaying and disrupting the flow through the cartridge. This was of great importance, as the extraction of the butyltins, the derivatisation reaction and the elution of the derivatives depended on the unobstructed flow of the water sample, the aqueous solution of the reagent and the eluting organic solvent through the cartridge.

5.4 Ethylation followed by liquid-liquid extraction

Another approach to the determination of TBT in water samples was ethylation followed by conventional liquid-liquid extraction to an organic solvent, as mentioned in Section 3.3.1. TBT ethylation with $NaBEt_4$ has been described elsewhere[147, 148] and in this project was used for the water samples produced by leaching sediment samples in water. It was chosen in order to avoid difficulties arising from cartridges blocking with the SPE/*in situ* ethylation method.

5.4.1 Method

The water sample (the volume is specified in each experiment) was poured in a glass separating funnel and 25 mL of 1 M pH 5 buffer solution (acetic acid/sodium acetate, described in Section 5.1.1) were added followed by 2 mL of the aqueous $NaBEt_4$ solution (2 % w/w) and 2 mL of the hexane extracting solvent, typically containing 0.1 µg Sn/mL TeBT.

Shaking the separating funnel promoted the mixing of the reagent with the sample and simultaneously extracted the ethylated TBT into the hexane.

The two phases were left then for 10 minutes to separate and the water phase was discarded. The hexane layer analysed for TBT by GC-PFPD.

All of the chromatographic operating conditions were specified in Section 4.2.

5.4.2 Calibration and sensitivity

Measurements of extracted/derivatised water samples spiked with TBTCl were carried out in order to establish the linear range.

For the experiment aliquots of 250 mL of deionised water were spiked with 10, 20 and 200 µL of a 0.1 µg/mL solution of TBTCl and 20 µL of a 10 µg Sn/mL solution of TBTCl in MeOH. The analytical procedure described in Section 5.4.1 was followed.

Good linearity was achieved within the range 0-400 ng Sn/L TBTEt (Figure 39).

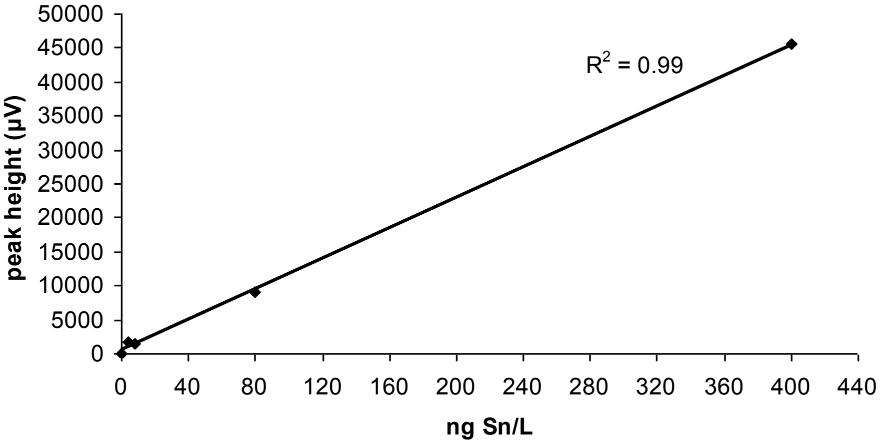


Figure 39. Calibration curve over the range of 0-400 ng Sn/L TBTEt

The absolute limit of detection (3 x noise signal) given the 1 µL injection to the GC-PFPD was 0.3 pg TBT as Sn. For a 250 mL sample of water the limit of detection is 6 ng Sn/L as TBT.

Lower (1-5 ng/L TBT) limits of detection have been achieved by 2 L of seawater LLE into hexane, Grignard hexylation, concentration of the extract to 0.1 mL and GC-FPD determination[237], but the method in the current study would achieve 0.04 ng Sn/L as TBT if the same concentration factors applied. Limits of detection of 0.038 pg/L of TBT for open ocean seawater have been reported by LLE of 1 L of seawater, $NaBEt_4$ derivatisation, concentration of the organic layer to 1mL followed by 100 µL injection to a GC-ICPMS system[172]. The method in the current study would achieve 0.03 ng Sn/L TBT if the same concentration factors applied.

5.4.3 Repeatability

A repeatability experiment was carried out at a TBT concentration level within the linear range established in the last experiment.

Five 100 mL samples of water spiked with 10 µL of a 10 µg/mL TBTCl in MeOH were shaken for 3 hours before analysis. This was done to simulate the procedure of a leaching test where a sediment/water mixture is shaken under fixed conditions. The analytical procedure described in Section 5.4.1 was followed.

The %RSD for the five samples after shaking, derivatisation and fast manual extraction was found to be 4%, which was considered satisfactory.

5.4.4 Mechanical shaking (low speed)

During the extraction of TBT from sediment leachates with hexane, an emulsion often formed. This emulsion was attributed to the presence of organic matter and surfactants and perhaps fine particulate matter in the leachate combined to the violent manual shaking during the extraction with hexane. The emulsion was formed due to the decrease in the surface tension[238] that would otherwise make all the organic matter to come together and separate from the water. The decrease might have been caused by surfactants present, resulting in the stability of droplets containing organic matter in the bulk of water. The procedure had to be modified to prevent the emulsion formation.

In order to break the emulsion or to prevent its formation several different techniques were used, which disrupt the stabilising forces in the emulsion, some of which had been reported before for dealing with emulsions formed at this step of the analysis for TBT: addition of salt[145], addition of conc. HCl[149], addition of iso-propanol as an anti-foaming agent[148], freezing the emulsion in liquid nitrogen and then thawing it, swirling the emulsion in the separating funnel, slow shaking during the extraction .

Of all the different techniques only slow shaking repeatedly gave an emulsion-free hexane layer. The extraction time was increased to 30 min instead of 1 min and an experiment was carried out to test the recovery of TBT with slow shaking compared to the fast manual shaking.

5.4.4.1 Recovery with mechanical low speed shaking

Three aliquots of 100 mL TBT-spiked water (10 µL of a 10 µg/mL TBTCl in MeOH) were derivatised and extracted with the slow mechanical extraction over 30 min and two identical aliquots were extracted with fast manual shaking for 1 min. The 30 min extraction time had been demonstrated to be sufficient for the extraction of organotins from water to iso-octane[174].

Recovery with the slow shaking was 67%±3% compared to that with fast shaking. The recovery was not entirely satisfactory but the repeatability was good, therefore a surrogate compound could be used to correct for the losses.

5.4.5 Surrogate compound for the extraction step

It was then decided to use tri(n-propyl)tin chloride (TPrTCl) as surrogate compound, to correct for incomplete extraction when using the slow shaking extraction as it had been reported as a suitable surrogate compound in procedures employing LLE followed by ethylation and GC-FPD[174] or PFPD[147] detection. At first, an experiment was carried out in order to establish the linear range of TPrT concentration.

5.4.5.1 Calibration and linearity for TPrT

The calibration curve for TPrT was based on the theoretical concentration of TPrTEt 0-0.004 µg Sn/mL. A 500 µg Sn/mL TPrTCl stock solution was prepared in MeOH and diluted up to the concentration of 10 µg Sn/mL TPrTCl. Four aliquots of 100 mL deionised water were spiked. The first two were spiked with 10 µL of 10 µg Sn/mL TPrTCl standard solution in MeOH, the third aliquot with 20 µL of this standard solution and the fourth with 40 µL of the same standard solution of TBTCl. The spiked samples were derivatised and extracted according to Section 5.4.1.

Good linearity was established in the range between 0 and 0.004 µg Sn/mL TPrT (Figure 40).

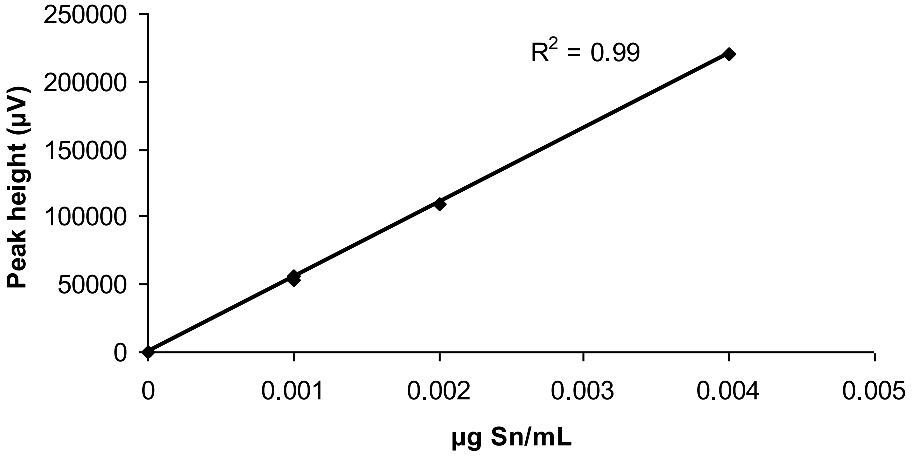


Figure 40. Calibration curve for ethylated TPrT 0-0.004 µg/mL

5.4.6 Recovery and repeatability of extraction with slow shaking

The repeatability of slow mechanical shaking, as well as the suitability of TPrT as the surrogate compound for correcting for incomplete extraction of TBT were then tested.

5.4.6.1 Experimental

Four aliquots of clean sediment were leached with deionised water for 3 hours and centrifuged to separate the leachates. The leachates were spiked with 10 μL from a 10 μg Sn/mL TBTCl solution in MeOH and 10 μL from a 10 μg Sn/mL TPrTCl solution in MeOH. The spiked solutions were buffered to pH 5 with acetic acid/sodium acetate buffer, 2 mL of a 2% (w/w) aqueous solution of $NaBEt_4$ was added and the separatory funnels were shaken vigorously. Then 2 mL of hexane spiked with TeBT (0.1 μg Sn/mL TeBT in hexane) were added and the separating funnels were shaken mechanically slowly for 30 min. 50 mL of deionised water were spiked at the same level with both TBTCl and TPrTCl, derivatised and extracted with fast manual shaking. The recoveries of TBT and TPrT in the slowly extracted aliquots were compared to that of the fast one.

5.4.6.2 Results and discussion

The average recovery yield was 59% ± 5% for TBT and 26% ± 2% for TPrT. Further use of TPrT as a surrogate compound for TBT was abandoned due to large difference in their recoveries and the very low recovery for the TPrT. Instead, measurement of a slowly extracted TBT-spiked water sample was incorporated in all the analyses, on which all the calculations were based, to correct for incomplete extraction of TBT.

The repeatability of TBT measurements was satisfactory. Higher % RSD has been reported[148] for water samples analysed with LLE, followed by $NaBEt_4$ ethylation and GC-PFPD measurement (15% RSD).

5.4.7 Accuracy of extraction with slow shaking

The accuracy of the procedure was tested using an external calibrant solution obtained from QUASIMEME[201] containing ethylated TBT in hexane.

5.4.7.1 Experimental

The ethylation/LLE procedure, described in Section 5.4.1 but with slow shaking, was applied to four 250 mL deionised water samples. The water samples were spiked with 10 μL of a 10 μg Sn/mL solution of TBTCl in MeOH resulting in 250 mL of 400 ng Sn/L water sample. A procedural blank was also analysed.

The calibrant solution was a 1.2 mL solution containing 10,200 μg/mL of TBTEt (molecular weight) in hexane. From this stock solution a 0.046 μg Sn/mL TBTEt solution in hexane was prepared and injected together with the derivatised samples of TBT-spiked water.

5.4.7.2 Results and discussion

The yield of SPE/ethylated TBT calculated according to the QUASIMEME external calibrant solution was on average 74% ± 1%.

The accuracy of this procedure was not entirely satisfactory but the advantages were simplicity and a lower detection limit than the SPE/ethylation procedure, explored earlier (Section 5.3). In order to overcome the discrepancy in the accuracy of the procedure a spiked sample was analysed with every batch of samples and the concentrations of the samples were calculated based on the spiked sample and not according to the QUASIMEME calibrant.

5.4.8 Conclusions on the ethylation/LLE method

TBT ethylation by $NaBEt_4$ followed by liquid-liquid extraction of the ethylated derivative into hexane was explored for the measurement of tributyltin in aqueous samples.

An example of the chromatography from a spiked water sample with a concentration of 400 ng Sn/L TBT can be seen in Figure 41. The hexane extract contained 0.05 μg Sn/mL TBT and 0.1 μg Sn/mL TeBT.

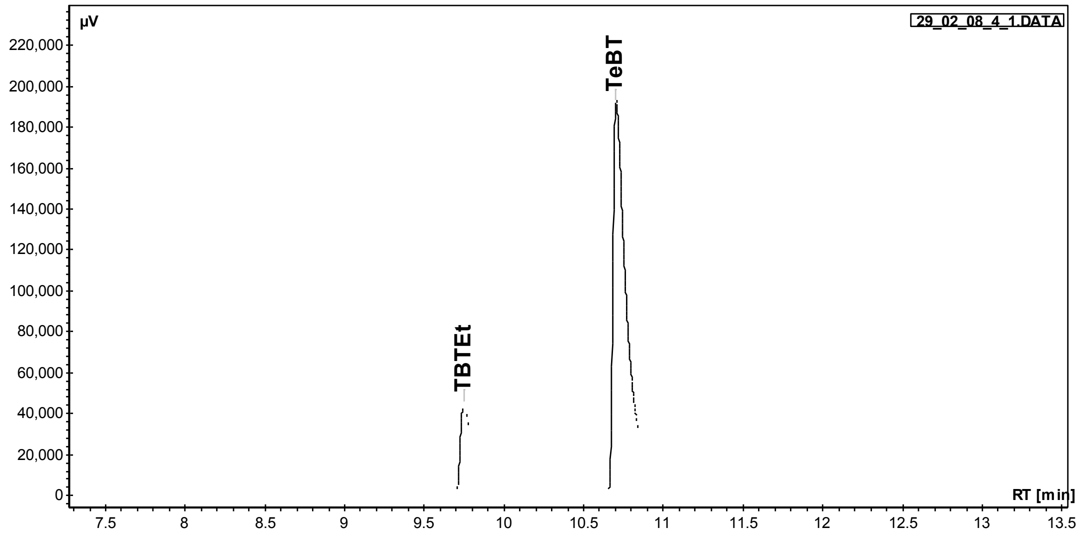


Figure 41. Partial chromatogram of the extract from a spiked derivatised water sample (0.05 μg Sn/mL TBT and 0.1 μg Sn/mL TeBT)

The procedure was fast and facile, repeatable and delivered a low detection limit for TBT (6 ng Sn/L TBT in water). The accuracy of the method could be improved by carrying out a second extraction of the sample. That way an additional amount of the ethylated TBT would be extracted. The disadvantage would be that the detection limit would deteriorate and also much more glassware would be necessary for isolating the hexane layer (upper layer) after the first extraction. Much more time per sample would be taken for carrying out the additional manipulations. Therefore, a spiked water sample was incorporated in every analysis to allow correction for losses of the analyte during the analytical procedure.

This method has been used for measuring TBT in the leachate from TBT-contaminated sediments and the efficiencies of TBT immobilisation approaches for TBT-contaminated sediments, as will be described in Chapter 6.

6 Remediation of butyltin-contaminated sediments and water

The current study focuses on the remediation of TBT-contaminated sludges. Some consideration has also been given to TBT contamination of water, as TBT-contaminated water may be generated during treatment.

The destruction approach was attractive because it eliminates the contamination and does not leave any legacy of contamination behind. Destruction techniques were therefore evaluated first. Two destruction approaches, combustion and ultrasonication were chosen for evaluation. The focus then moved to stabilisation approaches that are less energy-consuming and use familiar technologies.

6.1 Combustion

6.1.1 Introduction

The destruction of TBT-contaminated sediments by incineration under controlled conditions ideally converts the organotins to innocuous products (carbon, water and Sn(IV) oxide), rendering the material safe for reuse onsite or elsewhere, as aggregate or back filling material.

6.1.2 Experimental

A bulk surface (top 5 cm) sediment sample was collected on the 5/10/2005 from a small boatyard on the River Itchen, Southampton (UK). Three 15 g (wet weight) samples were taken and combusted at temperatures of 200, 500 and 1000 ºC in a muffle furnace for 10 hours. From each combusted sediment sample a 1.0 g sub-sample was taken. The sub-samples, and a control sediment sample that had been dried in an oven at 40ºC until constant weight, were analysed for butyltin compounds (Section 4.4.3). Teflon centrifuge tubes were used for the extraction step in order to avoid sorption of the butyltins on the walls of polypropylene tubes. For the quantification a standard solution of 0.1 μg Sn/mL of MHTBT, DHDBT and THMBT in hexane was used.

6.1.3 Results and discussion

It should be noted that the high temperatures in this experiment are expected to have eliminated the most volatile contents of the sediment sample and the total mass of the sample is likely to have been reduced. This experiment was designed to only give a rough estimate of the efficiency of combustion as a means of TBT elimination in sediments. More detailed experiments would follow where the ashed content of the sample would be determined, to allow more accurate quantification of the results. In the current experiment the burnt off mass of sample was not taken into account and the results are given as if 100% of the dry mass was involatile. The concentration of butyltins found in the sediment after combustion is expected to drop when the volatile fraction of mass is taken into account. Table 19 therefore shows the upper limit of concentration of organotins in the sediments after combustion. Sediment combustion effectively removed butylated tin species from the sediment with levels dropping below the detection limit at 1000 ºC.

(mg/kg dry wt)	**TBT**	**DBT**	**MBT**
Untreated sample	0.28	0.12	<0.006
200°C	0.03	0.09	<0.006
500°C	0.04	<0.004	<0.006
1000°C	<0.003	<0.004	<0.006

Table 19. Butyltin contaminated sediment samples combusted at 200, 500 and 1000°C for 10 h (single samples)

For disposal at sea the TBT concentration in sediments should not exceed 0.1-1 mg/kg (dry wt)[42] and on these grounds the combustion was effective for this sample, especially if only the TBT concentration is of interest and not the degradation product DBT. A 91% reduction of the TBT concentration was achieved even at 200ºC, while temperatures of 1000 ºC or higher were necessary to essentially eliminate all the butyltins. Whilst based on single analyses, this experiment confirms the results reported by Song *et al*[63], according to which sandblast waste containing TBT, DBT and MBT was completely detoxified after heat treatment for more than 1 hour at 1000 ºC (maximum treatment time not given) or just 1 hour at over 1000ºC (maximum treatment temperature not given).

During combustion several reactions can take place as the heat provides the energy for reactions that have a high energy barrier and do not occur spontaneously in ambient conditions.

At temperatures above 200ºC the Sn-C bond in organotins can be thermally cleaved[62] and the organotin compounds are thermally unstable above such temperatures[239]. Butyltin compounds are likely to combust before volatilising at standard atmospheric pressure (760 mm Hg), as the boiling point of TBTCl is: 171-173 ˚C at 10 mm Hg, that of DBTCl 135 ˚C at 10 mm Hg and that of MBT is 93 ˚C at 10 mm Hg.[240] The removal of the butyltins from the sediment at temperatures as low as 200 ˚C, though can be mainly attributed to volatilisation. At higher temperatures combustion is expected to cause the reduction of the butyltin concentration in the sediment.

The combustion of butyltins is expected to progress with debutylation of butyltins (Bu_xSnQ_{4-x}, Q = halide, polymer, OH^-). Studies of Sn-C bond dissociation energies for organotins indicate that the bonds dissociate stepwise and require different energies. In studies of dimethyltin dichloride the first Sn-C bond dissociation required 56 kcal/mol while the second Sn-C bond only 32 kcal/mol.[60] The thermal cleavage of the Sn-C bond, producing highly reactive butyl free radicals, results in inorganic forms of tin[241]:

$$Bu_3SnQ \longrightarrow Bu_2SnQ_2 \longrightarrow BuSnQ_3 \longrightarrow SnQ_4$$

In general, the most common species produced during combustion, other than water and those containing carbon, are widely regarded to be oxygen and hydrogen atoms together with radicals and HOO* and HO* radicals. Some of their formation reactions are shown below [227, 228]:

$$H^* + O_2 \longrightarrow O^* + {}^*OH$$

$$O^* + H_2 \longrightarrow H^* + {}^*OH$$

and also:

$$O_2 + H^* \longrightarrow HOO^*$$

$$HOO^* + H^* \longrightarrow H_2O_2$$

$$H_2O_2 \rightleftharpoons 2HO^*$$

Hydroxyl radicals can react with the tin atom when the tributyltin compounds (shown in the form of tributyltin chloride in the reactions below) are present:

$$Bu_3SnQ + {}^*OH \longrightarrow Bu_3SnOH + Q^*$$

and gradually debutylate them to tin oxide.

$$Bu_3SnOH + {}^*OH \longrightarrow Bu_2Sn(OH)_2 + Bu^*$$

$$Bu_2Sn(OH)_2 + {}^*OH \longrightarrow BuSnO_2H + H_2O + Bu^*$$

$$BuSnO_2H + {}^*OH \longrightarrow SnO_2 + H_2O + Bu^*$$

The *OH free radical may also degrade tributyltin according to the proposed mechanisms for the UV/TiO_2, UV-Fe(III) and ozone abiotic degradation of TBT (Chapter 2, Schemes 1-3).

The butyl radicals cleaved from the tin atom will react with *H or *OH free radicals to form compounds such as butane and butanol:

$$CH_3CH_2CH_2CH_2^* + {}^*H \longrightarrow CH_3CH_2CH_2CH_3$$

$$CH_3CH_2CH_2CH_2^* + {}^*OH \longrightarrow CH_3CH_2CH_2CH_2OH$$

that could then volatilise or combust to carbon dioxide and water. The mechanism of the combustion of butane and butanol has been studied extensively[227]:

$$CH_3CH_2CH_2CH_3 + 6.5O_2 \longrightarrow 4CO_2 + 5H_2O + \text{heat}$$

$$CH_3CH_2CH_2CH_2OH + 6O_2 \longrightarrow 4CO_2 + 5\ H_2O + \text{heat}$$

Song *et al*[63] collected the flue gases from the combustion of butyltins and the main compound that they could identify was CO_2 (further information on the detection system and operating parameters were not provided). They concluded that the butyl groups were oxidised to inorganic tin compounds and had not simply volatilised. This would support the hypothesis that butyltins are degraded during combustion and not simply removed by heat.

Volatilisation of toxic compounds including organotins would cause potential safety problems unless considered in the design of the incineration plant. The high temperature required together with the need for a suitable scrubber will have significant cost implications (> £50/tonne of wet sediment excluding haulage, estimate by Land and Water, 2007). Another parameter worth noting is the unfavourable predisposition of the public towards incinerators. That may prevent planning permission being granted for such an installation on a remediation site.

6.2 Ultrasonic destruction

6.2.1 Introduction

Ultrasound has been gaining interest for the treatment of organic pollutants because of its effectiveness.[242] The expansion and collapse of cavitation bubbles that takes place during ultrasonication can create extreme conditions (4000-5000 K and hundreds of bars of pressure)[243]. These conditions generate *OH and H* radicals from the dissociation of water, which can attack compounds contained in the same liquid and degrade them[244, 245].

As reported earlier (Sections 2.2.2-2.2.3), *OH radicals have been used for the debutylation of TBT in water. It was therefore believed that the generation of *OH radicals by ultrasonication of aqueous solutions spiked with TBT might lead to the degradation of the TBT molecules in the same way.

6.2.2 Experimental

The evaluation of ultrasonication as a TBT destruction technique was carried out using an MSE 150 W ultrasonic disintegrator (MK2 with a 9.5 mm probe of 20 kHz nominal output frequency). Deionised water (200 mL) was spiked with 20 μL of a TBTCl standard solution (10 μg Sn/mL in methanol). The spiked water was divided into four 50 mL aliquots. Three of these aliquots were ultrasonicated for 30 minutes in an iced water bath (to avoid evaporation of the TBTCl). The fourth was used as a control solution. The water samples were then analysed as described in Section 5.3.10.

6.2.3 Results and discussion

The TBT concentration was reduced from 2000 ng Sn/L to 1037±154 ng/L (48±3% reduction) after sonication, but this occurred with the appearance of 470 ng Sn/L as DBT. This was attributed to the degradation of TBT to DBT by debutylation. There was also chromatographic evidence, in two of the three treated samples, of another unknown compound (Figure 42).

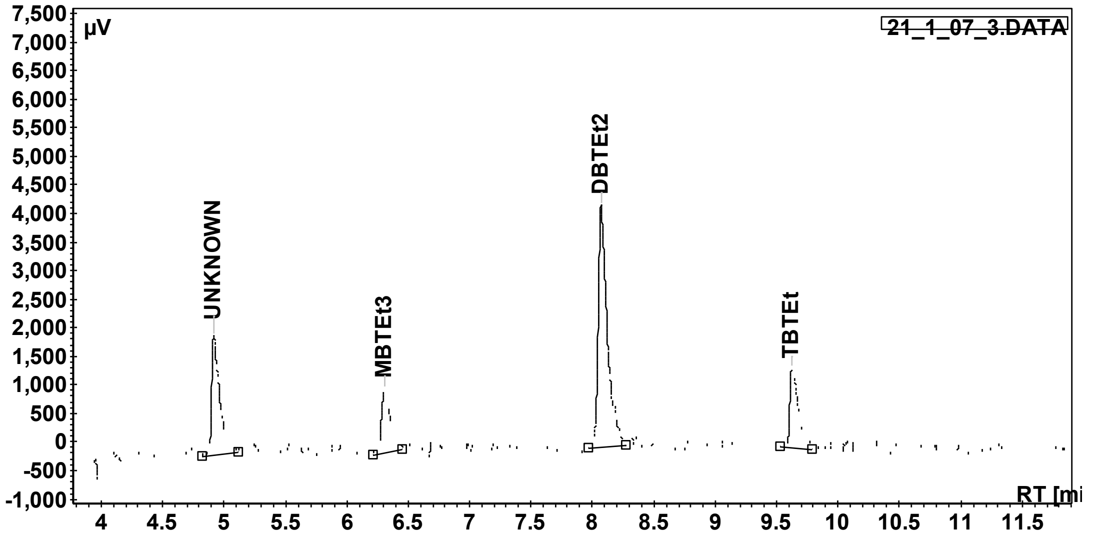


Figure 42. Partial chromatogram of ultrasonicated and derivatised TBT-spiked solution showing TBT, degradation products DBT and MBT and an unknown compound

The tailing of the unknown peak indicated that it was probably a tin compound. Its short retention time would support the unknown being an even lighter compound, with a lower boiling point, than MBT. It is possible that the unknown peak is that of tetra-ethyltin formed by ethylation of inorganic tin (resulting from the complete debutylation of the TBT).

$$Bu_3SnQ \longrightarrow Bu_2SnQ_2 \longrightarrow BuSnQ_3 \longrightarrow SnQ_4$$

A hypothesis that TBT could eventually be degraded to inorganic tin by debutylation was therefore supported by these preliminary results.

During ultrasonication cavitation bubbles are formed and their rapid expansion or collapse creates extreme conditions of temperature and pressure. It has been reported that up to 4000-5000 K and hundreds of bar pressure can be developed in the cavitation bubbles. Due to the high energy input hydrogen and hydroxyl radicals are formed from the dissociation of water[244]:

$$H_2O \rightarrow H^* + {}^*OH$$

The degradation of organic compounds, including organotins, in aquatic solutions is attributed to their oxidation by the *OH radicals[242, 245]. The degradation reactions of TBT by *OH, which are the proposed mechanisms for the UV/TiO_2, UV-Fe(III) and ozone abiotic degradation of TBT, may apply here as well (Chapter 2, Schemes 1-3).

The dissociation energy for the H-O bond in water (H-O-H) is *ca* 118 kcal/mol[246] and it is greater than the Sn-C bond dissociation energy in organotins (50-75 kcal/mol)[60]. It is therefore possible that the ultrasonication provides sufficient energy so that debutylation occurs by homolytic fission of the Sn-C bond. Rehorek and Janzen[245] have investigated the sonic degradation of some organotin compounds in benzene solutions and they found evidence of alkyl radicals formation after 20 min of ultrasonication (55kHz). The formation of alkyl radicals was attributed to Sn-C bond fission due to the cavitation effects of the sonication.

Despite the fact that some TBT was destroyed, the efficiency of ultrasonication was not satisfactory as more than 50% of the TBT still remained in the solution after 30 min treatment. Moreover, the treatment period of 30 minutes for such a small volume of sample was considered to be too long to be used in a commercial treatment plant. Even longer treatment times would be required for sludge samples. Destruction of TBT using ultrasonication would require costly specialised equipment, personnel and forbidding energy and time input to achieve acceptable results. This method was not explored further.

6.3 Assessment of stabilisation efficiencies

Stabilisation was the approach next examined in the present study. It was regarded as potentially more cost-effective as their energy and capital investment requirements were less, also it could be carried out on site without the need for transporting the contaminated material. Also, the company, Land and Water Ltd, had used this approach for other types of contamination encountered in dredgings and therefore the personnel were familiar with it. The equipment necessary was considered to be easily accessible and simple to use.

This approach is based on the prevention of leaching of TBT contamination into the environment by the fixation of TBT, so several different solid matrices were evaluated for this purpose.

The efficiency of materials was initially assessed using spiked water samples and later using spiked sediment samples. In order to determine the amount of TBT leaching, a standard leaching test, BSEN 12457_3:2002, was adapted for TBT.

The stabilisation of TBT was based on immobilisation of the contaminant on a solid matter with such efficiency that when the solid matter was flushed with water the contaminant would remain fixed on the solid matter and would not be mobilised. Fixation was achieved by physical and chemical adsorption of the TBT on the surface of the solid materials studied. From the materials evaluated here, some had been evaluated before (Chapter 2) while for others no published data for their effectiveness on immobilising TBT exist as yet. The categories of materials evaluated here are: carbon products, clays, organically modified clays, iron, cements and fly ash.

6.3.1 Leaching test

6.3.1.1 Introduction

The ability of a stabilisation material to prevent the leaching of TBT from contaminated sediments was assessed by mixing a TBT-contaminated sample with the candidate material and by subjecting the mixture to the BSEN 12457_3:2002 leaching test. BSEN 12457_3:2002 "Characterisation of waste-Leaching-Compliance test for leaching of granular waste materials and sludges. Part 3: Two stage batch test at a liquid to solid ratio to 2 L/kg (2L/S) and 8 L/kg (8L/S) for materials of a high solid content and with a particle size below 4 mm (without or with size reduction)" is the default test to be used for granular waste. The leachate produced was then analysed using the method described in Section 5.3.10.

The BSEN 12457_3:2002 leaching test is a 24 h test with two stages. During the 1st stage the sediment is shaken in a glass bottle (with PTFE-lined screw cap) with water at a ratio of 2 L/kg dry sediment wt for 6 h. During the second stage the sediment is re-shaken with water at a ratio 8 L/kg dry wt for 18 h. At the end of each stage the water (leachate) is separated from the solids and the TBT content is determined in the extract solution. A typical water-solids separation procedure is to stop agitating the glass bottle, leave the larger solid particles to settle and then filter through a 0.45 μm membrane filter under vacuum. The solids and filter from the first stage are then transferred to a larger bottle for the second stage. As this leaching test was not designed specifically for TBT contamination, some adaptations were found to be necessary.

6.3.1.2 Experimental

In order to test for butyltin losses during the water-solids separation step, 120 mL aliquots of deionised water were spiked with 40 μL of a 6.25 μg Sn/mL (as TBTCl) solution in methanol resulting in solutions of 0.002 μg Sn/mL (as TBTCl). The spiked-water samples were shaken for 3 hours, filtered and the filtered water was analysed according to Section 5.3.10. A control TBTCl solution of the same volume and spiking level was analysed (according to Section 5.3.10) without filtering after 3 hours of shaking.

The filters used were membrane and glass fibre filters of 47 mm diameter. The membrane filters were: cellulose (0.45 μm, HATF-Mixed cellulose esters, triton free, protein binding 150 μg/cm^2, Millipore), polyvinylidene fluoride (0.45 μm, HVLP-Durapore membrane, PVDF, hydrophilic, protein binding 4 μg/cm^2, Millipore), Teflon (0.5 μm, polypropylene backed, Whatman), Mitex (5 μm, PTFE, Millipore) and polycarbonate (0.4 μm, Nuclepore). The glass fibre filters were: MF300 (0.7 μm, Fisherbrand), GF/C (1.2 μm, Whatman) and GF/F (0.7 μm, Whatman).

6.3.1.3 Results and discussion

Significant losses of butyltins (up to 70%) were observed with all types of filters (Figure 43).

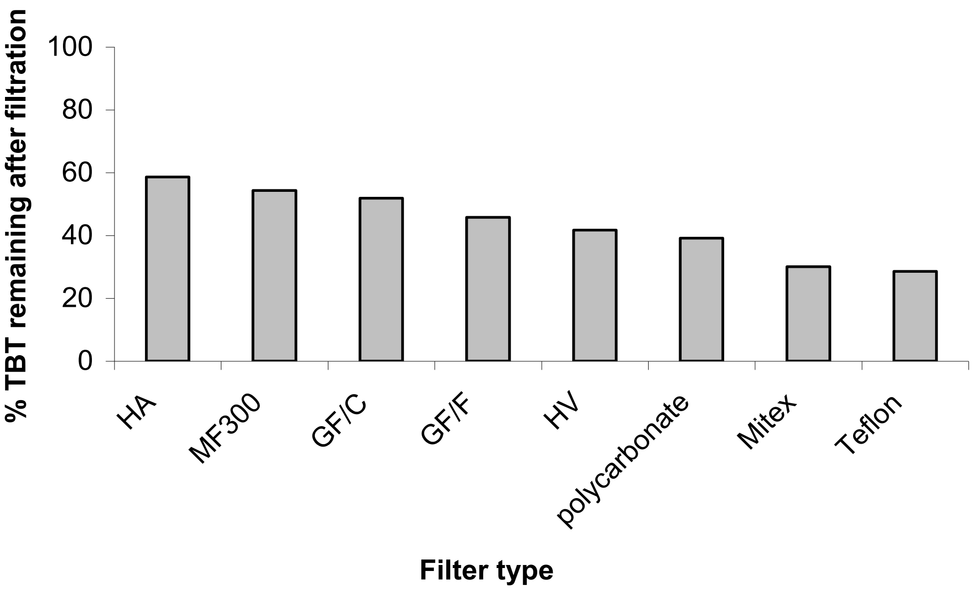


Figure 43. % TBT remaining compared to control (single measurements)

The losses were attributed to adsorption of the butyltins on the filters, which confirms findings reported elsewhere[247, 248], where TBT losses of up 50%, depending on the initial concentration, were observed using cellulose membrane filters (0.45 μm) for TBT-spiked solutions of 20-100 μg/L TBT. One of the studies[247] reports that the recovery was >85% in tests where centrifugation was used instead of filtration.

6.3.1.4 Conclusion and alternative procedure

Since TBT losses during filtration of the leachate were significant, it was decided to use centrifugation for water-solids separation. To test the recovery after centrifugation, 120 mL of deionised water was spiked with 0.04 mL of a 6.25 μg Sn/mL methanolic solution of the TBTCl. Instead of the filtration, the solution was decanted to 50 mL disposable polypropylene centrifuge tubes (Fisher, UK) and centrifuged at 6700 xg for 30 min. The supernatant was then transferred to glass flasks, to be analysed (Section 5.3.10). The recovery was 93% (single measurement) compared to a control solution of the same volume that had been spiked with TBT in the same way, but had not undergone centrifugation (or filtration). Thereafter, the centrifugation procedure was adopted instead of filtration.

6.3.2 Candidate materials

6.3.2.1 Coal and charcoal

Coal was created by the partial decomposition of plants under anaerobic conditions, which were buried. Coal can be found mixed with fossils, stratified and interbedded with sedimentary rocks. It is therefore a mixture of complex high molecular structures, containing a large amount of carbon and smaller amounts of other elements, such as hydrogen, oxygen, nitrogen and also sulfur, phosphorus and traces of other elements. Inorganic substances are also present, such as quartz, feldspar and clay minerals. The content varies and coal can be ranked according to the ratio of carbon content to volatile constituents (H, O and N). The rank is: lignite<subbituminous<bituminous coals.[98]

Charcoal is a black, porous, man-made material, which resembles coal and is generated by heating biomass (wood, bones and sugar) or polymers in the absence of oxygen.[249] It contains largely carbon but with some volatile constituents and inorganic substances.[250]

Commercial coal and charcoal, of unknown origin, were purchased from a local coal merchant (Southampton, UK).

6.3.2.2 Coke and OrganoDec

Coke is a porous material produced from the heating of bituminous coal in the absence of air.[251] Any volatile constituents of coal are driven off and recovered as useful compounds.

The solid carbon remaining is coke. Another useful by-product is a liquor recovered from the cooling of the gas, from which tar is extracted.[251, 252]

Two coke-related materials were evaluated in this study. One was commercial coke of unknown origin that was purchased from a local coal merchant (Southampton, UK) and the other was OrganoDec, a coke-derived material (grain size <1.5 mm, fixed carbon 86% wt, moisture content <0.05%), which is a remediation agent marketed by the dredging company DEC (UK).

6.3.2.3 Activated carbon materials

Activated carbon is a long-established material for the removal of organic contaminants from water[253] and has been also successfully used for TBT contamination (Section 2.3.1). The raw material for activated carbon is coal, nutshell such as coconut shells and palm-kernel shells, bamboo, wood chips, sawdust, corncob and seeds.[89] Activated carbon is produced by physical or chemical activation. Physical activation involves carbonisation (pyrolysis in argon or nitrogen atmosphere at 600-900 ˚C) and activation/oxidation, where raw or carbonised material is exposed to oxidising atmospheres (using CO_2, O_2 or steam) and temperatures of 600-1200 ˚C. Chemical activation is usually preferred due to the lower temperatures and shorter time necessary. It is performed by impregnating the material with acids (H_3PO_4) or bases (KOH, NaOH) or salts ($ZnCl_2$) and carbonising it at temperatures of 450-900 ˚C.

The granular activated carbons tested here were: a bituminous coal-based activated carbon material for the removal of organic compounds and pesticides from wastewater (Aquacarb 207 EA 12x40, mean particle diameter 0.8-1.2 mm, surface area 1000 m^2/g, moisture content <10%), provided by Chemviron-Calgon (UK) and a granular charcoal activated for gas adsorption (0.85-1.70 mm, 10-18 mesh) purchased from BDH (UK). Aquacarb was tested in its granular form and also after manually grinding to a fine powder.

The powdered carbons were: AP, a powdered activated carbon from bituminous coal (Aquacarb 207AP, grain size <0.074 mm, surface area 950-1100 m^2/g, moisture content <10%, pH 7-8) and CP, a powdered activated carbon from coconut shell (Aquacarb 203CP, grain size <0.074 mm, surface area 700-800 m^2/g, moisture content <10%, pH 9-11), both provided by Chemviron-Calgon (UK).

6.3.2.3.1 Particle size and thermogravimetric analysis (Aquacarb and OrganoDec)

A thermogravimetric analysis of both OrganoDec and Aquacarb and a particle size analysis of OrganoDec were carried out in order to explore their properties further.

6.3.2.3.2 Experimental

The particle size of OrganoDec was measured using a particle size analyser (Coulter N4 Plus) with a 10 mW laser operating at 90˚ angle. A thermogravimetric analysis (TGA) was carried out for both OrganoDec and Aquacarb (Thermogravimetric Analyser TGS-2, Perkin Elmer). Both materials were subjected to the same temperature program from 25 ºC to 950 ºC increasing at a 5 ºC/min rate, the analysis being carried out in air.

6.3.2.3.3 Results and discussion

The particle size analysis of the OrganoDec showed a bimodal distribution (Figure 44) of the particle size, with maxima at 417±168 nm (23%) and 2835±1059 nm (77%). The slightly higher maximum (2835±1059 nm) given in the particle analysis might imply a tendency of the particles to aggregate and therefore appear larger.

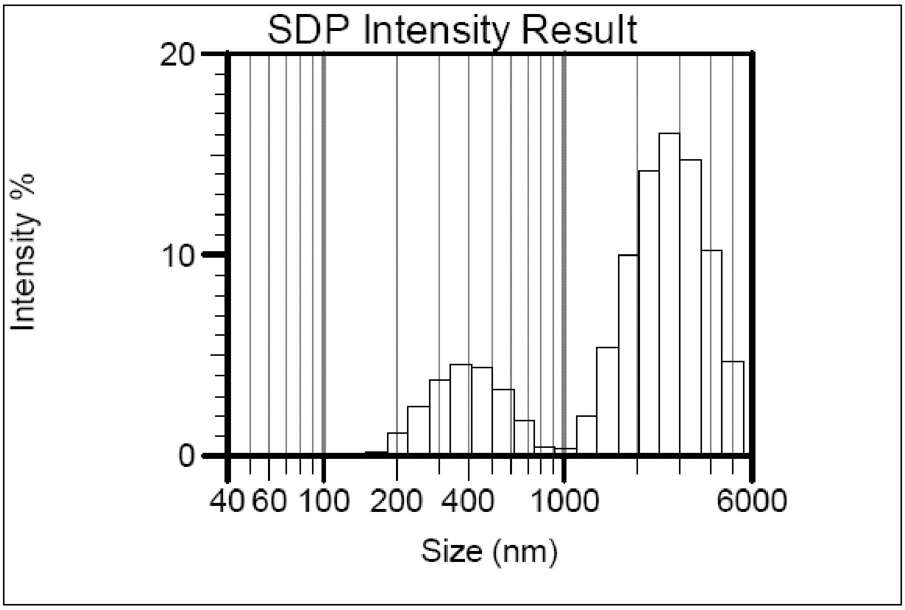


Figure 44. Particle size analysis results for OrganoDec

The TGA analysis of Aquacarb (Figure 45) showed an initial 5.5 % weight loss between 30 ˚C and 100 ˚C, which was assumed to be mainly due to evaporation of moisture adsorbed on the activated carbon material and perhaps other impurities with low boiling points. At the same temperatures OrganoDec had a 37.91% loss that was attributed to water (Figure 46). This assumption was supported by the fact that OrganoDec appeared wet. Even though the Material Data Sheet for OrganoDec specified that the moisture content was < 0.05 % the specification might refer to the initial form of the material. Water might have been mixed in to eliminate the risk of dust explosion and to make it more manageable. Further weight loss, characteristic of the combustion of carbon, was observed starting at *ca* 570 ˚C for Aquacarb (81.52 %) and *ca* 480 ˚C for OrganoDec (55.01 %). The remaining is the ash content of the material, such as metals and minerals. The ash content for Aquacarb was 12.96 % and for OrganoDec 7.08 %. The content of the two materials, apart from the water content, appears to be very similar, as expected as both materials mainly consist of carbon.

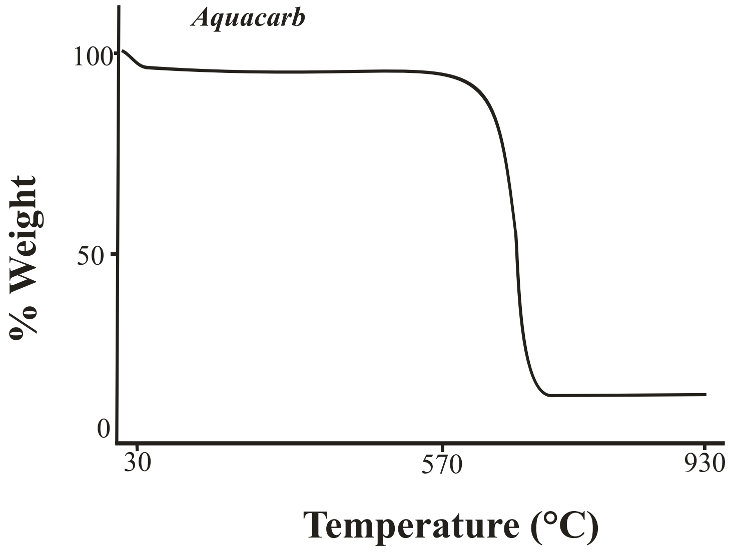


Figure 45. TGA analysis of Aquacarb

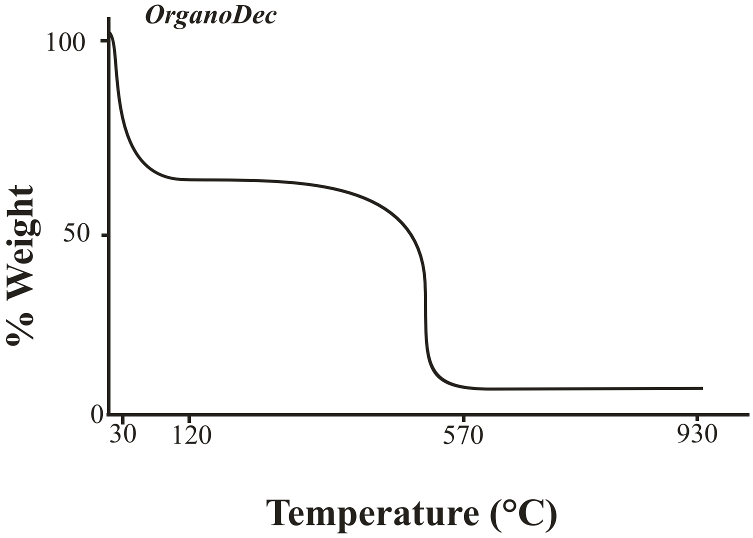


Figure 46. TGA analysis of OrganoDec

6.3.2.4 Clays

6.3.2.4.1 Bentonite

Bentonite is a general term for hydrated alumino silicates $Al_2O_3.4SiO_2.H_2O$ + x H_2O. They were formed by the weathering of volcanic materials or from rocks of sedimentary origin. Crude bentonite contains 75-85% montmorillonite, 5-10% illite and 5-10% other minerals. Bentonite clays have a layer structure. Their structure can be described as alumina sheets sandwiched between tetrahedral silica units. (Figure 47) The water penetrates between the alumina layers and the lattice structure expands resulting in swelling of the clay.

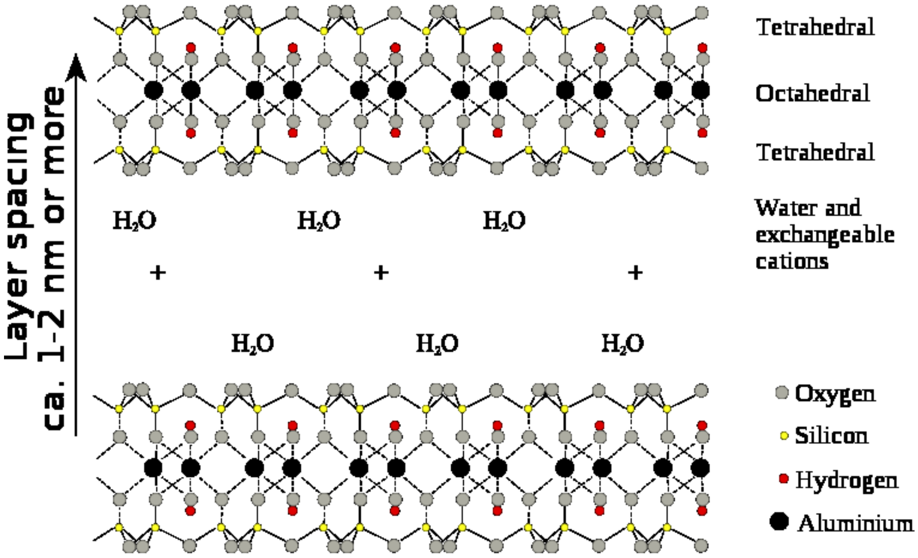


Figure 47. Crystal structure of montmorillonite[254] (main constituent of bentonite)

Bentonite minerals are usually complex, as ionic replacements take place within the lattice of the crystal. Due to the ionic replacements the layers are charged. More specifically, if an ion of Mg^{2+} replaces an ion of Al^{3+} then a negative charge is created on the surface. Usually, this negative charge is neutralised by exchangeable cations that adsorb on the bentonite surface. The amount of this kind of ions is defined as the Cation Exchange Capacity (CEC) of the clay and it is expressed as meq per 100 g. There are two types of bentonite: sodium bentonite and calcium bentonite. One of the main characteristics of bentonite is its high CEC value (70-100 meq/100 g). Bentonite adsorbs water resulting to swelling of the clay.

The rheological properties of the bentonite suspension are used in geotechnical engineering, as it is often used to create a viscous material or gel for sealing purposes e.g. drilling. Calcium bentonite does not swell when wet, but has greater adsorption characteristics. Wet calcium bentonite can be converted by ion exchange to sodium bentonite through mixing with sodium carbonate.

The bentonite tested in this project was Steebent CE (100% bentonite, impurities: up to 1% free crystalline silica, up to 2% sodium carbonate, pH 9-10) provided by the company "Steetley Bentonite" (UK).

6.3.2.4.2 Sepiolite

Sepiolite, a hydrated magnesium silicate $Si_{12}Mg_8O_{30}(OH)_4(OH_2)_4.8H_2O$, is a secondary mineral associated with serpentine. It has a very high surface area of 320 m^2/g (B.E.T.) due to pores and channels that resemble zeolithic channels (Figure 48).

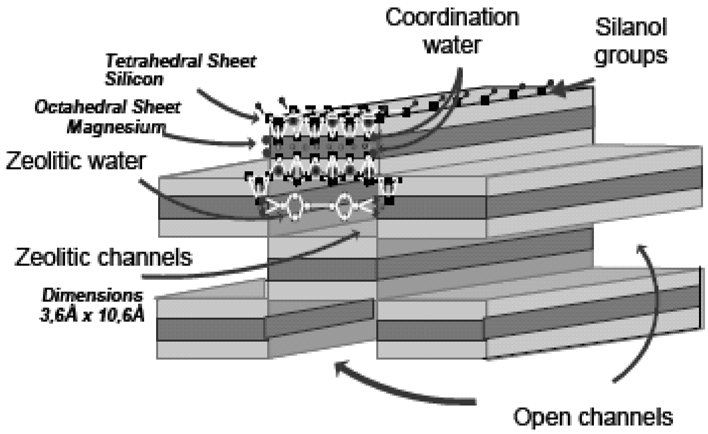


Figure 48. Structure of sepiolite[255]

The pores and channels are created due to ionic replacement in the structure of the clay. The very high surface area makes it a very good adsorbent and its structure gives useful rheological properties. Due to the difference in the chemical structure of sepiolite compared to bentonite (it is not layered), sepiolite is not a swelling clay and its exchange capacity is only 10-15 meq/100 g.

The sepiolite tested in this project was Pangel S9 (sepiolite clay >99%, crystalline silica <1%, pH (10% in water) 8.5±0.5), provided by "Steetley Bentonite" (UK).

6.3.2.5 Organically modified clays

Organically modified forms of sepiolite were also provided by the company "Steetley Bentonite" (UK) for evaluation. The modified sepiolites had differences in polarity: Pangel B5 had the lowest polarity, followed by Pangel B10, Pangel B20 and Pangel B40 that had the highest polarity. The ingredients of the Pangel B series are shown in Table 20.

Material	**Contents**
Pangel B5	quarternary ammonium compound, dimethyl benzyl hydrogenated tallow alkyl chloride < 20 % sepiolite clay > 80%, quartz <1%
Pangel B10	quarternary ammonium compound, dimethyl benzyl hydrogenated tallow alkyl chloride < 15 % sepiolite clay > 80%, quartz <1%
Pangel B 20	quarternary ammonium compound, dimethyl benzyl hydrogenated tallow alkyl chloride < 15 % sepiolite clay > 85%, quartz <1%
Pangel B40	quarternary ammonium compound, methyl benzyl bis (hydrogenated tallow alkyl) chloride < 15 % sepiolite clay > 85%, quartz <1%

Table 20. Contents of the organically modified clays Pangel B

6.3.2.6 Iron

Zero valent iron (ZVI) has been used for the removal of numerous pollutants[256] mainly chlorinated organic compounds or Cr(VI). As a strong reducing agent, zero valent iron is reacting with oxidizing pollutants converting them to less toxic forms. ZVI particles exist in many forms, such as carbon supported ZVI nanoparticles[257], Fe(0)/Fe_3O_4 composites[258], Fe(0)-Ti[259] or nanoscale Pd/Fe particles[260].

Some idea of the mechanism by which Fe(0) reduces metals is given in the example below, in which zero valent iron in the form of a Fe(0)/Fe_3O_4 composite reduces Cr(VI).

According to Coelho *et al*[258], Fe(0) reduces Fe (III) to Fe(II) by an electron transfer via the metal-oxide interface of a Fe(0)/Fe_3O_4 composite prepared with mechanical alloying, according to the following thermodynamically favoured reaction:

$Fe^0 + 2Fe^{3+} \rightarrow 3Fe^{2+}$ ΔE=1.12 V

and Fe(II) reduces Cr(VI) to less toxic forms of chromium:

Fe^{2+} + Cr (VI) → Fe^{3+} + reduced forms of Cr

The Fe(III) generated from the reduction of Cr(VI) receives an e^- from Fe(0) which generates new Fe(II) for the reduction of Cr(VI). The magnetite's octahedral structure allows both Fe(II) and Fe(III) to be accommodated. Coehlo *et al* argue that the magnetite surface increases the reactivity of Fe(0), as it had been found that the surface of Fe(0) quickly oxidised in the environment and became inactive.

The cost of ZVI materials depends on the quantity purchased and their type, according to a study by the US Navy 20-77$ per pound was the price range in 2005.[261] Apart from ZVI other forms of iron are often used which are more economical solutions as they are by-products of other processes, e.g. iron chips.

The ZVI used in this work was from two sources. One material was an aqueous suspension from the company Toda Kogyo (US). The average particle size was 70 nm, the average reactive surface area 30 m^2/g, particles had an iron oxide (Fe_3O_4) shell and an elemental iron core.[262] The other material was a clean ground iron product, of unknown origin, from the company Connelly-GMP (US).

6.3.2.7 Cements

6.3.2.7.1 Portland cement

The most common form of cement is Portland cement. It is made by heating a mixture of limestone, clay and other materials that may include fly ash and shale. The materials are fired together in a kiln to about 1400 ˚C. The heat drives off water and CO_2. The clinker is then mixed with a small amount of gypsum and the mixture is ground to produce cement.[263]

The typical composition of Portland cement[263, 264] is: 67% CaO ("C"), 22% SiO_2 ("S"), 5%

Al_2O_3 (“A”), 3% Fe_2O_3 (“F”) and 3% of some other compounds (MgO, TiO_2, Na_2O, K_2O, SO_3, lime and chloride). Normally four main groups are formed:

- Alite, 50-70% Ca_3SiO_5 (“C_3S”)
- Belite, 15-30% Ca_2SiO_4 (“C_2S”)
- Aluminite, 5-10% $Ca_3Al_2O_6$ (“C_3A”)
- Ferrite, 5-15% $Ca_4Al_2Fe_2O_{10}$ (“C_4AF”)

The compressive strength of cement is mainly due to alite and belite. The cementing effect of Portland cement derives from the hydration reaction of alite and belite. The reaction of cement with water is a direct addition of water molecules and a hydrolysis which is usually also referred to as hydration for convenience. C_3S and C_2S are believed to undergo hydrolysis and the final products are $Ca_3Si_2O_7.3H_2O$ and $Ca(OH)_2$.

The hydrolysis reactions given below are by approximation and are not stoichiometric:

For alite (C_3S): $2\ Ca_3SiO_5 + 6\ H_2O \rightarrow Ca_3Si_2O_7.3H_2O + 3\ Ca(OH)_2$

For belite (C_2S): $2\ Ca_2SiO_4 + 4\ H_2O \rightarrow Ca_3Si_2O_7.3H_2O + Ca(OH)_2$

The reaction of aluminite with water is very violent and results in immediate stiffening of the paste (flash set). To prevent this, gypsum is added to the cement clinker. The hydration reaction can be represented by approximation:

$$Ca_3Al_2O_6 + 6\ H_2O \rightarrow Ca_3Al_2O_6.6\ H_2O$$

Ferrite is believed to hydrate into tricalcium aluminate hydrate and an amorphous phase, probably $CaO.Fe_2O_3.aq$.

Typically in Portland cement the hydration is 75% complete within 28 days.

The remediation of inorganic and organic pollutants by stabilisation/solidification using cement has been reported. For inorganic pollutants many different additives and ways of solidification have been employed. These include solidification by cement, pozzolans, thermoplastic method, organic polymerisation, encapsulation and organophilic clay. In the case of pollution by organics, pure cement was used for the remediation or in some cases together with organophilic clay, natural bentonite, activated carbon, activated carbon combined with H_2O_2, Fe(II), carbon black and activated carbon combined with organophilic clays.[265]

6.3.2.7.2 Alumina cement

Alumina cement is a totally different type of cement that was created in order to solve the problem of the degradation of Portland cement by gypsum-bearing waters. Even though its composition differs from Portland cements, the concreting techniques are similar.

As its name implies, alumina cement contains a high percentage of alumina. More specifically, alumina cement consists of approximately equal amounts of lime and alumina (40% each) and about 8% silica. The raw materials are limestone or chalk and bauxite, an erosion product consisting of hydrated alumina, iron and titanium oxides and small amounts of silica. During manufacturing of alumina cement, bauxite and limestone are crushed to lumps of about 100 mm and fed into the furnace. The temperature in the furnace goes up to fusion temperature of about 1600 °C. The product is cooled and then ground in tube mills. Because of the high cost of bauxite and high temperature of firing during manufacturing and the hardness of the alumina cement that requires high power consumption and considerable wear of the tube mills, the cost of this cement is much higher than Portland cement.[263]

A typical composition of alumina cement[263] is 3-8% SiO_2, 37-41% Al_2O_3, 36-40% CaO, 9-10% Fe_2O_3, 5-6% FeO and smaller amounts of TiO_2 and MgO. The main groups are CA and C_5A_3. The main hydration products are CAH_{10}, C_2AH_8, alumina gel and no $Ca(OH)_2$ exists. The absence of $Ca(OH)_2$ is responsible for the resistance of the cement to sulphate attack.

Desiccated aluminous cement concrete has very high resistance to dry heat and it is often used for the construction of furnaces. Temperatures as high as 1800°C can be withstood by concrete made from special white calcium aluminate cement and a fused alumina aggregate. This cement consists of 72% alumina, 26% lime, 1% iron and silica.[263]

6.3.2.8 Fly ash

Fly ash or pulverised fuel ash (PFA) is a residue from the combustion of coal, which is trapped in the chimneys of power stations, to reduce atmospheric pollution. It contains silica and lime but its exact composition varies according to the composition of coal burnt. Fly ash has been found to be useful as a component of concrete, mixed in with cement, for construction purposes. Fly ash is the most common artificial pozzolanic material (reacts with $Ca(OH)_2$ to form compounds with cementitious properties) and is therefore used as a Portland cement replacement material (15-40% Portland cement wt) not only because it is often cheaper but also because of its strength development and resistance against sulphate attack and some other destructive elements.[263] Other uses of fly ash include filling of embankments, grouting and road construction.[266]

Fly-ash has been found to reduce the mobility of Cu by 98.2% and Pb by 99.9% in Cu and Pb contaminated soils in batch trials and also reduced the bioavailability of the metals in a two year field trial. [267]

6.3.2.9 Comparison of the properties of candidate materials

The candidate materials that were assessed were sorbent materials and solidifying additives. Not all the sorbents had the same properties as some adsorbed through van der Waals forces while others through ionic forces or hydrophobic interaction (Table 21). The solidifying additives were not expected to contribute to the adsorption of TBT but their effect on the amount of TBT that leached out of the sediment after their addition was studied instead.

Candidate materials	***Properties assessed***
Sorbents	
Activated carbon materials	Adsorption (van der Waals forces)
Coal and charcoal	Adsorption (van der Waals forces)
OrganoDec and coke	Adsorption (van der Waals forces)
Bentonite	Adsorption (ionic forces)
Pangel S9 (sepiolite)	Adsorption (zeolithic chanels)
Pangel B (B5, B10, B20, B40)	Adsorption (hydrophobic forces)
Iron	Adsorption (ionic forces)
Solidification additives	
Portland cement	Effect on the leaching of TBT
Alumina cement	Effect on the leaching of TBT alone and combined with Portland cement
Fly ash	Effect on the leaching of TBT alone and combined with Portland cement

Table 21 Comparison of the properties of the candidate materials

6.3.3 Assessment of sorbent materials using spiked water solutions

6.3.3.1 Introduction

The efficiencies of candidate stabilisation materials were initially tested using butyltin-spiked water solutions. Each stabilisation material was added to a TBT-spiked aliquot of water. The volume of water was the typical amount of water necessary to carry out the leach test (BSEN 12457_3:2002).

6.3.3.2 Materials

The materials assessed were OrganoDec, Aquacarb in its original granular form and also in a (manually) ground form and granular activated carbon for gas absorption. Also, a series of organically modified sepiolite (clay) with increasing polarity (Pangel B5<B10<B20<B40) and pure sepiolite clay (Pangel S9) were evaluated. Bentonite clay was also tested. Additionally, zero valent iron, in granular ZVI and ground iron form, was evaluated.

6.3.3.3 Experimental

As this step was mainly used as a screening tool for choosing the most promising materials, and in order to minimise the analysis time and consumption of materials, only the first step of adding water to a liquid (L) to solid (S) ratio of 2L/S of the leaching step was carried out and the leachate was analysed after 3 hours of shaking.

For these experiments 120 mL aliquots of deionised water were spiked with 30-40 µL of a 6.25 µg Sn/mL methanolic solution of the TBTCl (or 10 µL of a 10 µg Sn/mL solution for Aquacarb tests). A small amount (see Table 22) of each material to be assessed was added. For each material three replicates were analysed, together with a control aliquot of water without the sorbent material. The mixture was shaken on a roller bed (Luckham, Multimix Major) at maximum speed for 3 h and then centrifuged for 30 min at 6700 xg to separate the solids. In the case of Pangel B5, B10 and B20, to prevent blocking of the SPE cartridges during the extraction step of the analysis, 5g of NaCl was added to assist the aggregation and settlement of the clay particles and a second 30 min centrifugation at 6700 xg was carried out. The leachates were analysed according to Section 5.3.10.

In order to determine the pH of some of the materials to be tested, a small amount of each one (5-10% w/v) was diluted in deionised water. The pH of the suspension was measured with a pH meter (model 8521, Hanna Instruments).

6.3.3.4 Results and discussion

The limit of detection for each batch of samples may have differed slightly and it was calculated each time according to the performance of the GC-PFPD and the exact volume of sample treated. The concentration and the proportion of the butyltins remaining in the leachates, compared with an untreated (control) butyltin solution, are shown in Table 22.

The partition coefficient Kd shown is defined as:

$Kd=[TBT]_{ads}/[TBT]_{sol}$

where: $[TBT]_{ads}$ is the concentration of TBT calculated to be adsorbed on the additive at equilibrium and $[TBT]_{sol}$ is the concentration of TBT measured in solution at equilibrium.

The materials tested are ranked according to their decreasing Kd values. The higher the Kd, the higher the adsorption of butyltins on the solid material, the more efficient the material in removing the butyltins from the aqueous solution.

Material in water -% (w/v)	**Initial concentration of each butyltin (ng/L)**	**TBT in treated solutions: (ng/L) (%) Kd(L/kg)**	**DBT in treated solutions: (ng/L) (%) Kd(L/kg)**	**MBT in treated solutions: (ng/L) (%) Kd(L/kg)**
OrganoDec-**8%**	2100	8±5 (0.4%±0.2%) Kd=3138	19±7 (0.6%±0.3%) Kd=1314	45±27 (1.4%±1.3%) Kd=548
Pangel B10-**2.5%**	1600	27±2 (1.7%±0.2%) Kd=2330	82±1 (5.2%±0.1%) Kd=740	<33 ng/L (<2.06%) Kd>901
Pangel B5-**2.5%**	1600	28±3 (1.8%±0.2%) Kd=2246	137±21 (8.8%±1.3%) Kd=427	68±13 (4.3%±0.8%) Kd=901

Material in water -% (w/v)	**Initial concentration of each butyltin (ng/L)**	**TBT in treated solutions: (ng/L) (%) Kd(L/kg)**	**DBT in treated solutions: (ng/L) (%) Kd(L/kg)**	**MBT in treated solutions: (ng/L) (%) Kd(L/kg)**
Aquacarb ground-**4%**	1050	<13 ng/L (<1.24%) Kd>1914	Not added	Not added
Pangel B20-**2.5%**	1600	36±2 (2.3%±0.1%) Kd=1738	138±9 (8.9%±0.6%) Kd=424	598±55 (38%±4%) Kd=67
Pangel B40-**2.5%**	1600	56±9 (3.6%±0.6%) Kd=1103	73±12 (4.7%±0.8%) Kd=321	50±10 (3.2%±0.6%) Kd=480
Aquacarb granular-**8%**	1050	<16 ng/L (<1.52%) Kd>957	Not added	Not added
Pangel S9-**2.5%**	1600	117±13 (7.5%±0.8%) Kd=507	158±22 (10%±1.4%) Kd=365	229±19 (15%±0.2%) Kd=239
Aquacarb granular-**4%**	1050	50±20 (5%±2%) Kd=480	Not added	Not added
Ground Iron-**8%**	2100	228±324 (11%±15%) Kd=99	498±800 (24%±38%) Kd=39	139±57 (6.6%±3%) Kd=169
Activated C (for gas absorption)-**8%**	2100	273±133 (13%±7%) Kd=80	86±23 (4%±1%) Kd=281	473±152 (23%±6%) Kd=41
Granular ZVI-**8%**	2100	851±85 (41%±4%) Kd=18	1377±192 (66%±9%) Kd=6	224±81 (11%±2%) Kd=101
Bentonite-**2.5%**	1600	1192±39 (74%±2%) Kd=14	1546±37 (103%±2%) Kd=1	77±1 (5.0%±0.04%) Kd=791

Table 22. Partitioning of butyltins between candidate additives and water

The partition of butyltins should be discussed taking into account the pH of the solution where the partitioning took place, as the pH value determines the form of the butyltins in water and the nature of the adsorbent surfaces. The pH values of the suspension of the materials in water are shown in Table 23 below.

Material	**pH** (±0.5)
OrganoDec	8-9
Aquacarb	6
Gran. charcoal activated for gas absorption	9
Pangel B5	8
Pangel B10	8
Pangel B20	8.5
Pangel B40	8.5
Pangel S9	8.5
Bentonite	9-10
Ground Iron	6.5-7
Granular ZVI	9.5-10

Table 23. The pH values of candidate additives in water

Carbon materials

OrganoDec performed very well. The adsorption of all three butyltins from solution was exceptionally good.

Aquacarb, initially tested in its granular form, also exhibited excellent TBT-adsorbing properties when added as an 8% mix with water. It was less effective however when mixed in the granular form at 4%. After grinding, to reduce the particle size and increase the surface area, its adsorption efficiency recovered resulting in TBT levels in solution dropping below the detection limit of *ca* 15 ng/L.

OrganoDec and Aquacarb performed significantly better than activated carbon marketed for gas absorption. The activated carbon for gas adsorption that was tested was however rather old and potentially deactivated. It was therefore not expected to be efficient.

In general, forces that may contribute to adsorption of an adsorbate onto an adsorbent are: coulombic forces (attraction, repulsion), ionic species-neutral species attraction, covalent bonding, ionic species-dipole attraction, dipole-dipole attraction, dipole-induced dipole attraction, hydrogen bonding and van der Waals attraction. In water, some of these forces, such as hydrogen bonding, are not expected to contribute to the adsorption of an adsorbate on an adsorbent because water can always bind more strongly. Attraction between organic compounds and activated carbon is believed to be due to van der Waals forces between the crosslinked graphitic crystallite plates that form micropores and the organic compounds.[253] Compounds that are non polar and are large tend to adsorb to activated carbon better. The removal of TBT from solution was therefore attributed to such adsorption forces on the Aquacarb.

In general, differences can be attributed to the total surface area difference as well as the potential difference in the carbon activation procedure and to the source of carbon in each case.[268] These factors would result in a difference in the shape, size of its pores and the chemical groups on the carbon surface that would determine its behaviour towards the butyltins. As activated carbons are rarely pure materials it is likely that secondary binding mechanisms may also be responsible for TBT adsorption.

Organically modified sepiolite products

The TBT removal efficiencies of the Pangel series ranged from 98.3% for Pangel B10 to 96.4% for Pangel B40.

The removal of organotins from solution (pH≈8) by the Pangel B products was attributed to the hydrophobic attraction forces of the organic additives together with the adsorption capacity, due to the zeolithic structure of sepiolite. As expected the decreasing efficiency of Pangel B products for TBT followed their decreasing hydrophobicity because as their hydrophobicity decreased, less hydrophobic sites were available for adsorbing the TBT.

Clays

According to Hoch *et al*[95, 269], adsorption of organotins on clays is attributed to the ionic attraction by functional groups on the surface of clays. Such sites can be: hydroxyl (-OH), carboxyl (-COOH), phenolic ($-C_6H_4OH$) and amine ($-NH_2$) groups including the SiOH or AlOH surface sites. This type of site can be negatively charged depending on the pH. Other sites are the cation exchange sites of the clays with a permanent negative charge. The cation exchange sites of clays have been created due to isomorphic substitution of a cation of higher valence within the crystal lattice by one with a lower valence.[270]

The optimum pH for the adsorption of TBT is between pH values 6-7, as this is the area that the maximum concentration of negative charges in clays overlaps with the area where the TBT^+ predominates.[29] At higher pH conditions (pH=7-9) hydrophobic forces have been shown by Hoch *et al*[271] to be the main mechanism of TBT adsorption as only small amounts of TBT remain in the ionic form.

Pure sepiolite, at pH 8, was not as efficient as organically modified sepiolite in adsorbing the organotins from water. The removal of TBT by Pangel S9 (92.5% removed) was attributed to the amount of TBT^+ still in solution at pH 8.

Bentonite adsorbed the TBT very poorly (22.4% removed) and had no significant affinity for DBT. In the case of bentonite clay the adsorption of TBT is reported to be pH dependant, as the main mechanism is the binding of TBT^+ to pH-dependant negatively charged sites at the mineral edges. TBT binds less efficiently to the permanent negatively charged interlayer sites, by cation exchange[269], due to its large size (374 $Å^3$) which prevents it from reaching the interlayer adsorption sites. As the pH of bentonite is 9-10, when left without buffering as in the current study, the TBT is converted to its neutral form and the adsorption on bentonite is predicted to decrease. This has been confirmed by partition experiments of TBT between montmorillonite clay and deionised water by Hoch *et al*[269].

MBT has a lower molecular volume[29] which allows better adsorption on the negatively charged sites of the clay and intercalation in the interlamellar areas of smectite-type clays, such as bentonite. Clusters of adsorbed MBT are known to extend some montmorillonite layers from 14 to 22 Å[272]. For MBT the removal efficiency by bentonite is therefore much higher (94.9%) and this has been attributed by Hermosin *et al*[272] primarily to adsorption by cation-exchange and then additional neutral MBT is attracted by hydrophobic forces to the first moiety adsorbed.

Iron

Some removal of TBT was observed, which was attributed to adsorption due to ionic attraction and not reduction of TBT to tin(0). The surface of granular ZVI was vastly higher than that of the ground iron and ZVI was therefore expected to adsorb more TBT. The higher removal efficiency of ground iron (11% TBT remaining) compared to granular ZVI (41% TBT remaining) was attributed to the fact that granular ZVI had an alkaline pH (9-10). Since the point of zero charge (pzc) for the Fe_3O_4, which covers the surface of granular ZVI is at pH 6.5[273] the surface would be negatively charged. Under alkaline conditions most of the TBT is in its neutral form and not much adsorption takes place. In the case of ground iron, its surface appeared to be rust and potential iron oxides are FeOOH, $Fe(OH)_3$ and Fe_2O_3 which have their points of zero charge at pH 7.8-8.5[273] while the solution had a pH of 6.5-7. At these acidic conditions TBT is in its ionic form but the iron oxides and hydroxides are mostly in their positively charged form and they do not have an affinity for TBT^+. Weidenhaupt *et al*[29] did not find any significant adsorption of TBT on FeOOH, neither at pH 4 nor at pH 7. These observations confirm the findings of the current study.

6.3.3.5 Conclusion

The materials OrganoDec, Pangel B10 and ground Aquacarb lowered the TBT concentration to levels only 4-8 times higher than the EQS of 2 ng Sn/L TBT in coastal and estuarine water[53]. Ground Aquacarb, OrganoDec and Pangel B10 were the best performers and were selected for further testing.

6.3.4 Assessment of Pangel B10 using spiked sediments

6.3.4.1 Introduction

The stabilisation of TBT-spiked sediment samples using Pangel B10 was assessed as it was found to be one of the best performing sorbent materials for TBT (Section 6.3.3.4). The experiments were carried out using two different types of sediment as well as different levels of TBT in the sediments. The spiking levels of TBT in the stabilisation experiments were representative of the low and high ends of typical TBT contamination. The typical TBT concentration in sediments in the UK, as reported by Thomas *et al, 2000*[274], was 0.04-5.8 mg/kg dry wt in coastal and off-shore sediments. In Spain Arambarri *et al*, 2003[119] reported 0.05-5.48 mg/kg dry wt TBT in estuarine sediments and Kan-Atireklap et al, 1997[275] reported 0.004-4.5 mg/kg dry wt TBT in coastal sediments in Thailand.

6.3.4.2 Experimental

Fresh surface (upper 5 cm) sediment for spiking was collected (18/2/2007) from a small boatyard on the River Itchen. This sediment was found not to leach out any measurable TBT (< 15 ng/L) in experiments using the leaching test (Section 6.3.1.4). Fresh surface (upper 5 cm) sediment was also collected (5/3/2007) from the Beaulieu estuary (New Forest, UK), which was also found to be suitable for spiking based on the same criteria.

After determining the water content of each sediment according to EN 12880:2000[276] a suitable amount of wet sediment was mixed with Pangel B10 (5% or 20% dry wt Pangel B10). Standard solutions of TBTCl in MeOH (50 and 500 μg Sn/mL) were used for the spiking of the mix. For each set of conditions shown in Table 23, three replicate samples (87.5 g dry wt) of the spiked mix and a control spiked sediment sub-sample (87.5 g dry wt) not containing Pangel B10 were subjected to the leaching test (Section 6.3.1.4).

The necessary amount of water to achieve the 2L/S water/solids ratio was added to each aliquot. After 6 hours of agitation on a roller bed at maximum speed, each sample was centrifuged in polypropylene disposable centrifuge tubes for 1 hour at 4000 xg and 50 mL of the leachate of each sub-sample was analysed for TBT (Section 5.3.10).

6.3.4.3 Results and discussion

In Table 24, the concentration of TBT measured in the leachates of treated samples at equilibrium is shown. The concentration of TBT measured in the leachates of sediment samples that had not been treated is also shown, as this was taken as the baseline against which the treated sediments are judged and to reflect day-to day variation. The Kd values of the TBT partitioning between the mixes of sediment/Pangel B10 and the water are shown, together with the impact that the additive had on the release of TBT into solution expressed as %TBT leaching from the treated samples compared to the untreated.

Sample	**TBT (μg)**	**Pangel B10 added (%)**	**Initial TBT in sediment (mg/kg dry wt)**	**Kd (L/kg)**	**TBT in leachate of treated samples (ng/L)**	**TBT in leachate compared to control (%)**
1 (Itchen sed.)	0.5	5	0.006	200	28±8	53±15
2 (Itchen sed.)	0.5	20	0.006	299	19±5	27±12
3 (Itchen sed.)	2	20	0.024	1378	17±3	14±3
4 (Beaulieu sed.)	500	20	5.7	4861	1175±1103	120±113

Table 24. Leaching test results for samples treated with Pangel B10

The adsorption coefficient (Kd=[TBT]ads/[TBT]sol) for the sediment/Pangel B10 mix was very similar in samples of low TBT contamination (0.006 mg/kg) (Table 24). In samples of higher TBT contamination (0.024 and 5.7 mg/kg) the Kd increased, but as the concentration of TBT in the leachate of treated samples was 20% more on average compared to the leachate of the control, Pangel B10 was not considered efficient enough as it appear to mobilise instead of immobilising the TBT.

The proportion of the spike of TBT that was measured in the leachate of treated samples as well as in samples that were left untreated is shown in Table 25:

Sample	**TBT spike (μg)**	**Proportion of TBT spike in the leachate of the treated samples**	**Proportion of TBT spike in the leachate of the untreated samples**
1 (Itchen sediment)	0.5	0.98 %	1.8 %
2 (Itchen sediment)	0.5	0.67 %	2.5 %
3 (Itchen sediment)	2	0.15 %	1.1 %
4 (Beaulieu sediment)	500	0.04 %	0.03 %

Table 25. Proportion of mass of TBT found in the leachates of untreated and treated samples

Less than 1 % of spike of TBT added in all samples was released into solution during the leaching test. As TBT has a very high affinity for solid matter and also a very low solubility in water (8-10 ppm for TBTO, 6 ppm for TBTF) the fact that most of it (99.97%-97.54%) is adsorbed by the sediment itself is not surprising. The addition of Pangel B10 appeared to result in even lower levels of TBT in solution. Sample 4, prepared from the Beaulieu sediment, adsorbed a higher % of TBT, which could be attributed to a range of parameters like particle size, geochemistry and organic matter content.

Significant variability was also observed for all the experiments. It was attributed to inadequate mixing of the spike of TBT or/and of Pangel B10 in the mix before the sub-sampling. The variability is very prominent in Sample 4, which had the most TBT added.

The immobilisation of TBT with the use of Pangel was attributed to hydrophobic absorption of TBT on the organic additive, which has a long carbon chain. It appears that in Sample 4 the sediment was as efficient at adsorbing TBT as Pangel B10 and therefore the concentration in the leachates of treated and untreated samples was not any different.

Sample 4, despite having the highest Kd for TBT, had levels of TBT in the leachate that were much higher than any regulatory limit. For Samples 1-3, Pangel B10 achieved leachate concentrations just one order of magnitude higher than the 2 ng/L EQS. Its performance was not satisfactory for higher levels of TBT contamination.

6.3.4.4 Conclusion (Pangel B10)

Because of its poor performance with highly TBT contaminated samples, and also the potential of the organic additive contained in Pangel B10 to leach or degrade over time releasing the adsorbed TBT and other potentially toxic leachates from the Pangel B10 itself, this material was not considered further.

6.3.5 Assessment of other candidate materials using spiked sediments

6.3.5.1 Introduction

Ordinary Portland cement (OPC) is a common additive employed to achieve reduction of the % water content of sludges prior to their disposal or re-use. Commonly, cement is added at approximately 6-10% wet wt ratio with the sludges to solidify them, resulting in material that, whilst not entirely solid, can be safely transported. Apart from safe transportation, the solidification allows disposal in landfill sites, as liquids are banned and liquid wastes must be pre-treated, since October 2007 (according to the Landfill Directive[49]).

Some potential additive combinations involving cement as the solidifying agent were evaluated using TBT-spiked sediment samples from the River Itchen.

6.3.5.2 Experimental

The materials tested as sorbents were ground Aquacarb (AqC), ground coal, ground charcoal, ground coke, fly ash and OrganoDec. OPC, as a solidifying agent, was also added to some samples.

For each sample 45 g of wet Itchen sediment was spiked with 1 mL of a 500 µg Sn/mL TBTCl solution in methanol resulting in sediment samples with 11.11 mg Sn/kg TBT wet weight. Then, 10 g sorbent material (~20% w/w wet weight), 3 g of OPC (in the samples specified in Tables 25-26) and 54g of deionised water were added and the leaching procedure in Section 6.3.1.4 was followed. A 45 g aliquot of the same sediment, also spiked with TBTCl at the same level and containing no sorbent material, was leached (according to Section 6.3.1.4) with 54 g of deionised water, to be used as a control. A blank analysis, the analysis of deionised water, was also carried out. A TBTCl solution in water was also extracted, derivatised and analysed to correct for losses of the analyte during the analysis. Samples of the same sediment (45 g) spiked with TBTCl at the same level and containing 3g cement, but no stabilising material, were leached with 54g of deionised water each to test the effect of cement on untreated sediment. The materials used for the analysis and the analytical procedure followed are as described in Section 5.4. The pH of the suspension of the additives was determined as in Section 6.3.3.3. The average mineral content of 29 samples taken from the same area of the River Itchen as the spiked sediment used in this experiment (determined by XRF as described in Section 4.8) was used in order to interpret the results of the current stabilisation experiment.

6.3.5.3 Results and discussion

In Table 26, the concentration of TBT measured in the leachates of treated samples at equilibrium is shown. The concentration of TBT measured in the leachates of sediment samples that were not treated is shown, as this was taken as the baseline against which the treated sediments are judged. It also reflects small day-to day variations in the analysis. The Kd values of the TBT partitioning between the mixes of sediment/additives and the water are shown, together with the impact that the additives had on the release of TBT from the sediment into water expressed as %TBT leaching from the treated samples compared to the untreated.

Material	TBT in leachate of treated samples (ng/L)	TBT in leachate of untreated samples (ng/L)	Kd (L/kg)	TBT in leachate of treated samples compared to that of untreated (%)
OPC	23600	3200	571	823±40 %
AqC/OPC	600	3200	20832	27±0 %
Coal/OPC	20200	2400	617	829±161 %
Coal	2800	2400	4825	115±31 %
Charcoal/OPC	3400	1800	3675	191±38 %
Charcoal	3600	1800	3752	201±8 %
Coke/OPC	33700	2300	370	1469±1156 %
Coke	3800	2300	3555	166±57 %
Fly ash/OPC	17500	1200	713	1476±0 %
Fly ash	1600	1200	8444	134±10 %
OrganoDec/OPC	100	1800	124999	5±2 %
OrganoDec	100	1800	135134	8±1 %

Table 26. Leaching test results for candidate stabilising agents and cement combinations

Table 27 below, shows the proportion of TBT measured at equilibrium (100 ng/L-33700 ng/L) in the leachate of treated samples (60 mL), compared to the TBT added to the mix of sediment/additives (500 μg). In brackets, the proportion of TBT measured at equilibrium (2117 ng/L on average) in the leachate of untreated samples (60 mL), compared to the TBT added to the samples (500 μg) is shown. The differences between the proportion of TBT leaching with and without treatment demonstrate the impact that each additive had on the immobilisation of TBT.

Material	**Proportion of TBT spike in the leachate of the treated samples**	**Proportion of TBT spike released in the leachate of the corresponding untreated samples**
AqC/OPC	0.007 %	0.038 %
OPC	0.283 %	0.038 %
Coal/OPC	0.242 %	0.029 %
Coal	0.034 %	0.029 %
Charcoal/OPC	0.041 %	0.022 %
Charcoal	0.043 %	0.022 %
Coke/OPC	0.404 %	0.028 %
Coke	0.046 %	0.028 %
Fly ash/OPC	0.210 %	0.014 %
Fly ash	0.019 %	0.014 %
OrganoDec/OPC	0.001 %	0.022 %
OrganoDec	0.001 %	0.022 %

Table 27. Proportion of TBT spike found in the leachates of untreated and treated samples

As expected from the stabilisation experiments carried out with Pangel B10, the control analyses indicate that more than 99.9% (99.975 % on average) of the TBT spike was adsorbed on the sediment when left untreated (Table 27). Some of the additives immobilised the TBT further, while most of the additives tested had the opposite impact and the TBT levels in the leachate increased. In all cases however more than 99.5% (99.889 % on average) of the added TBT was still immobilised.

In Table 28 the pH values of water solutions containing the combination of additives in this experiment are shown:

Material	**pH** (± 0.5)
OPC	12
AqC/OPC	11.5
Coal/OPC	11.1
Coal	7.6
Charcoal/OPC	6.9
Charcoal	5.5
Coke/OPC	11.3
Coke	6.6
Fly ash/OPC	11.6
Fly ash	7.8
OrganoDec/OPC	11.7
OrganoDec	8.8

Table 28. The pH of candidate additives for TBT-spiked sediments

The mineral content of sediments from the same area as the sample sediment in the current experiment is shown in Table 29:

Mineral	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	MnO
%	52.8	7.8	5.7	2.2	12.8	2.9	1.7	0.7	0.04

Table 29. Average mineral content of sediments in the area of origin of the sediment sample

For most combinations, the amount of TBT detected in solution in the leachates of additive(s)-treated samples compared to the control (Table 27) can be related on the pH of the solutions (Table 27). The exceptions are those with Aquacarb and OrganoDec.

Cement only-treated samples

The concentration of TBT in the leachate of the cement-treated samples was more than 800% that of the control (untreated) sample. From the 500 μg of TBT added in each sediment sample 1.18 μg of TBT leached out when the sediment sample was treated with cement, while only 0.16 μg TBT leached out when the sediment was left untreated (no cement).

This increase in the mobility of TBT in the presence of cement was attributed to the sharp increase of the pH of leaching water to pH 12. Under such pH conditions (pH> TBT pKa=6.25[19]) TBT is mostly in the TBTOH form and is therefore de-sorbed from the charged surface of the minerals in the sediment, according to adsorption studies[269] conducted with pure montmorillonite and a sediment containing 80% montmorillonite ($Na_x((Al_{2-x}Mg_x)Si_4O_{10}(OH)_2)$)[270], 10% Na^+-kaolinite ($Al_2Si_2O_5(OH)_4$)[270], 10% illite $(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$[266] and 5% amorphous SiO_2.

The typical composition of soil clay minerals is:

Mineral (%)	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O
Montmorillonite (France)	51	20	0.8	3.2	1.6	0.04	0.1
Kaolinite (Virginia, US)	45	38	0.8	0.1	0.1	0.7	0.1
Illite (Scotland, UK)	49	29	3	1.3	0.7	0.1	7.5

Table 30. Composition of soil clay minerals[277]

Sediments are the products of weathering of different rocks and they vary in composition. The sediments from the area where sediment selected for this experiment originated have a higher content of Ca^{2+} (Table 29) compared to the typical composition of soil clay minerals (Table 30). The sediment selected for the current experiment could adsorb TBT with the same mechanism as montmorillonite, kaolinite and illite clay minerals do (electrostatic attraction of the TBT^+ on the negatively charged sites of the clays). Organic matter in the sediment also adsorbs TBT, mainly in its neutral form by hydrophobic forces, or by electrostatic forces through functional groups such as -COOH, -OH. The pH dependence of the charge of many adsorption sites on minerals explains the changes in the adsorption capacity of the sediment with changes in the pH brought about by additives. In the case of cement, its hydration reactions release Ca^{2+} which may compete with TBT^+ for the adsorption sites on the sediment. This might be an additional factor contributing to TBT de-sorption from sediments with the addition of cement.

Aquacarb/cement-treated samples

Addition of Aquacarb in TBT-containing samples resulted in extremely low concentrations in the leachate, as it was also seen in the screening experiments with TBT-spiked water samples in Section 6.3.3.4. Treatment of TBT-contaminated samples with Aquacarb in addition to cement resulted in only 0.03 μg TBT leaching out compared to 1.18g μg TBT leaching out with OPC- only treatment and compared to 0.16 μg TBT leaching out with no treatment at all. The pH of the AqC/OPC suspension was 11-12, in which the TBTOH species predominates. This species is neutral and has minimum solubility in water. According to these characteristics its high adsorption on activated carbon can be explained.

When AqC was added to the cement/sediment mix, it appeared to reduce the leaching of TBT by approximately 800%, which is similar to the findings of Hebatpuria *et al*, during experiments assessing the immobilisation of phenol on phenol-spiked sand using a mix of cement and 2 % (w/w sand) regenerated activated carbon (F400, Calgon)[278], where the addition of the carbon resulted in 600% less phenol leaching out. Lacking studies of the immobilisation efficiency of activated carbon on TBT-contaminated sediments, the phenol study could be an indication of the effectiveness of activated carbon in the presence of cement, despite the huge difference between the properties of phenol and TBT.

OrganoDec-treated and OrganoDec/cement treated samples

OrganoDec, consisting of a coke-derived material and 38% w/w water (Section 6.3.2.3.3), removed TBT equally or more effectively than Aquacarb. The pH of OrganoDec in solution is 8-9 and when OPC was added increased to pH 11-12. The efficiency appeared unaffected by the change in pH. In both cases the TBTOH species is expected to predominate. OrganoDec is believed to be a highly porous carbon material therefore TBT removal is based on adsorption. Its removal efficiency is therefore attributed to Van der Waal forces between TBTOH and the micropores of graphitic planes, similarly to the adsorption of TBTOH on AqC. Other forces that may contribute to the removal of TBT from OrganoDec may be attraction of any TBT^+ species on potentially present negatively charged functional groups on the surface of OrganoDec. At pH 8-9 though, this type of forces are not expected to contribute much as above pH 7 oxygen containing functional groups largely lose their charge.[253]

Other carbon materials

The commercial coal, charcoal and coke samples that were assessed as cheaper alternatives to Aquacarb were not as efficient. Their addition to TBT-spiked sediment with OPC or alone did not appear to reduce the TBT in the leachate compared to the control.

The concentration of TBT in the water of the treated samples seemed to depend largely on the pH of the solution. When coal, charcoal/OPC, charcoal and coke were added the pH was within the range of 5-8. Under such pH conditions there is known to be an overlap of high concentrations of TBT^+ and negatively charged sites on the sediment minerals.[271] TBT was therefore most probably retained by the sediment, as the addition of the carbon products did not reduce the concentration of TBT in solution. In the cases of charcoal/OPC, charcoal and coke the concentration of TBT in solution was higher than that of the control leachate. This can be attributed to cations introduced by the additives (e.g. Ca^{2+}) which would compete with TBT^+ for adsorption on the negatively charged sites of the minerals of the sediment. In the cases of coal/OPC and coke/OPC the pH increased to 11-11.5. Under such pH conditions TBT is converted to its neutral form and is re-released to solution.

Coke was expected to perform better than all the alternatives to activated carbon, because of its high porosity, but failed to do so in practice. The pH value in the case of coke was 6-

7, which is very close to the pKa of TBT (pKa=6.25). This transitional pH for TBT might explain what appears to be a non-existent removal capacity of the coke tested. It could be expected that a significant number of TBT molecules still existed in their ionic form, which might not be well retained by the surface of the coke, as a high proportion of any functional groups may have converted to their neutral forms at this pH. Additionally, hydrophobic interaction with the surface of the coke would be limited due to still largely ionic character of TBT at this pH.

Fly ash-treated and fly ash/cement treated samples

Fly ash (obtained from the Tilbury coal-fired power station), when mixed with cement, failed to prevent the mobilisation of TBT. This was attributed to the lack of any significant adsorption properties that could reverse the leaching of TBT into the water after the cement driven pH increase. Fly ash, when added alone, mobilised less TBT than OPC did when added alone. That might be an indication that fly-ash could be used to replace cement to some extent as this could lead to less TBT leaching out even with no other additive present. This kind of replacement has been often used in cement-based solidification/stabilisation treatments.[279] The reason for the improved leaching levels is attributed to the much lower pH (~8), as in pH 7-8 the TBT is still largely retained by the sediment as TBT^+. It should be noted that the pH may differ according to the source of fly ash. In the current study, as fly ash was not efficient in reducing the TBT below the control levels, it was not tested any further.

6.3.5.4 Conclusion

Sediment appears to retain more than 99.9% of the added TBT. The adsorption of TBT from the sediment appears to be strongly dependant on pH in all the cases. In highly alkaline conditions such as pH 11-12 when cement was added, only OrganoDec and Aquacarb were capable of re-adsorbing the re-released TBT from solution. It was decided to explore the adsorption capabilities of Aquacarb further.

6.3.6 Testing with different spiked sediments

Additional sediments, from different sources, were tested to confirm that Aquacarb reduces the TBT levels in the leachates of TBT-spiked sediments from different origins.

Fresh coarse sediment from the River Itchen was tested as well as fresh wet silt sediments from Inverness and Bristol. Sampling for all sediments was carried out in February 2008. The spiking, mixing and the leaching tests carried out using the procedure described in Section 6.3.5.2, with 5 g (10% w/w) or 10g (20% w/w) ground AqC and 3 g OPC. The materials and method used for the measurement are as described in Section 5.4.

In Table 31, the concentration of TBT measured in the leachates of treated and untreated samples at equilibrium and the Kd values of the TBT partitioning between the water and the mixes of sediment/additives are shown, together with %TBT leaching from the treated samples compared to the untreated (taken as baseline).

Sediment	**ground Aquacarb %**	**TBT in leachate of treated samples (ng/L)**	**TBT in control leachate (ng/L)**	**Kd (L/kg)**	**% TBT in leachate compared to control**
Southampton coarse	20%	1200	7600	10415	16±2 %
	10%	4700	7600	3038	62±0 %
Inverness	20%	20	5220	624999	3±2 %
	10%	150	5220	95237	1±1 %
Bristol	15%	400	11300	33782	4±0 %
	10%	1900	11300	7517	17±4 %

Table 31. Leaching test results for different sediments

The highest amount of TBT was detected in the leachate of the spiked Southampton sediment sample and the lowest in the spiked Inverness sample. The higher amount of TBT found in the leachate of the coarse Southampton sediment can be attributed to a higher percentage of sand present, which has lower surface area than silt and therefore contributes less to the TBT retention.

A study[280] investigating the parameters that influence the adsorption of TBT to mineral clays (kaolinite, montmorillonite and illite) has concluded that the mineralogy, the salinity, the pH, grain size and also the organic matter content influence the uptake of TBT from the sediments. According to that study, adsorption decreases with an increase in salinity when tested over the range of 0-32 ‰. Also, a correlation has been found for adsorption increasing with an increase in organic matter content, attributed to partitioning of TBT in the organic matter[271] as well as complexation to carboxylate and phenolate groups[281]. These findings demonstrate that it is extremely difficult to predict the adsorption of TBT in sediments, unless a thorough investigation of all these parameters is carried out.

Ground Aquacarb reduced the TBT concentration below the concentration in the control leachate for all three sediment types, but not close to or below the 2 ng/L EQS[53]. It was therefore decided to evaluate the adsorption efficiency of the material in its powder form.

6.3.7 Dosing experiments with powdered carbon products

Powdered carbon products were used to enhance the mixing of the carbon stabilising product and to also increase the surface area of the carbon.

The powdered materials were: AP and CP. Dosing experiments were carried out using the Bristol sediment as the substrate. This sediment was selected from the three available as being more representative because ground Aquacarb demonstrated intermediate stabilisation efficiency when combined with that type of sediment. Spiking the sandy Southampton sediment would be a stricter test, but in the environment it is mostly the silty/clayey sediments that are in need of immobilisation techniques, because for sandy sediments cheaper physical treatments, such as soil washing, are usually effective.

The experimental part was carried out as in Section 6.3.5.2 with the addition of 20-2.5% (w/w) of activated carbon and 3 g of cement. The materials used for the analysis and the analytical procedure followed are as described in Section 5.4.

In Table 32, the concentration of TBT measured in the leachates of treated and untreated samples at equilibrium and the Kd values of the TBT partitioning between the water and the mixes of sediment/additives are shown, together with %TBT leaching from the treated samples compared to the untreated (taken as baseline).

Material - % (w/w)	**TBT in leachate (ng/L)**	**TBT in control leachate (ng/L)**	**Kd (L/kg)**	**TBT in leachate compared to control**
AP-20%	<50 ng/L	Not determined	>249999	Not determined
CP-20%	<50 ng/L	Not determined	>249999	Not determined
AP-10%	<30 ng/L	5400	>490194	<0.56 %
CP-10%	<30 ng/L	5400	>490194	<0.56 %
AP-5%	<40 ng/L	14100	>384614	<0.28 %
CP-5%	<40 ng/L	14100	>384614	<0.28 %
AP-2.5%	<20 ng/L	8800	>793649	<0.23 %
CP-2.5%	700	8800	22674	8±2 %

Table 32. Leaching test results with powdered carbon products

A significant increase in the removal efficiency was observed with the use of powdered Aquacarb products (Table 32) compared to the efficiency of the manually ground

Aquacarb. Both the powdered products were very efficient at the 20%, 10% and 5% ratio. This was attributed to the larger surface area of the smaller particles and perhaps better mixing with the sample due to the smaller particle size. CP was not as efficient as AP at the 2.5% ratio, perhaps due its lower surface area, therefore it was not tested any further.

6.3.8 Increased cement ratio

The cement dose was increased from 6% to 10% to provide a harder end material with better geotechnical properties. The improved geotechnical properties would allow use of the stabilised sediment as a construction material increasing its value.

TBT-spiked Bristol sediment was mixed with 2.5% and 5% AP and 10% cement w/w wet wt.

The experimental part was carried out as in Section 6.3.5.2 after increasing the amount of cement to 4.5 g (10%). The materials used for the analysis and the analytical procedure followed are as described in Section 5.4.

In Table 33, the concentration of TBT measured in the leachates of treated and untreated samples at equilibrium and the Kd values of the TBT partitioning between the water and the mixes of sediment/additives are shown, together with %TBT leaching from the treated samples compared to the untreated (taken as baseline).

Material – % w/w	**Spiking**	**TBT in leachate (ng/L)**	**TBT in control leachate (ng/L)**	**Kd (L/Kg)**	**TBT in leachate compared to that of control**
AP-2.5%	500 μg	90	9100	168349	0.99±0.1 %
AP-5 %	500 μg	90	9100	163397	0.99±0.2 %

Table 33. Leaching test results of spiked sediment with AP (2.5-5%) and 10% OPC

The increased dose of cement did not make any significant difference to the amount of TBT in the leachate as the increase of TBT in the leachate was about 1%.

The dose of 2.5% AP as the sorbent material and 10% cement as the solidifying agent was tested over a longer term to permit the cement to undergo hydration.

6.3.9 Long term leachability experiment

As AP (powdered Aquacarb) at 2.5% had demonstrated very good efficiency even at the increased cement ratio (10%) it was necessary to investigate the adsorption behaviour over a longer period of time.

6.3.9.1 Experimental

The long term leachability of TBT from a 2 kg TBT-spiked wet Bristol sediment sample was tested. The spiking was done in a glass container (beaker) by mixing 50 mL of a 500 μg as Sn/mL TBTCl methanolic solution into 100 mL deionised water and adding the mixture slowly to the sediment, while stirring vigorously. To the mixture was added 2.5 % (50 g) Aquacarb powder (AP) and 10% (200 g) OPC. Mixing of the materials with the sediment took place until the mixture was homogenous under visual inspection. The mixture was then transferred to a large container lined with aluminium foil (to avoid absorption of TBT on the plastic walls of the container) and was left to dry outdoors with a lid to protect it from the rain while allowing the circulation of air.

Before spiking the sediment was found to contain 63% water, according to EN 12880:2000[276]. After spiking the sediment it contained approximately 12 mg/kg (wet wt) or 34 mg/kg (dry wt) of added TBT.

The full procedure of leaching test BSEN 12457_3:2002 was applied with the adaptation described in Section 6.3.1.4. This leaching test is a two-step procedure and the results for each step are given below. Sampling of the mixture took place on the 1st, 7th and 33rd day after the mixing. For each 45g aliquot of wet mud 54 g of deionised water was added for the first step and 240 mL for the second step. A blank analysis, the analysis of deionised water, was incorporated into the procedure. A TBTCl solution in water was also derivatised and analysed to correct for losses of the analyte during the analysis.

6.3.9.2 Results and discussion

The results from each step of the leaching tests carried out 1, 7 and 33 days after the mixing of the TBT-spiked sediment with cement and powdered activated carbon are shown in Table 34. The concentration of TBT in the total volume of leachate (10L/S) calculated from the mass of TBT leached out during each leaching step is given, as well as the total concentration of TBT leached out, in mg/kg (wet wt) of sediment.

	TBT in leachate (ng/L)	**Combined leachate (10 L/S) (ng/L)**	**Leached from sediment (mg/kg wet wt)**	**Proportion of TBT spike**
Day 1 step 1	200±50	50±0	0.0004±0.00005	0.0030 %
Day 1 step 2	20±1			
Day 7 step 1	100±30	10 ±0	0.0001±0.00000	0.0008 %
Day 7 step 2	10±0			
Day 33 step 1	< 30 ng/L	< 30 ng/L	< 0.0002	0.0000 %
Day 33 step 2	< 5 ng/L			

Table 34. Leaching test results from Days 1, 7, 33 after mixing spiked sediment with cement and activated carbon

The TBT content in the leachate did not appear to increase over time after the mixing was carried out. To the contrary, TBT concentrations showed a reducing pattern. The reduction was attributed to further immobilisation of TBT by complexation with cement hydration products, which form slowly over 28 days after the mixing of cement with water.

In a study of immobilisation of phenol in cement based solidified/stabilised hazardous wastes using regenerated activated carbon Hubatpuria *et al*[278] reported that analyses of pore fluids of cement paste containing phenol suggested formation of a phenol-cement complex, which further reduced the presence of phenol in the pore water. The decreasing leaching out of TBT over time may be attributed to complexes forming between the cement and TBTOH.

It is worth noting that in the same phenol study it was also examined whether the hydration of cement hinders the adsorption of phenol on the activated carbon. It was found that after 10h the phenol that could adsorb on the carbon when activated carbon was coated in cement was only 4% of the phenol that would adsorb on uncoated activated carbon. This was attributed to the solidifying processes of cement, which create a gel-like semi-permeable membrane of calcium silicate hydrate that constantly expands. This membrane would prevent the adsorption of phenol by blocking its path. It was found, however, that 98% of the added phenol was adsorbed on the activated within the first 10 hours. The two materials cement and activated carbon could, therefore, be added at the same time when applying the solidification/stabilisation as the adsorption was essentially completed before the solidification would start obstructing it. It was also found that once the cement had encapsulated the carbon it also prevented desorption of the adsorbed phenol. More specifically, about 8 hours after coating of the activated carbon particles with cement less than 2% of the adsorbed phenol leached out from the cement-coated carbon than from uncoated. The amount of phenol desorbed from cement-coated activated carbon dropped to zero 14 hours after coating.[282]

The ability of activated carbon to adsorb TBT after its encapsulation with cement is of high importance. As TBT is commonly found in sediments in the form of paint flakes slowly releasing TBT, the fact that once encapsulated activated carbon looses the ability to adsorb TBT means that the newly released TBT might be a pollution source. It is however also possible that cement encapsulates the paint flakes in the same way and prevents the release of TBT to the environment.

6.3.10 Alumina cement/powdered Aquacarb

As the high leachability of TBT from OPC-treated sediments in this work was attributed to the alkaline conditions created during the hydration of OPC, alumina cement and more specifically furnace alumina cement was assessed as a cement replacement material because of its lower alkalinity. Its combination with AP was also tested.

Two aliquots of 45g of wet mud (Bristol sediment) were spiked with 1 mL of a 500 μg Sn/mL TBTCl solution. 10g of alumina cement and 54g of deionised water were added. A 45 g aliquot of the same sediment, spiked with TBTCl at the same level, and 54 g of deionised water, but no alumina cement, was leached as a control sample.

Also, two 45 g aliquots of the same sediment spiked with TBTCl at the same level containing 5 g alumina cement (11%) and 2.5g (~ 5%) of AP were leached with 54 g of deionised water. A blank analysis (using deionised water) was also carried out. A TBTCl solution was also derivatised and analysed to correct for losses of the analyte during the analysis. The materials used for the analysis and the analytical procedure followed are as described in Section 5.4. The pH of alumina cement and alumina cement/AP suspensions was measured as in Section 6.3.3.3.

In Table 35, the concentration of TBT measured in the leachates of treated and untreated samples at equilibrium and the Kd values of the TBT partitioning between the water and the mixes of sediment/additives are shown, together with %TBT leaching from the treated samples compared to the untreated (taken as baseline).

Material	**TBT in leachate of treated samples (ng/L)**	**TBT in control leachate (ng/L)**	**Kd (L/Kg)**	**% TBT in leachate compared to control**
Alumina cement	6600	Not determined	2046	Not determined
Alumina cement/AP-5%	< 30ng/L	6400	>483090	<0.47

Table 35. Leaching test results for alumina cement and alumina cement/AP treated samples

Alumina cement, added alone, did not appear to improve the TBT concentration in the leachate. The concentration was not however as high as in the case of OPC addition (Section 6.3.5.3). When AP (5%) was added, no TBT was found in the leachate, which was the same or marginally better than when OPC was used with 5% AP (Section 6.3.7). The pH of alumina cement and alumina cement/AP solutions was 7.5-8, which is lower than the pH of cement and Aquacarb/OPC solutions (pH 11-12). It appears that TBT is better adsorbed on the sediment and AP when alumina cement is used instead of OPC. This is attributed to the lower pH which allows stronger electrostatic adsorption of the TBT on the sediment.

Alumina cement is known[263, 283], however, to have weaker geotechnical properties after setting, compared to OPC and it should not be used for structural purposes. Another disadvantage is the much higher price: £400 per tonne for alumina cement compared to £100 per tonne for OPC (quotation for a minimum of a 30 tonne delivery within 100 miles in bulk 1 tonne bags, by Castle Cement Ltd July 2008). Its combination with AP could be investigated further, in case the amount of AP can be optimised and a more cost-effective mix than the one for OPC/AP can be found. Even then, alumina cement should only be used when no significant structural strength is required for the end product.

6.4 Conclusions

In this chapter the remediation of TBT-contaminated sediments and water by several different ways was assessed. The two main methods were destruction of the pollutant and immobilisation of TBT in sediments.

6.4.1 Destruction

The thermal treatment (incineration) of TBT-contaminated sediments was successful after heating the sediments at 1000 °C. As a destruction technique, the most prominent advantage of this method is the elimination of TBT by combustion and volatilisation. Substantial reduction of the volume of the material is also achieved but the material that remains usually contains potentially toxic compounds, such as heavy metals, in high concentrations and should be treated or disposed of accordingly. Despite the advantages of this technique, the high energy and all the safety and pollution control measures required make it expensive.

Another destruction method evaluated was ultrasonication. This method removed 40% of the TBT after a 30 minute treatment from TBT-spiked solutions. Even though this method could be optimised or tested in combination with other methods (like flocculation and adsorption[94] or ZVI, as it has been investigated for other organic compounds[284]) for wastewater treatment, it was not considered to have the potential to be an efficient technique for contaminated sludges, which are expected to require massively higher energy and time. Additionally, hiring or purchasing special equipment and hiring or training personnel should be added to the cost of this technique.

6.4.2 Immobilisation

From the technologies examined in this work, the most promising technology appears to be solidification/stabilisation. Removal of TBT from TBT-spiked water as a screening tool and then immobilisation of TBT in TBT-spiked sediment was investigated using different materials. The materials belonged to the categories of: carbon products, pure clays, organically modified clays, fly ash, cements and iron (in the form of ground iron and granular zero valent iron). Combinations of additives with cement (OPC), which is typically used as a solidifying agent, were also tested. TBT was expected to adsorb on these materials and therefore TBT leaching to drop. It was found that >99.95% of the TBT was adsorbed by the sediment itself. Cement appeared to inhibit the adsorption of TBT by increasing the pH value to 11-12 and converting the TBT to its neutral form and perhaps by increasing the concentration of Ca^{2+} competing with any remaining TBT^{+}. TBT showed very good affinity for some of the materials and more specifically for activated carbon and coke (in the form of OrganoDec), even when cement was added, and for low/medium polarity organophilic clays. The option of activated carbon was preferred as it is cheaper than the organically modified clays and non degradable. A powdered activated carbon product (AP) had the best performance. No TBT was detected (< 5 ng Sn/L TBT) in the leachate in tests carried out 33 days after treating TBT-spiked sediments with activated carbon (2.5%) and cement (10%). This technique is therefore considered to be a viable way forward for the remediation of TBT.

The advantages of this technology, apart from eliminating the leaching of TBT, is the fact that it employs familiar, for the dredging industry, practices and equipment (excavation and mixing), relatively inert and non-toxic materials (cement, activated carbon), large volumes can be treated in a short period of time on site and, finally, the end product can be reused as a construction material on site or elsewhere. The disadvantage of this method is that it does not destroy TBT and this can result in a drop of the value of the land where it is reused. Also, before this technology is applied, geotechnical and leaching tests should be carried out determining the amount of cement and activated carbon to be added in order to create an end product with the desired properties. The amount of activated carbon necessary may vary according to the amount of TBT in the sludge, as well as other parameters unique for each sample, like the levels of other contaminants.

7 Final conclusions and future work

The main aim of this project was to assess the efficiency of technologies for the remediation of TBT-contaminated sediments and water. Suitable analytical techniques were developed for the determination of TBT in sediments and water that allowed the assessment of destruction and stabilisation remediation technologies.

The use of XRF for the determination of total tin in sediments, as a TBT contamination screening technology, has also been explored.

7.1 Analytical methods

The analysis of sediment and water samples for TBT is scientifically challenging due to the many different forms in which it exists (halide, oxide, in polymers), its organometallic nature and its very high affinity for solid matter. The analysis of environmental samples for TBT has been the subject of a very large number of published papers, which is indicative of the many different issues the researchers had to overcome. In this project gas chromatography with a pulsed flame photometric detector (GC-PFPD) was chosen, owing to the low detection limit that could be achieved with relatively low maintenance and purchase costs. For the use of such instrumentation a derivatisation step is necessary, after the extraction of the butyltins from the environmental matrices, to convert them to suitable species for the gas chromatography. Several changes were found to be necessary in order to optimise the analysis procedure, to obtain satisfactory performance.

7.1.1 Detector and injector optimisations

An early observation of irreproducible results, while measuring solutions of pure hexylated butyltins in hexane, initiated experiments for the improvement of the GC-PFPD operation. The lack of reproducibility was initially attributed to deposition of tin oxide (butyltin combustion product) in the detector chamber causing drift of the signal over time. Several sets of gas flow rates other than the initial values set by the Varian engineers (Air1 17, H_2 14, Air2 10) were tested to improve repeatability between injections but none of them was found to be suitable. A 100% increase of the gas flows improved the repeatability but it also reduced the sensitivity as the residence time of the butyltin compounds in the detector was reduced. The gas flow rates were finally left unchanged. The PTV (programmed temperature vaporisation) function of the injector was also put to use with a ramped temperature program. Sensitivity doubled as the compounds were gradually volatilised and better separation of the three butyltins was achieved. The initial temperature of the PTV was optimised (150°C) to achieve the highest sensitivity. These setting were employed for the analysis of water and sediment samples.

Future work on the GC-PFPD settings could concern the gas flow rates, as it is believed that the three gas flow rates could be finely optimised to achieve even higher sensitivity. A, more structured such as a, "Simplex" type of approach used for optimisation of variables[285] could be employed to explore combinations of the three flow rates that would lead to the highest sensitivity for the measurement of the alkylated butyltins using the GC-PFPD system.

7.1.2 Analytical procedures for the measurement of butyltins in sediments

An analytical procedure has been developed based on the hexane/tropolone extraction of butyltins followed by Grignard derivatisation to give tetralkylated butyltins. This approach was chosen because of the reported specificity of the extraction for the butyltins and stability of the hexylated compounds. The instrument's detection limits were approximately: 0.3 pg for TBT, 0.4 pg for DBT and 0.6 pg for MBT (as Sn). Its repeatability for the analysis of contaminated sediments was 10%-18% RSD, which was within the reported values in the literature for TBT in sediments.[185, 215] The projected detection limits for the analysis of 0.5 g dry wt sediment and a final extract volume of 20 mL were: TBT=0.037 mg/kg, DBT=0.047 mg/kg and MBT=0.073 mg/kg dry wt (as Sn) in sediments. As the Action Levels for disposal at sea according to OSPAR Commission[42] for TBT in the dredged materials are 0.1-1 mg/kg dry wt, the detection limits achieved by the method are satisfactory. The overall accuracy of the method was confirmed using the reference harbour sediment PACS-2.

7.1.3 Extraction from sediments assessment

Ball-milling of the dry sediment, which was assessed as a means of promoting the extraction of TBT from sediments and to improve sample homogeneity, increased the yields but failed to increase the repeatability, as the %RSD unexpectedly increased from 10%-21% (without ball-milling) to 29% (with ball-milling). An alternative approach of extraction, using dichloromethane/acid leaching of the sediment followed by a solvent exchange with hexane and a Grignard derivatisation, was also explored. This approach was compared with the hexane method. The hexane extraction method gave lower yields (even though within the experimental error) and lower %RSD for TBT (29%) than the DCM method (38%). This may be attributed to the ability of DCM to penetrate the paint flakes present in the sediment and extract more TBT. But in this the lack of homogeneity of the sample due to paint flakes becomes more apparent. Also, losses of TBT were observed during the exchange of DCM with hexane just before the derivatisation, which were believed to contribute to the increased variability. It should be noted that DCM seemed to increase the extraction of MBT from the sediment, potentially due to the more ionic character of MBT compared with DBT and TBT, and would be preferred when the concentration of MBT in the sediment is of interest.

Future work could include testing the extraction yields of butyltins from sediments with a hexane/acid combination with a longer contact time.

7.1.4 Identification of hot-spots

A technique that can quickly identify hot-spots of TBT contamination can be a valuable technological asset to a civil engineering company such as Land and Water Ltd. This technique would be used for the fast and facile zoning of suspected TBT contamination. A disadvantage of this technique can be that any tin-made object present in the sediments by deposition can potentially lead to wrong conclusions. This could be overcome if the technique is used in order to detect if the OSPAR Commission[42] criterion (1 mg Sn/kg TBT), for dumping dredged material back at sea, is breached or not for total Sn. This will allow the exclusion of the sediments with Sn <1 mg/kg from the need to be further sampled or unnecessarily subjected to remediation. The result is potentially great economic benefit.

7.1.5 Determination of TBT in water

After investigating the option of a tributyltin hydride generation derivatisation procedure, it was decided not to adopt it due to several issues including uncertainty over the linearity of the detector's response as well as poor sensitivity of the detector to these species (300 ng/L for a 25 mL water sample).

Instead, a new solid-phase extraction method was developed based on on-column ethylation. The fact that the pre-concentration, derivatisation and isolation take place *in-situ* is a great advantage of the method since it saves time, effort and minimises the amount of glassware required. It also potentially minimises losses that would be inevitable during transfers to other vessels as well as cross-contamination problems. The suitability of ethyl acetate as the eluting solvent and a sample flow rate of 5-10 mL/min were established and a solvent volume of 4 mL was found to be necessary for the complete elution of the derivatives. The injected estimated limits of detection for this method are 0.2 pg for TBT and DBT and 0.3 pg for MBT and TPrT (surrogate) as Sn. For 250 mL water samples, the estimated limits of detection (10 ng/L TBT, 12 ng/L DBT, 20 ng/L MBT, as Sn) are similar to the reported limits of detection for these species in water (10-40 ng/L)[127, 197]. The %RSD of this method was approximately 7% for artificially spiked samples. The method was tested with satisfactory results with sea water and acidified (pH 2) water samples. The accuracy of the method was confirmed using the QUASIMEME calibrant solutions. The only difficulty during the use of this method had arisen from the analysis of water samples with high particle content, as the ones produced from the leaching tests of TBT-contaminated sediments. Suspended matter was found to block the SPE cartridges at times, stopping the flow.

Another analytical approach was then adopted. The procedure involves ethylation in glass separating funnels and slow liquid-liquid extraction, to avoid emulsion formation, of the derivatives into hexane. Good repeatability (~ 5% RSD) and satisfactory recovery, after correction with an internal standard, were achieved. The detection limit was 6 ng Sn/L TBT. This detection limit was regarded satisfactory, as a concentration step could be later incorporated, if necessary for the assessment of the remediation techniques.

7.2 Destruction of the TBT present in contaminated sediments

The advantage of a successful destruction of the TBT that is present in sediment dredgings is the potential for the safe re-use of the material and elimination of the risk of potential leaching of TBT. The two destruction techniques that were assessed are combustion and ultrasonication.

The removal of butyltins in sediments was tested on sediments of low butyltin contamination (0.28 mg/kg TBT) at temperatures of 200°C, 500°C and 1000°C. The butyltins were undetectable (<0.003 mg/Kg TBT, <0.004 mg/Kg DBT, <0.006 mg/Kg MBT (as Sn) dry wt) in sediments only after combustion at 1000°C. The butyltins are expected to have volatilised and combusted under these conditions. The main concern regarding the implementation of this approach at a TBT-contaminated site would be the high plant costs and energy requirements, which make it expensive.

If incineration were to be part of scheme to recycle material that would probably reduce the overall cost and make it more sustainable as a technique. An example of such a scheme has involved the recycling of oil, hydrocarbons and heavy metals waste materials, including contaminated sediments for the production of construction-grade cement.[286] During processing all the material is fed into furnaces at 1200-1400°C which convert the organic pollutants into CO_2 and H_2O. Similar applications in brick[287] or glass manufacturing. Usually the quality or price of such materials is no different from others in the market that come from pure materials but the obstacle to their commercial success is the public safety fears.

The other destruction technique assessed was ultrasonication. Solutions of 2000 ng/L TBT were treated and TBT content fell by 48% after a 30 minute treatment. This reduction was not satisfactory and it showed that the total removal of TBT from sludges would not be viable using this technique.

As destruction methods require highly specialised equipment the main focus of this project shifted to the exploration of stabilisation options.

7.3 Immobilisation of TBT in sediments

The binding of TBT to any additive material is normally a reversible process and the objective of this work was to identify acceptable additive materials that maximise the binding efficiency and therefore minimise TBT leaching.

The TBT-binding efficiencies of candidate additives were screened using the BSEN 12457_3:2002 leaching test adapted for the assessment of TBT leaching. Adaptation was necessary as filtration was causing losses of the analyte that were attributed to adsorption on the membrane and glass fibre filters tested. Centrifugation of the samples was adopted instead.

The stabilisation materials tested were carbon materials (Aquacarb, OrganoDec, coal, coke, charcoal and carbon marketed for gas absorption), zero valent iron (in suspension and as iron chip), clays (bentonite, sepiolite), organically modified clays (organophilic sepiolite), fly ash and cements (OPC and high alumina cement).

An important finding of the work was that the sediment itself adsorbed more than 99% of the TBT present. The proportion of the TBT leaching into water was pH dependent in most cases, which is attributed to the change of the hydrophobicity of TBT at pH 6.3. Aquacarb, OrganoDec and organophilic sepiolite had the best immobilisation performance, while cement appeared to have the opposite effect significantly increasing the leaching of TBT. The use of organophilic clays was dismissed as the long term behaviour and toxicity of the organic additive was unknown. Aquacarb appeared as a good competitor to OrganoDec which is a marketed remediation agent. Powdered Aquacarb (AP), an activated carbon material, based on bituminous coal (added at 2.5 % wet weight) eliminated the leaching of TBT even when combined with cement, added at 10% wet weight to obtain better geotechnical properties. Tests were carried out after a month from the mixing date and no TBT was detected (< 5 ng Sn/L) in the water. This combination of additives was therefore regarded as having successfully immobilised TBT.

Stabilisation trials using sediments from different areas are necessary. They will allow the assessment of the materials under more realistic conditions. As sediments are complex matrices and their exact content is often unpredictable, it is possible that issues will arise at that stage (potentially interference from other pollutants) that will require further laboratory work.

Activated carbon generally has lower affinity for heavy metals than organic compounds but those would be immobilised by precipitation in the alkaline pH of the cement. Activated carbon has a great affinity for organic compounds and these often co-exist in TBT-contaminated sediments as pollutants. Combination of cement and activated carbon has been shown effective for some of them, such as phenols[288]. Studies of the in-situ treatment of PCBs[289], PAHs[290], DDT[291]-contaminated sediments with activated carbon show promising results. This means that activated carbon can treat a wide range of compounds at the same time as TBT.

Instead of cement, expanding clays, such as bentonite, could be mixed with activated carbon. Expanding clays do not offer the geotechnical properties of cement but offer very low permeability. By preventing the penetration of water they stop the movement of the leached contaminants towards potential receptors. Another alternative worth exploring is fly ash. Uncontaminated fly ash could be used to partially replace cement as it is often cheaper and it has been found to provide the same final strength in concrete. Mixing of fly ash with cement offers better packing as fly ash particles cover the gaps between cement particles and reduces the permeability[263].

As nature is a complex environment where a multitude of elements and compounds move almost freely and in different forms, it is certain that, unless some isolation measures are taken, even the vast surface area of activated carbon will be eventually saturated. It is possible though that the saturation rate is slower than the natural degradation of compounds held on it. In that case some compounds will be desorbed, in their degraded forms, allowing others to adsorb. Activated carbon could continue to be an active adsorbent for a long period of time but that would be determined by the conditions of each site.

Another concern regarding the immobilisation of TBT-contaminated sediments is the behaviour of TBT present in slow-release paints. As these paints have a release rate of at least 0.5-1.5 μg TBT/cm^2/day[4] and last 3-5 years or more from when they are applied, it is likely that they would still leach TBT from paint flakes present in the sediments. A long term capacity of the immobilising system is therefore necessary to ensure that TBT leaching out from paint flakes long after the application of the treatment, will also be immobilised. In the current study, all the treatment experiments were carried out using spiked samples. In the spiked samples the TBT was free to adsorb on the surface of activated carbon, which is not the case for all TBT in the environment. Experiments with sediments containing TBT paints would be necessary to determine their behaviour when treated with activated carbon/cement mixes for immobilisation purposes. Then any necessary optimisations or adaptations of the treatment should be tested. A drainage system that would collect and filter (using activated carbon filters) all run off water from areas where treated sediments have been used could be set up. That however increases the complexity and cost of the treatment option and should be factored in.

Cost

The proportions of materials used in this work could be used as a rough cost guide. Approximately 10% OPC and 2.5% AP wet wt of sediment was added. For cement the cost is about £0.1/kg (£100/tonne, Castle Cement Ltd July 2008) and the cost for AP is £1.25/kg (£1250/tonne, Chemviron-Calgon, 2008). The cost for the additives would therefore be £41.25 for 1000 kg of contaminated sludge. To reduce the cost, regenerated activated carbon should be considered as it has been shown, in the case of F400 (Calgon), to be a cost-effective alternative as it usually costs less than 25% of the cost of virgin activated carbon[282].

It is highly advisable to always evaluate the scope of a pre-treatment, like soil washing (scrubbing contaminated sediment with water to separate the larger-grained, cleaner, fractions of sediment), that can immensely reduce the quantity of material requiring treatment and thus the cost of expensive additives like activated carbon.

7.4 A comparison of options

It should be noted that changes in the legislation and fuel prices together with many hidden costs and savings make the cost comparison between remediation techniques rather complicated.

Remediation techniques can be applied on-site and off-site. When examining off-site techniques the cost of transportation is relative to the distance of the treatment or disposal area. Other consequences or costs of transferring the contaminated material to the treatment plant or site, such as greenhouse gas emissions, noise, dust and soiling of the surrounding roads, should be also taken into account. If the TBT concentration is < 0.1 mg/kg a sea disposal is possible. Then the levels of other potentially present contaminants should be investigated and again the costs for transporting the sludges to a suitable off-shore area should be examined.

When treating material on-site, permits, like a mobile treatment plant licence, should be in place and the cost and time implications of those should also be considered. The material can be reused on site if there is potential for it to be used as a filling material or as a substrate e.g. for a parking area. If not, then its use is considered as disposal activity and the relevant permits should be in place.

As not all site-specific circumstances can be anticipated, a general framework for comparing on a disposal route or remediation of TBT contaminated sludges is shown in Table 36. A complementary decision table which can be used together with Table 36 follows (Table 37).

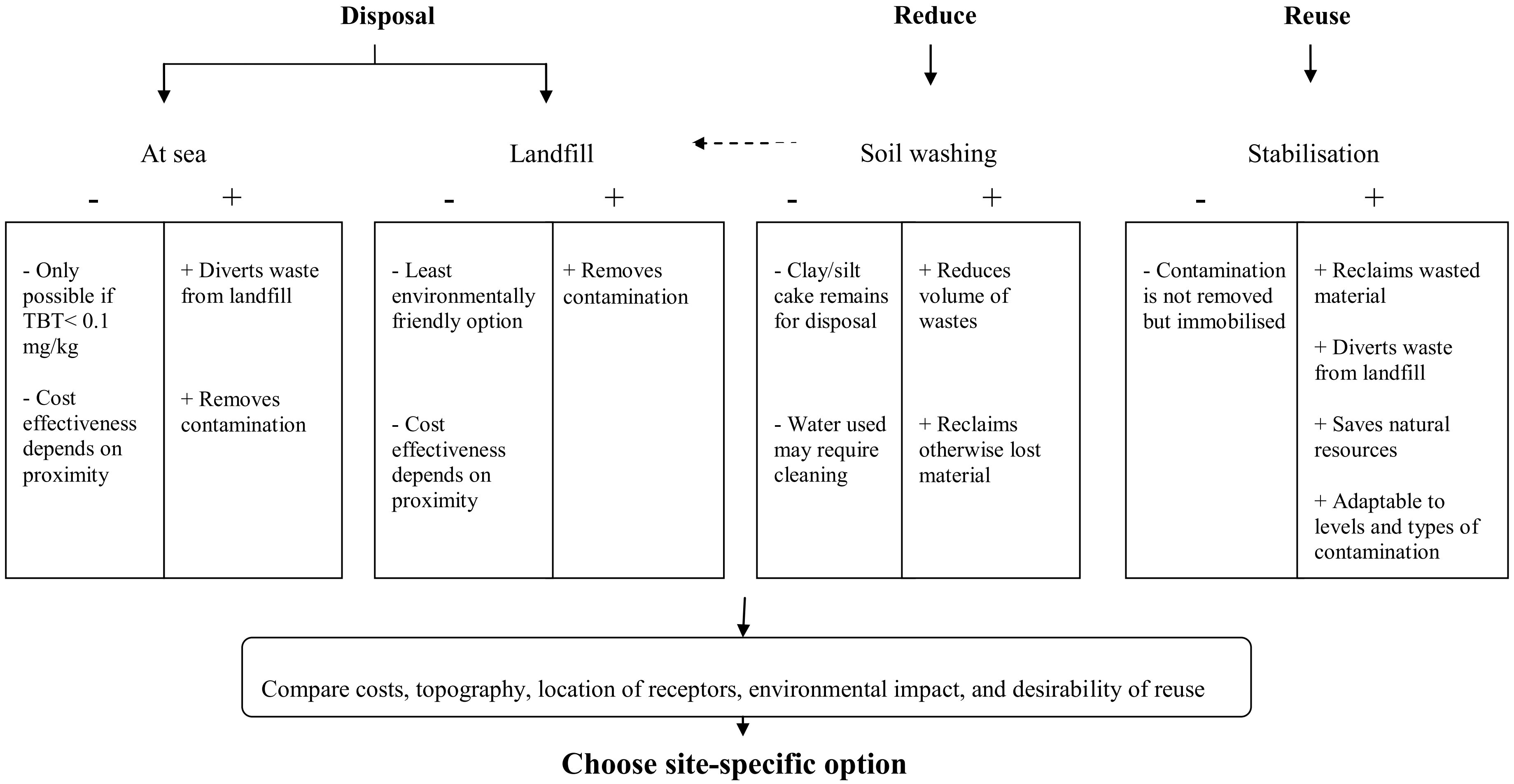


Table 36 Comparison of options for the remediation or disposal of TBT-contaminated sludges

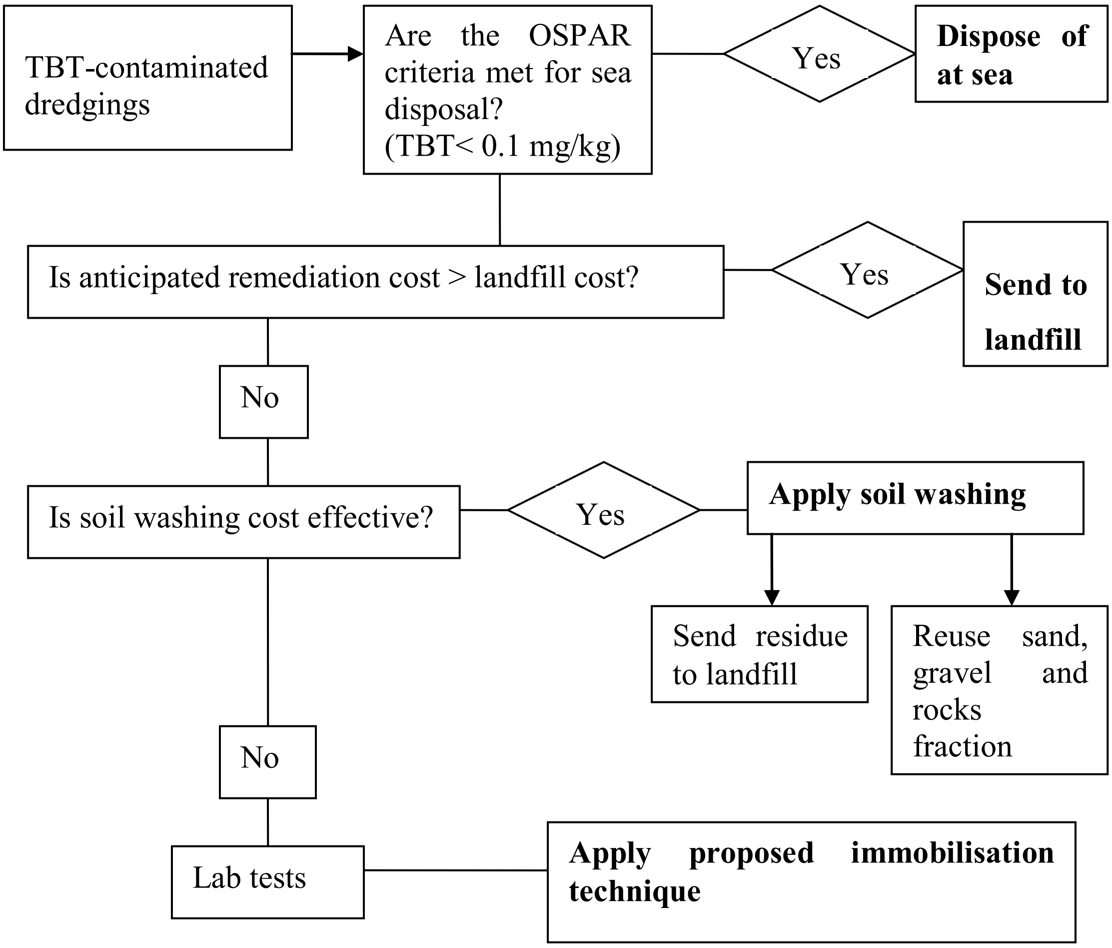


Table 37 Decision table for the remediation or disposal of TBT-contaminated dredgings

7.5 Overall conclusion

During this project, analytical methods have been developed for the analysis of TBT-contaminated sediments and water. These analytical procedures have been successfully used for the assessment of remediation technologies (destruction and stabilisation) for TBT contamination. As the most efficient destruction method (combustion) is considered too expensive at present, the stabilisation option was explored. A combination of an activated carbon product with cement gave a satisfactory end product of immobilised TBT-spiked sediment. The technique was regarded as having been successful even though longer term verification would be necessary.

8 References

1. A. Abbott, P. D. Abel, D. W. Arnold and A. Milne, Cost-benefit analysis of the use of TBT: the case for a treatment approach, *Science Of The Total Environment*, 2000, **258**, 5-19.

2. M. A. Champ, Economic and environmental impacts on ports and harbors from the convention to ban harmful marine anti-fouling systems, *Marine Pollution Bulletin*, 2003, **46**, 935-940.

3. M. E. Waite, M. J. Waldock, J. E. Thain, D. J. Smith and S. M. Milton, Reductions in TBT concentrations in UK Estuaries following legislation in 1986 and 1987, *Marine Environmental Research*, 1991, **32**, 89-111.

4. I. Omae, Organotin antifouling paints and their alternatives, *Applied Organometallic Chemistry*, 2003, **17**, 81-105.

5. M. Callow, Ship fouling - problems and solutions, *Chemistry & Industry*, 1990, 123-127.

6. M. H. Gitlitz, Recent developments in marine antifouling coatings, *Journal Of Coatings Technology*, 1981, **53**, 46-52.

7. S. Kiil, C. E. Weinell, M. S. Pedersen and K. Dam-Johansen, Analysis of self-polishing antifouling paints using rotary experiments and mathematical modeling, *Industrial & Engineering Chemistry Research*, 2001, **40**, 3906-3920.

8. V. J. D. Rascio, Antifouling coatings: Where do we go from here, *Corrosion Reviews*, 2000, **18**, 133-154.

9. P. Howe and P. Watts, Tin and inorganic tin compounds, in *Concise International Chemical Assessment*, World Health Organisation, Geneva, 2005.

10. M. Hoch, Organotin compounds in the environment - an overview, *Applied Geochemistry*, 2001, **16**, 719-743.

11. C. Alzieu, J. Sanjuan, J. P. Deltreil and M. Borel, Tin contamination in Arcachon Bay-Effects on oyster shell anomalies, *Marine Pollution Bulletin*, 1986, **17**, 494-498.

12. E. D. Goldberg, TBT - an environmental dilemma, *Environment*, 1986, **28**, 17.

13. P. Matthiessen, R. Waldock, J. E. Thain, M. E. Waite and S. Scropehowe, Changes in periwinkle (*Littorina littorea*) populations following the ban on TBT-based antifoulings on small boats in the United Kingdom, *Ecotoxicology And Environmental Safety*, 1995, **30**, 180-194.

14. INCHEM, Tributyltin compounds, ed. International Programme on Chemical Safety, World Health Organisation, Geneva, 1999, vol. PIM G018.

15. T. F. Lytle, C. S. Manning, W. W. Walker, J. S. Lytle and D. S. Page, Life-cycle toxicity of dibutyltin to the sheepshead minnow (*Cyprinodon variegatus*) and implications

of the ubiquitous tributyltin impurity in test material, *Applied Organometallic Chemistry*, 2003, **17**, 653-661.

16. C. Bancon-Montigny, G. Lespes and M. Potin-Gautier, Organotin survey in the Adour-Garonne basin, *Water Research*, 2004, **38**, 933-946.

17. C. A. Impellitteri, O. Evans and B. Ravel, Speciation of organotins in polyvinyl chloride pipe via X-ray absorption spectroscopy and in leachates using GC-PFPD after derivatisation, *Journal Of Environmental Monitoring*, 2007, **9**, 358-365.

18. INCHEM, Tributyltin compounds, ed. International Programme on Chemical Safety, World Health Organisation, Geneva, 1990, vol. 116.

19. C. G. Arnold, A. Weidenhaupt, M. M. David, S. R. Muller, S. B. Haderlein and R. P. Schwarzenbach, Aqueous speciation and 1-octanol-water partitioning of tributyl- and triphenyltin: Effect of pH and ion composition, *Environmental Science & Technology*, 1997, **31**, 2596-2602.

20. D. M. Di Toro, C. S. Zarba, D. J. Hansen, W. J. Berry, R. C. Swartz, C. E. Cowan, S. P. Pavlou, H. E. Allen, N. A. Thomas and P. R. Paquin, Technical basis for establishing sediment quality criteria for nonionic organic chemicals using equilibrium partitioning *Environmental Toxicology And Chemistry*, 1991, **10**, 1541-1584.

21. R. B. Laughlin, H. E. Guard and W. M. Coleman, Tributyltin in seawater - Speciation and octanol water partition coefficient, *Environmental Science & Technology*, 1986, **20**, 201-204.

22. T. Tsuda, S. Aoki, M. Kojima and H. Harada, The influence of pH on the accumulation of tri-normal-butyltin chloride and triphenyltin chloride in carp, *Comparative Biochemistry And Physiology C-Pharmacology Toxicology & Endocrinology*, 1990, **95**, 151-153.

23. J. P. Meador, in *Reviews of Environmental Contamination and Toxicology*, 2000, vol. 166, pp. 1-48.

24. R. J. Maguire and R. J. Tkacz, Degradation of the tri-normal-butyltin species in water and sediment from Toronto harbor, *Journal of Agricultural and Food Chemistry*, 1985, **33**, 947-953.

25. M. A. Unger, W. G. Macintyre and R. J. Huggett, Sorption behavior of tributyltin on estuarine and fresh-water sediments, *Environmental Toxicology And Chemistry*, 1988, **7**, 907-915.

26. J. P. Meador, C. A. Krone, D. W. Dyer and U. Varanasi, Toxicity of sediment-associated tributyltin to infaunal invertebrates: Species comparison and the role of organic carbon, *Marine Environmental Research*, 1997, **43**, 219-241.

27. K. E. Day, R. J. Maguire, D. Milani and S. P. Batchelor, Toxicity of tributyltin to four species of freshwater benthic invertebrates using spiked sediment bioassays, *Water Quality Research Journal Of Canada*, 1998, **33**, 111-132.

28. J. Poerschmann, F. D. Kopinke and J. Pawliszyn, Solid phase microextraction to study the sorption of organotin compounds onto particulate and dissolved humic organic matter,

Environmental Science & Technology, 1997, **31**, 3629-3636.

29. A. Weidenhaupt, C. Arnold, S. R. Muller, S. B. Haderlein and R. P. Schwarzenbach, Sorption of organotin biocides to mineral surfaces, *Environmental Science & Technology*, 1997, **31**, 2603-2609.

30. P. F. Seligman, J. G. Grovhoug, P. M. Stang, A. O. Valkirs, M. O. Stallard and R. F. Lee, Distribution and fate of tributyltin in the marine environment, *Abstracts Of Papers Of The American Chemical Society*, 1988, **195**, 70-GEOC.

31. W. J. Langston and N. D. Pope, Determinants of TBT adsorption and desorption in estuarine sediments, *Marine Pollution Bulletin*, 1995, **31**, 32-43.

32. P. M. Sarradin, Y. Lapaquellerie, A. Astruc, C. Latouche and M. Astruc, Long term behavior and degradation kinetics of tributyltin in a marina sediment, *The Science of The Total Environment*, 1995, **170**, 59-70.

33. K. Fent, Ecotoxicology of organotin compounds, *Critical Reviews In Toxicology*, 1996, **26**, 3-117.

34. W. J. Langston and G. R. Burt, Bioavailability and effects of sediment-bound TBT in deposit-feeding clams, Scrobicularia plana, *Marine Environmental Research*, 1991, **32**, 61-77.

35. R. J. Maguire, J. H. Carey and E. J. Hale, Degradation of the tri-normal-butyltin species in water, *Journal of Agricultural and Food Chemistry*, 1983, **31**, 1060-1065.

36. D. Barug and J. W. Vonk, Studies on the degradation of bis-(tributyltin) oxide in soil, *Pesticide Science*, 1980, **11**, 77-82.

37. D. Barug, Microbial degradation of bis(tributyltin) oxide, *Chemosphere*, 1981, **10**, 1145-1154.

38. P. F. Seligman, A. O. Valkirs and R. F. Lee, Degradation of tributyltin in San Diego Bay, California waters, *Environmental Science & Technology*, 1986, **20**, 1229-1235.

39. P. J. Graig, *Comprehensive organometallic chemistry*, Pergamon Press, New York, 1981.

40. *International Convention on the Control of Harmful Anti-fouling Systems on Ships* International Maritime Organisation, 2001.

41. *Harmful ships' paint systems to be outlawed as international convention meets entry-into-force criteria*, International Maritime Organisation, http://www.imo.org/Newsroom/mainframe.asp?topic_id=1472&doc_id=8473, 2008.

42. *Overview of contracting parties' national action levels for dredged material*, OSPAR Commission, 2004.

43. *List of chemicals for priority action-Update 2007 (Reference number 2004-12)*, OSPAR Commission, 2007.

44. *Directive 2006/12/EC on waste*, European Commission, 2006.

45. *Commission decision 2000/532/EC establishing a list of hazardous waste*, European Commission, 2002.

46. *Environmental Protection Act 1990*, Parliament of the United Kingdom, 1990.

47. *Statutory Instrument 1991 No. 2839: The Environmental Protection (Duty of Care) Regulations 1991* Parliament of the United Kingdom, 1991.

48. *Statutory Instrument 2002 No. 1559: The Landfill (England and Wales) Regulations 2002*, Parliament of the United Kingdom, 2002.

49. *The Landfill Directive 1999/31/EC*, European Economic Community, 1999.

50. *Directive 91/689/EEC on hazardous waste*, European Economic Community, 1991.

51. *Approved Supply List. Information approved for the classification and labelling of substances and preparations dangerous for supply*, Health and Safety Commission, 2005.

52. HM Revenue and Customs, *HMRC Notice LFT1: A general guide to landfill tax*, 2007.

53. *Directive 76/464/EEC on the disposal of dangerous substances*, European Economic Community, 1976.

54. *2000/60 Framework Directive for Water*, European Economic Community, 2000.

55. *Model procedures for the management of land contamination*, Environment Agency and Department for Environment Food and Rural Affairs, 2004.

56. L. Goethals and A. Pieters, *TBT Clean (LIFE02 ENV/B/000341):Task 3550: Remediation of sediments-Treatment of the solid phase*, Envisan, Belgium, 2005.

57. S. J. Blunden, L. A. Hobbs and P. J. Smith, *The environmental chemistry of organotin compounds-Environmental Chemistry*, Royal Society of Chemistry, London, 1984.

58. H. A. Skinner, *Advances in organometallic chemistry*, Academic Press, New York, 1964.

59. A. L. Allred and E. G. Rochow, A scale of electronegativity based on electrostatic force, *Journal of Inorganic and Nuclear Chemistry*, 1958, **5**, 264-268.

60. R. C. Poller, *The chemistry of organotin compounds*, Logos Press Limited, London, 1970.

61. W. P. Neumann, *The organic chemistry of tin*, Wiley, New York, 1970.

62. E. A. Clark, R. M. Sterritt and J. N. Lester, The fate of tributyltin in the aquatic environment - A look at the data, *Environmental Science & Technology*, 1988, **22**, 600-604.

63. Y. C. Song, J. H. Woo, S. H. Park and I. S. Kim, A study on the treatment of antifouling paint waste from shipyard, *Marine Pollution Bulletin*, 2005, **51**, 1048-1053.

64. C. Mostofizadeh, *Elimination of TBT compounds from dredged material by means of*

pressure thermolysis, Institute of energy and process technology, Bremerhaven, 2001.

65. K. Duhamel, G. Blanchard, G. Dorange and G. Martin, Recovery of all species from photolytic degradation of tributyltin compounds TBTX (X = Cl, OSn Bu_3), *Applied Organometallic Chemistry*, 1987, **1**, 133-142.

66. J. A. Navio, C. Cerrillos, F. J. Marchena, F. Pablos and M. A. Pradera, Photoassisted degradation of n-butyltin chlorides in air- equilibrated aqueous TiO2 suspension, *Langmuir*, 1996, **12**, 2007-2014.

67. G. Mailhot, M. Astruc and M. Bolte, Degradation of tributyltin chloride in water photoinduced by iron(III), *Applied Organometallic Chemistry*, 1999, **13**, 53-61.

68. G. Breeveld, G. Haug and B. V. Vangelsten, *Removal of organotin compounds in dockyard wastewater by photolysis*, Norwegian Geotechnical Institute, 2005.

69. O. Grievson, *The removal of permethrin and tributyltin from wastewater using advanced oxidation processes and adsorption*, MSc Thesis, Cranfield University, 2007.

70. G. C. Schafran, *Evaluate Pilot and Full-Scale Treatment Processes to Remove TBT from Industrial Wastewater*, Center for advanced ship repair, Old Dominion University, 2002.

71. S. Pensaert, G. DeBecker, B. DeClercq, S. DePuydt, K. VandeVelde, S. Trapp and J. Novak, *TBT Clean (LIFE02 ENV/B/000341): Treatment of sediment*, DEC, http://www.portofantwerp.be/tbtclean/htm/Pub_mainset.htm.

72. J. A. Navio, F. J. Marchena, C. Cerrillos and F. Pablos, UV photolytic degradation of butyltin chlorides in water, *Journal of Photochemistry and Photobiology a-Chemistry*, 1993, **71**, 97-102.

73. H. Stichnothe, W. Calmano, E. Arevalo, A. Keller and J. Thoming, TBT-contaminated sediments - Treatment in a pilot scale - Dedicated to Prof. Dr. Ulrich Forstner on his 65th birthday, *Journal Of Soils And Sediments*, 2005, **5**, 21-29.

74. H. Stichnothe, A. Keller, J. Thoming, N. Lohmann and W. Calmano, Reduction of tributyltin (TBT) and other organic pollutants of concern in contaminated sediments by means of an electrochemical oxidation, *Acta Hydrochimica Et Hydrobiologica*, 2002, **30**, 87-93.

75. H. Stichnothe, J. Thoming and W. Calmano, Detoxification of tributyltin contaminated sediments by an electrochemical process, *Science Of The Total Environment*, 2001, **266**, 265-271.

76. A. Hansen, Ferric iron remediation stabilisation, in *Exploring innovative remediation techniques for contaminated land and groundwater conference*, London Technology Network, London, 2008.

77. G. Ciucani, H. Mosbaek and S. Trapp, Uptake of tributyltin into willow trees, *Environmental Science And Pollution Research*, 2004, **11**, 267-272.

78. J. Novak and S. Trapp, Growth of plants on TBT-contaminated harbour sludge and

effect on TBT removal, *Environmental Science And Pollution Research*, 2005, **12**, 332-341.

79. N. F. Y. Tam, A. M. Y. Chong and Y. S. Wong, Removal of tributyltin (TBT) by live and dead microalgal cells, *Marine Pollution Bulletin*, 2002, **45**, 362-371.

80. J. E. Landmeyer, T. L. Tanner and B. E. Watt, Biotransformation of tributyltin to tin in freshwater river-bed sediments contaminated by an organotin release, *Environmental Science & Technology*, 2004, **38**, 4106-4112.

81. H. Inoue, O. Takimura, K. Kawaguchi, T. Nitoda, H. Fuse, K. Murakami and Y. Yamaoka, Tin-carbon cleavage of organotin compounds by pyoverdine from *Pseudomonas chlororaphis*, *Applied And Environmental Microbiology*, 2003, **69**, 878-883.

82. P. Bernat and J. Dlugonski, Acceleration of tributyltin chloride (TBT) degradation in liquid cultures of the filamentous fungus *Cunninghamella elegans*, *Chemosphere*, 2006, **62**, 3-8.

83. P. Bernat and J. Dlugonski, Degradation of tributyltin by the filamentous fungus *Cunninghamella elegans*, with involvement of cytochrome P-450, *Biotechnology Letters*, 2002, **24**, 1971-1974.

84. T. G. Luan, J. Jin, S. M. N. Chan, Y. S. Wong and N. F. Y. Tam, Biosorption and biodegradation of tributyltin (TBT) by alginate immobilized *Chlorella vulgaris* beads in several treatment cycles, *Process Biochemistry*, 2006, **41**, 1560-1565.

85. Ellis L. B. M., Roe D. and Wackett L. P., The University of Minesotta biocatalysis/biodegradation database: The first decade. Nucleic acids research. D517-D521, University of Minnesota, 2006.

86. A. S. Stasinakis, N. S. Thomaidis, A. Nikolaou and A. Kantifes, Aerobic biodegradation of organotin compounds in activated sludge batch reactors, *Environmental Pollution*, 2005, **134**, 431-438.

87. R. Brandsch, K.-E. Nowak, N. Binder and B. Jastorff, Investigations concerning the sustainability of remediation by land deposition of tributyltin contaminated harbour sediments, *Journal Of Soils And Sediments*, 2001, **1**, 234-236.

88. *Treatment technologies for site clean up. Annual Status report*, US Environmental Protection Agency, 2007.

89. S. Baksi, S. Biswas and S. Mahajan, *Activated Carbon from Bamboo - Technology Development towards Commercialisation*, http://www.tifac.org.in/news/accarbon.htm, 2007.

90. T. J. Gremm and F. H. Frimmel, Determination of organotin compounds in aqueous samples by means of HPGC-AED, *Water Research*, 1992, **26**, 1163-1169.

91. R. Prasad and G. C. Schafran, Characterization of tributyltin in shipyard waters and removal through laboratory and full-scale treatment, *Water Research*, 2006, **40**, 453-462.

92. A. Maes and S. Vreysen, *Use of Sorbent Materials for the Removal of Cu, Zn and*

Organotin Compounds from Dockyard Wastewaters, Faculty of Bioscience engineering, Katholikie Universiteit Leuven, 2005.

93. G. C. Schafran, T. M. Tekleab, R. Prasad, T. Fox, M. A. Champ and D. A. Johnson, *TBT removal paper-Removal of tributyltin (TBT) from shipyard waters: Laboratory evaluations and one year of full-scale, shipyard-based treatment*, Center for advanced ship repair, Old Dominion University, 2001.

94. S. Vreysen, A. Maes and H. Wullaert, Removal of organotin compounds, Cu and Zn from shipyard wastewaters by adsorption - flocculation: A technical and economical analysis, *Marine Pollution Bulletin*, 2008, **56**, 106-115.

95. M. Hoch, J. Alonso-Azcarate and M. Lischick, Adsorption behavior of toxic tributyltin to clay-rich sediments under various environmental conditions, *Environmental Toxicology And Chemistry*, 2002, **21**, 1390-1397.

96. G. M. Walker, J. A. Hanna and S. J. Allen, Treatment of hazardous shipyard wastewater using dolomitic sorbents, *Water Research*, 2005, **39**, 2422-2428.

97. Envirotreat, *Technology overview*, http://www.envirotreat.com/technology_overview.html, 2007.

98. K. B. Krauskopf, *Introduction to geochemistry*, 2nd edn., McGraw-Hill, New York, 1979.

99. Envirotreat, *Mylor Harbour-Cornwall (case study)*, http://www.envirotreat.com/Mylor-Harbour-Cornwall.pdf, 2007.

100. P. Lahtinen, *Development of mass stabilisation technique for contaminated sediments*, 5th International SedNet Conference, Oslo, 2008.

101. *BS EN 197-1:2000, Cement. Compositions, specifications and conformity criteria for common cement*, British Standard.

102. J. Havukainen, M. Lepannen and A. Piispanen, *Mass Stabilisation-A method for reuseof TBT-contaminated sedimentsas part of the harbour field in Helsinki*, 5th European Conference on Contaminated Sediments: Reuse of waterways and remediation of sediments, London, United Kingdom, 2008.

103. A. Piispanen and A. Makinen, *Removal of tributyltin from the seabed of Vuosaari harbour*, Ramboll Finland, 2004.

104. T. Abbott, Cost-effective treatment of TBT-contaminated wash water, *Mer-Marine Engineers Review*, 1996, 33-34.

105. A. Eschenbach, J. Höhne, Z. Söding and G. Luther, *The steam stripping process: A remediation technique for TBT- and PAH-contaminated dredged sediments and soils*, Containment and remediation technology conference and exhibition, Orlando, Florida, 2001.

106. J. Wilson, Tyne capping trial, in *TBT's treatment and disposal*, CEDA, London, 2007.

107. S. Diez, S. Lacorte, P. Viana, D. Barcelo and J. M. Bayona, Survey of organotin compounds in rivers and coastal environments in Portugal 1999-2000, *Environmental Pollution*, 2005, **136**, 525-536.

108. A. C. Almeida, A. D. R. Wagener, C. B. Maia and N. Miekeley, Speciation of organotin compounds in sediment cores from Guanabara Bay, Rio de Janeiro (Brazil) by gas chromatography-pulsed flame photometric detection, *Applied Organometallic Chemistry*, 2004, **18**, 694-704.

109. M. Abalos, J. M. Bayona, R. Compano, M. Granados, C. Leal and M. D. Prat, Analytical procedures for the determination of organotin compounds in sediment and biota: a critical review, *Journal Of Chromatography A*, 1997, **788**, 1-49.

110. J. A. J. Thompson, S. Douglas, Y. K. Chau and R. J. Maguire, Recent studies of residual tributyltin in coastal British Columbia sediments, *Applied Organometallic Chemistry*, 1998, **12**, 643-650.

111. A. J. Bartlett, U. Borgmann, D. G. Dixon, S. P. Batchelor and R. J. Maguire, Tributyltin uptake and depuration in *Hyalella azteca*: Implications for experimental design, *Environmental Toxicology And Chemistry*, 2004, **23**, 426-434.

112. T. Suzuki, H. Yamada, I. Yamamoto, K. Nishiura, K. Kondo, M. Murayama and M. Uchiyama, Chemical species of organotin compounds in seawater and their seasonal variations, *Journal of Agricultural and Food Chemistry*, 1996, **44**, 3989-3995.

113. K. Takahashi, Measurement of the leaching rates of tributyltin and triphenyltin compounds from antifouling paint by gas-chromatography, *Jocca-Surface Coatings International*, 1991, **74**, 331.

114. M. Abalos, J. M. Bayona and P. Quevauviller, Comprehensive evaluation of the extraction variables affecting the determination and stability of native butyl- and phenyl-tin compounds from sediment, *Applied Organometallic Chemistry*, 1998, **12**, 541-549.

115. F. Smedes, A. S. deJong and I. M. Davies, Determination of (mono-, di- and) tributyltin in sediments. Analytical methods, *Journal Of Environmental Monitoring*, 2000, 541-549.

116. Y. Hattori, H. Yamamoto, K. Nagai, K. Nonaka, H. Hashimoto, S. Nakamura, M. Nakamoto, K. Annen, S. Sakamori, H. Shiraishi and M. Morita, Determination of tributyltin and triphenyltin compounds in industrial wastewater by GC, *Bunseki Kagaku*, 1991, **40**, 25-31.

117. E. Graupera, C. Leal, M. Granados, M. D. Prat and R. Compano, Determination of tributyltin and triphenyltin in sediments by liquid chromatography with fluorimetric detection - Assessment of spiking procedures, *Journal Of Chromatography A*, 1999, **846**, 413-423.

118. P. Schubert, E. Rosenberg and M. Grasserbauer, Optimization of a sample preparation procedure for the speciation of organotin compounds in sediment samples using GC- AED, *International Journal of Environmental Analytical Chemistry*, 2000, **78**, 185-204.

119. I. Arambarri, R. Garcia and E. Millan, Assessment of tin and butyltin species in

estuarine superficial sediments from Gipuzkoa, Spain, *Chemosphere*, 2003, **51**, 643-649.

120. F. Suehiro, T. Kobayashi, L. Nonaka, B. C. Tuyen and S. Suzuki, Degradation of tributyltin in microcosm using Mekong River sediment, *Microbial Ecology*, 2006, **52**, 19-25.

121. B. Lalere, J. Szpunar, H. Budzinski, P. Garrigues and O. F. X. Donard, Speciation analysis for organotin compounds in sediments by capillary gas-chromatography with flame photometric detection after microwave-assisted acid leaching, *Analyst*, 1995, **120**, 2665-2673.

122. J. R. Encinar, P. R. Gonzalez, J. I. G. Alonso and A. Sanz-Medel, Evaluation of extraction techniques for the determination of butyltin compounds in sediments using isotope dilution-GC/ICPMS with Sn-118 and Sn-119-enriched species, *Analytical Chemistry*, 2002, **74**, 270-281.

123. O. F. X. Donard, B. Lalere, F. Martin and R. Lobinski, Microwave-assisted leaching of organotin compounds from sediments for speciation analysis, *Analytical Chemistry*, 1995, **67**, 4250-4254.

124. L. Yang and J. W. H. Lam, Microwave-assisted extraction of butyltin compounds from PACS-2 sediment for quantitation by high-performance liquid chromatography inductively coupled plasma mass spectrometry, *Journal Of Analytical Atomic Spectrometry*, 2001, **16**, 724-731.

125. Y. Cai, R. Alzaga and J. M. Bayona, In-situ derivatization and supercritical fluid extraction for the simultaneous determination of butyltin and phenyltin compounds in sediment, *Analytical Chemistry*, 1994, **66**, 1161-1167.

126. Y. Cai, M. Abalos and J. M. Bayona, Effects of complexing agents and acid modifiers on the supercritical fluid extraction of native phenyl- and butyl-tins from sediment, *Applied Organometallic Chemistry*, 1998, **12**, 577-584.

127. S. Diez, L. Ortiz and J. M. Bayona, Off-line solid-phase extraction procedure for the determination of phenyl and butyltin compounds from aqueous matrices followed by GC-FPD determination, *Chromatographia*, 2000, **52**, 657-663.

128. A. M. Caricchia, S. Chiavarini, C. Cremisini, R. Morabito and C. Ubaldi, Analytical methods for the determination of organotins in the marine environment, *International Journal of Environmental Analytical Chemistry*, 1993, **53**, 37-52.

129. E. Gonzalez-Toledo, R. Compano, M. Granados and M. D. Prat, Determination of butyltin and phenyltin species by reversed- phase liquid chromatography and fluorimetric detection, *Journal Of Chromatography A*, 2000, **878**, 69-76.

130. J. L. Gomezariza, R. Beltran, E. Morales, I. Giraldez and M. Ruizbenitez, Use of cartridges for speciation of organotin compounds in environmental samples, *Applied Organometallic Chemistry*, 1994, **8**, 553-561.

131. R. Alzaga and J. M. Bayona, Supercritical-fluid extraction of tributyltin and its degradation products from seawater via liquid-solid phase extraction, *Journal Of Chromatography A*, 1993, **655**, 51-56.

132. S. Aguerre, G. Lespes, V. Desauziers and M. Potin-Gautier, Speciation of organotins in environmental samples by SPME-GC: comparison of four specific detectors: FPD, PFPD, MIP-AES and ICP-MS, *Journal Of Analytical Atomic Spectrometry*, 2001, **16**, 263-269.

133. C. Bancon-Montigny, P. Maxwell, L. Yang, Z. Mester and R. E. Sturgeon, Improvement of measurement precision of SPME-GC/MS determination of tributyltin using isotope dilution calibration, *Analytical Chemistry*, 2002, **74**, 5606-5613.

134. M. Gallego-Gallegos, R. Munoz-Olivas, A. Martin-Esteban and C. Camara, Synthesis and evaluation of molecularly imprinted polymers for organotin compounds: a screening method for tributyltin detection in seawater, *Analytica Chimica Acta*, 2005, **531**, 33-39.

135. W. Dirkx, R. Lobinski, M. Ceulemans and F. Adams, Determination of methyltin and butyltin compounds in waters of the Antwerp harbor, *Science Of The Total Environment*, 1993, **136**, 279-300.

136. S. Tsunoi, T. Matoba, H. Shioji, L. T. H. Giang, H. Harino and M. Tanaka, Analysis of organotin compounds by grignard derivatization and gas chromatography-ion trap tandem mass spectrometry, *Journal Of Chromatography A*, 2002, **962**, 197-206.

137. L. M. Allan, D. K. Verma, F. Yang, Y. K. Chau and R. J. Maguire, A method for the analysis of butyltin chlorides in air by gas chromatography with atomic emission detection, *Aihaj*, 2000, **61**, 820-824.

138. P. L. Pauson, Tropones and tropolones, *Chemical Reviews*, 1955, **55**, 9-136.

139. G. Lespes, Direct gas chromatographic determination of organotins as halide forms, *Analusis*, 1995, **23**, 382-388.

140. S. Hashimoto and A. Otsuki, Determination of mono-substituted, di-substituted and tri-substituted butyltin, phenyltin and methyltin compounds as free halides using gas chromatography with flame photometric detection, *Hrc-Journal of High Resolution Chromatography*, 1991, **14**, 397-400.

141. J. A. Stab, W. P. Cofino, B. Vanhattum and U. A. T. Brinkman, Comparison of GC MSd and GC AED for the determination of organotin compounds in the environment, *Fresenius Journal Of Analytical Chemistry*, 1993, **347**, 247-255.

142. I. Tolosa, J. Dachs and J. M. Bayona, Tributyltin speciation in aquatic matrices by cGC-FPD and cGC- MS confirmation, *Mikrochimica Acta*, 1992, **109**, 87-91.

143. M. Kawarai, T. Shirasaki and K. Mizuishi, Analysis of organotin compounds in seawater using GC/pulsed flame photometric detection, *Bunseki Kagaku*, 2002, **51**, 959-964.

144. J. L. Gomez-Ariza, E. Morales, I. Giraldez and R. Beltran, Acid leaching solvent extraction treatment of sediment samples for organotin speciation, *International Journal of Environmental Analytical Chemistry*, 1997, **66**, 1-13.

145. M. B. delaCalleGuntinas, R. Scerbo, S. Chiavarini, P. Quevauviller and R. Morabito, Comparison of derivatization methods for the determination of butyl- and phenyl-tin

compounds in mussels by gas chromatography, *Applied Organometallic Chemistry*, 1997, **11**, 693-702.

146. R. J. Maguire, Butyltin compounds and inorganic tin in sediments in Ontario, *Environmental Science & Technology*, 1984, **18**, 291-294.

147. J. A. Jacobsen, F. StuerLauridsen and G. Pritzl, Organotin speciation in environmental samples by capillary gas chromatography and pulsed flame photometric detection (PFPD), *Applied Organometallic Chemistry*, 1997, **11**, 737-741.

148. M. Leermakers, J. Nuyttens and W. Baeyens, Organotin analysis by gas chromatography-pulsed flame-photometric detection (GC-PFPD), *Analytical And Bioanalytical Chemistry*, 2005, **381**, 1272-1280.

149. P. Pinel-Raffaitin, P. Rodriguez-Gonzalez, M. Ponthieu, D. Amouroux, I. L. Hecho, L. Mazeas, O. F. X. Donard and M. Potin-Gautier, Determination of alkylated tin compounds in landfill leachates using isotopically enriched tin species with GC-ICP-MS detection, *Journal Of Analytical Atomic Spectrometry*, 2007, **22**, 258-266.

150. S. Tsunoi, H. Shioji and M. Tanaka, Derivatization of tributyltin with sodium tetrakis(4-fluorophenyl)borate for sensitivity improvement of tandem mass spectrometry, *Analytical Sciences*, 2004, **20**, 101-105.

151. M. G. Ikonomou, M. P. Fernandez, T. He and D. Cullon, Gas chromatography-high-resolution mass spectrometry based method for the simultaneous determination of nine organotin compounds in water, sediment and tissue, *Journal Of Chromatography A*, 2002, **975**, 319-333.

152. J. P. Meador, T. K. Collier and J. E. Stein, Determination of a tissue and sediment threshold for tributyltin to protect prey species of juvenile salmonids listed under the US Endangered Species Act, *Aquatic Conservation: Marine and Freshwater Ecosystems*, 2002, **12**, 539-551.

153. A. G. Howard, (Boro)hydride techniques in trace element speciation - Invited lecture, *Journal Of Analytical Atomic Spectrometry*, 1997, **12**, 267-272.

154. V. A. MaciasCarranza, J. V. MaciasZamora and J. A. VillaescusaCelaya, Organotin compounds in marine water and sediments from the port of Ensenada, Baja California, Mexico, *Ciencias Marinas*, 1997, **23**, 377-394.

155. M. J. Waldock and M. E. Waite, The performance of an analytical method for determination of TBT during a 6-year monitoring program, *Applied Organometallic Chemistry*, 1994, **8**, 649-658.

156. K. Takahashi, Determination of dibutyltin and tributyltin compounds in seawater and the distribution of them in seawater of several bays, *Nippon Kagaku Kaishi*, 1991, 367-374.

157. N. B. Bhosle, A. Garg, S. Jadhav, R. Harjee, S. S. Sawant, K. Venkat and A. C. Anil, Butyltins in water, biofilm, animals and sediments of the west coast of India, *Chemosphere*, 2004, **57**, 897-907.

158. C. L. Matthias, J. M. Bellama, G. J. Olson and F. E. Brinckman, Comprehensive method for determination of aquatic butyltin and butylmethyltin species at ultratrace levels using simultaneous hydridization extraction with gas-chromatography flame photometric detection, *Environmental Science & Technology*, 1986, **20**, 609-615.

159. J. J. Chen, Y. C. Lou and C. W. Whang, Determination of tributyltin in seawater by hydride generation-atomic absorption spectrometry, *Journal of the Chinese Chemical Society*, 1992, **39**, 461-464.

160. E. S. Garcia, J. I. G. Alonso and A. SanzMedel, Determination of butyltin compounds in sediments by means of hydride generation cold trapping gas chromatography coupled to inductively coupled plasma mass spectrometric detection, *Journal of Mass Spectrometry*, 1997, **32**, 542-549.

161. R. Ritsema, T. de Smaele, L. Moens, A. S. de Jong and O. F. X. Donard, Determination of butyltins in harbour sediment and water by aqueous phase ethylation GC-ICP-MS and hydride generation GC- AAS, *Environmental Pollution*, 1998, **99**, 271-277.

162. G. B. Jiang, Q. F. Zhou, J. Y. Liu and D. J. Wu, Occurrence of butyltin compounds in the waters of selected lakes, rivers and coastal environments from China, *Environmental Pollution*, 2001, **115**, 81-87.

163. J. C. Wu, Z. Mester and J. Pawliszyn, Determination of tributyltin by automated in-tube solid-phase microextraction coupled with HPLC-ES-MS, *Journal Of Analytical Atomic Spectrometry*, 2001, **16**, 159-165.

164. P. Quevauviller, F. Martin, C. Belin and O. F. X. Donard, Matrix effects in the determination of butyltin compounds in environmental-samples by GC-AA after hydride generation, *Applied Organometallic Chemistry*, 1993, **7**, 149-157.

165. M. Iijima and Y. Hoshino, Determination of tributyltin and triphenyltin compounds in fish by derivatization with sodium tetraethylborate, *Japanese Journal of Toxicology and Environmental Health*, 1998, **44**, 371-377.

166. M. Nagase, M. Toba, H. Kondo and K. Hasebe, Determination of dibutyltin compounds in soft polyurethane foam by gas chromatography with flame photometric detection, *Analyst*, 1998, **123**, 1091-1094.

167. R. M. Coloso and I. G. Borlongan, Significant organotin contamination of sediment and tissues of milkfish in brackish water ponds, *Bulletin Of Environmental Contamination And Toxicology*, 1999, **63**, 297-304.

168. P. Schubert, I. Fernandez-Escobar, E. Rosenberg and J. M. Bayona, Evaluation of desulfurization procedures for the elimination of sulfur interferences in the organotin analysis of sediments, *Journal Of Chromatography A*, 1998, **810**, 245-251.

169. J. M. F. Nogueira, B. Simplicio, M. H. Florencio and A. M. M. Bettencourt, Levels of tributyltin in sediments from Tagus estuary nature reserve, *Estuaries*, 2003, **26**, 798-802.

170. N. Voulvoulis, M. D. Scrimshaw and J. N. Lester, Removal of organotins during sewage treatment: A case study, *Environmental Technology*, 2004, **25**, 733-740.

171. C. CarlierPinasseau, G. Lespes and M. Astruc, Determination of butyl- and phenyltin compounds in sediments by GC-FPD after NaBEt4 ethylation, *Talanta*, 1997, **44**, 1163-1171.

172. H. Tao, R. B. Rajendran, C. R. Quetel, T. Nakazeto, M. Tominaga and A. Miyazaki, Tin speciation in the femtogram range in open ocean seawater by gas chromatography/inductively coupled plasma mass spectrometry using a shield torch at normal plasma conditions, *Analytical Chemistry*, 1999, **71**, 4208-4215.

173. S. Inoue, S. Abe, Y. Oshima, N. Kai and T. Honjo, Tributyltin contamination of bivalves in coastal areas around northern Kyushu, Japan, *Environmental Toxicology*, 2006, **21**, 244-249.

174. C. CarlierPinasseau, G. Lespes and M. Astruc, Determination of butyltin and phenyltin by GC-FPD following ethylation by NaBEt(4), *Applied Organometallic Chemistry*, 1996, **10**, 505-512.

175. E. Millan and J. Pawliszyn, Determination of butyltin species in water and sediment by solid-phase microextraction-gas chromatography-flame ionization detection, *Journal Of Chromatography A*, 2000, **873**, 63-71.

176. J. Dwivedi and L. D. Trombetta, Acute toxicity and bioaccumulation of tributyltin in tissues of *Urolophus jamaicensis* (yellow stingray), *Journal of Toxicology and Environmental Health-Part a-Current Issues*, 2006, **69**, 1311-1323.

177. A. Amirav and H. W. Jing, Pulsed flame photometer detector for gas-chromatography, *Analytical Chemistry*, 1995, **67**, 3305-3318.

178. H. W. Jing and A. Amirav, Pulsed flame photometric detector - a step forward towards universal heteroatom selective detection, *Journal Of Chromatography A*, 1998, **805**, 177-215.

179. A. F. L. Godoi, R. Favoreto and M. Santiago-Silva, GC analysis of organotin compounds using pulsed flame photometric detection and conventional flame photometric detection, *Chromatographia*, 2003, **58**, 97-101.

180. J. Strand, J. A. Jacobsen, B. Pedersen and A. Granmo, Butyltin compounds in sediment and molluscs from the shipping strait between Denmark and Sweden, *Environmental Pollution*, 2003, **124**, 7-15.

181. M. Bravo, G. Lespes, I. De Gregori, H. Pinochet and M. Potin-Gautier, Identification of sulfur interferences during organotin determination in harbour sediment samples by sodium tetraethyl borate ethylation and gas chromatography-pulsed flame photometric detection, *Journal Of Chromatography A*, 2004, **1046**, 217-224.

182. J. Nuyttens, *Evaluation of the GC-PFPD for the determination of organotin compounds in environmental samples*, PhD Thesis, Vrije Universiteit Brussel, 2004.

183. C. Marcic, I. Le Hecho, L. Denaix and G. Lespes, TBT and TPhT persistence in a sludged soil, *Chemosphere*, 2006, **65**, 2322-2332.

184. M. Le Gac, G. Lespes and M. Potin-Gautier, Rapid determination of organotin

compounds by headspace solid-phase microextraction, *Journal Of Chromatography A*, 2003, **999**, 123-134.

185. A. F. L. Godoi, R. C. Montone and M. Santiago-Silva, Determination of butyltin compounds in surface sediments from the Sao Paulo State coast (Brazil) by gas chromatography-pulsed flame photometric detection, *Journal Of Chromatography A*, 2003, **985**, 205-210.

186. L. H. Hassani, A. G. Frenich, M. H. Benajiba, M. J. G. Rodriguez, J. L. M. Vidal and A. Debdoubi, Assessment of butyltin and phenyltin pollution in the sea mullet, *Mugil cephalus*, along the Moroccan and Spanish coasts (Mediterranean Sea), *Archives Of Environmental Contamination And Toxicology*, 2006, **51**, 608-614.

187. H. Serra and J. M. F. Nogueira, Organotin speciation in environmental matrices by automated on-line hydride generation-programmed temperature vaporization-capillary gas chromatography-mass spectrometry detection, *Journal Of Chromatography A*, 2005, **1094**, 130-137.

188. H. Shioji, S. Tsunoi, H. Harino and M. Tanaka, Liquid-phase microextraction of tributyltin and triphenyltin coupled with gas chromatography-tandem mass spectrometry - Comparison between 4-fluorophenyl and ethyl derivatizations, *Journal Of Chromatography A*, 2004, **1048**, 81-88.

189. P. Rodriguez-Gonzalez, J. R. Encinar, J. I. G. Alonso and A. Sanz-Medel, Contamination of the coastal waters of Gijon on (North West Spain) by butyltin compounds, *Water Air and Soil Pollution*, 2006, **174**, 127-139.

190. S. Aguerre, C. Pecheyran and G. Lespes, Validation, using a chemometric approach, of gas chromatography-inductively coupled plasma-atomic emission spectrometry (GC-ICP-AES) for organotin determination, *Analytical And Bioanalytical Chemistry*, 2003, **376**, 226-235.

191. J. I. Garciaalonso, A. Sanzmedel and L. Ebdon, Determination of butyltin ion species by ion-exchange chromatography with inductively-coupled plasma-mass spectrometric and spectrofluorometric detection, *Analytica Chimica Acta*, 1993, **283**, 261-271.

192. M. Grotti, P. Rivaro and R. Frache, Determination of butyltin compounds by high-performance liquid chromatography-hydride generation-electrothermal atomization atomic absorption spectrometry, *Journal Of Analytical Atomic Spectrometry*, 2001, **16**, 270-274.

193. X. P. Wang, L. Ding, H. R. Zhang, J. H. Cheng, A. M. Yu, H. Q. Zhang, L. Liu, Z. H. Liu and Y. Li, Development of an analytical method for organotin compounds in fortified flour samples using microwave-assisted extraction and normal-phase HPLC with UV detection, *Journal of Chromatography B-Analytical Technologies in the Biomedical and Life Sciences*, 2006, **843**, 268-274.

194. P. Vinas, I. Lopez-Garcia, B. Merino-Merono, N. Campillo and M. Hernandez-Cordoba, Liquid chromatography-hydride generation-atomic absorption spectrometry for the speciation of tin in seafoods, *Journal Of Environmental Monitoring*, 2004, **6**, 262-266.

195. K. Bekri, R. Saint-Louis and E. Pelletier, Determination of tributyltin and 4-hydroxybutyldibutyltin chlorides in seawater by liquid chromatography with atmospheric

pressure chemical ionization-mass spectrometry, *Analytica Chimica Acta*, 2006, **578**, 203-212.

196. B. Fairman, T. Catterick, B. Wheals and E. Polinina, Reversed-phase ion-pair chromatography with inductively coupled plasma-mass spectrometry detection for the determination of organo-tin compounds in waters, *Journal Of Chromatography A*, 1997, **758**, 85-92.

197. E. Gonzalez-Toledo, A. Ortuno, R. Compano, M. Granados and M. D. Prat, Solid-phase extraction-liquid chromatography-fluorimetry for organotin speciation in natural waters, *Chromatographia*, 2002, **55**, 19-24.

198. P. BermejoBarrera, R. M. SotoFerreiro, R. DominguezGonzalez and A. BermejoBarrera, Determination of tributyltin, dibutyltin and total tin in the galicia estuaries by HPLC-ETAAS, *Annali Di Chimica*, 1996, **86**, 495-508.

199. P. Rivaro and R. Frache, Extraction of butyltins from sediments and their determination by liquid chromatography interfaced to inductively coupled plasma atomic emission detector, *Annali Di Chimica*, 2000, **90**, 299-306.

200. P. Quevauviller and O. F. X. Donard, Organotin stability during storage of marine waters and sediments, *Fresenius Journal Of Analytical Chemistry*, 1991, **339**, 6-14.

201. QUASIMEME, *Quality assurance of information for marine environmental monitoring in Europe* Project office at FRS.

202. M. A. Unger, *A manual for the analysis of butyltins in environmental samples*, Virginia Institute of Marine Science, 1996.

203. T. L. Wade, B. Garciaromero and J. M. Brooks, Tributyltin contamination in bivalves from united-states coastal estuaries, *Environmental Science & Technology*, 1988, **22**, 1488-1493.

204. S. H. Zhang, Y. K. Chau, W. C. Li and A. S. Y. Chau, Evaluation of extraction techniques for butyltin compounds in sediment, *Applied Organometallic Chemistry*, 1991, **5**, 431-434.

205. A. Amirav, H. Jing and J. J. Robinson, *Pulsed flame photometric detector for gas chromatography*, Varian, USA, 2000.

206. C. G. Flinn and W. A. Aue, Gas-chromatographic detection of organogermanium compounds by surface or gas-phase luminescence, *Journal of Chromatography*, 1979, **186**, 299-306.

207. G. B. Jiang, P. S. Maxwell, K. W. M. Siu, V. T. Luong and S. S. Berman, Determination of butyltins in mussel by gas chromatography with flame photometric detection using quartz surface induced luminescence, *Analytical Chemistry*, 1991, **63**, 1506-1509.

208. R. W. B. Pearse and A. G. Gaydon, *The identification of molecular spectra*, Chapman and Hall, London, 1976.

209. C. Bancon-Montigny, G. Lespes and M. Potin-Gautier, Improved routine speciation of organotin compounds in environmental samples by pulsed flame photometric detection, *Journal Of Chromatography A*, 2000, **896**, 149-158.

210. W. A. Aue, X. Y. Sun and B. Millier, Inter-elementary selectivity, spectra and computer-generated specificity of some main-group elements in the flame photometric detector, *Journal of Chromatography*, 1992, **606**, 73-86.

211. M. D. Mueller, Comprehensive trace level determination of organotin compounds in environmental samples using high-resolution gas chromatography with flame photometric detection, *Analytical Chemistry*, 1987, **59**, 617-623.

212. S. Cheskis, E. Atar and A. Amirav, Pulsed-flame photometer-A novel gas-chromatography detector, *Analytical Chemistry*, 1993, **65**, 539-555.

213. M. Kira, L. C. Zhang, C. Kabuto and H. Sakurai, Structure of (tropolonato)(4)M-type compounds (M = Si, Ge, Sn), *Organometallics*, 1998, **17**, 887-892.

214. M. J. F. Leroy, P. Quevauviller, O. F. X. Donard and M. Astruc, Determination of tin species in environmental samples (Technical Report), *Pure And Applied Chemistry*, 1998, **70**, 2051-2064.

215. W. J. Shim, S. H. Hong, U. H. Yim, N. S. Kim and J. R. Oh, Horizontal and vertical distribution of butyltin compounds in sediments from shipyards in Korea, *Archives Of Environmental Contamination And Toxicology*, 2002, **43**, 277-283.

216. A. Phenix, Building models: comparative swelling powers of organic solvents on oil paint and the cleaning of paintings, *V & A*, 2002, **40**.

217. N. Stolow, The action of solvents on drying oil films, *Journal of the Oil and Colour Chemists Association*, 1967, **40**.

218. I. Tolosa and J. W. Readman, Simultaneous analysis of the antifouling agents: Tributyltin, triphenyltin and IRGAROL 1051 in marina water samples, *Analytica Chimica Acta*, 1996, **335**, 267-274.

219. National Research Council Canada, *Marine sediment reference materials for trace metals and other constituents (HISS-1, MESS-3, PACS-2)*, Canada, 2000.

220. P. Konieczka, B. Sejeroe-Olsen, T. P. J. Linsinger and H. Schimmel, Determination of tributyltin (TBT) in marine sediment using pressurised liquid extraction-gas chromatography-isotope dilution mass spectrometry (PLE-GC-IDMS) with a hexane-tropolone mixture, *Analytical And Bioanalytical Chemistry*, 2007, **388**, 975-978.

221. J. F. Felizzola, A. D. R. Wagener, A. C. Almeida and W. O. Lin, Butyltin speciation in sediments from Todos os Santos Bay (Bahia, Brazil) by GC-PFPD, *Quimica Nova*, 2008, **31**, 89-93.

222. K. K. Turekian and K. H. Wedepohl, Distribution of the elements in some major units of the Earth's crust, *Geological Society of America Bulletin*, 1961, **72**, 175-191.

223. W. A. Aue and C. G. Flinn, Photometric tin detector for gas chromatography, *Journal*

of Chromatography, 1977, **142**, 145-154.

224. J. F. McGaughey and S. K. Gangwal, Comparison of 3 commercially available gas-chromatographic flame photometric detectors in the sulfur mode, *Analytical Chemistry*, 1980, **52**, 2079-2083.

225. S. O. Farwell and C. J. Barinaga, Sulfur-selective detection with the FPD-Current enigmas, practical usage, and future directions, *Journal of Chromatographic Science*, 1986, **24**, 483-494.

226. M. Dressler, *Selective Gas Chromatographic Detectors*, Elsevier, Amsterdam, 1986.

227. D. J. Hucknall, *Chemistry of hydrocarbon combustion*, Chapman and Hall, London, 1985.

228. R. M. Fristrom and A. A. Westenberg, *Flame Structure*, McGraw-Hill, New York, 1965.

229. G. B. Jiang and J. Y. Liu, Determination of butyltin compounds in aqueous samples by gas chromatography with flame photometric detector and headspace solid-phase microextraction after in-situ hydride derivatization, *Analytical Sciences*, 2000, **16**, 585-588.

230. F. M. Martin and O. F. X. Donard, Aqueous ethylation of organotin compounds in simple solution for speciation analysis by cryofocusing and detection by atomic-absorption spectrometry - Comparison with hydride generation, *Fresenius Journal Of Analytical Chemistry*, 1995, **351**, 230-236.

231. Y. Cai and J. M. Bayona, Simultaneous speciation of butyltin, phenyltin, and cyclohexyltin compounds in aqueous matrices using ethylation followed by solid-phase trace enrichment, SFE, and Cc Determination, *Journal of Chromatographic Science*, 1995, **33**, 89-97.

232. P. Bermejo-Barrera, G. Gonzalez-Campos, M. Ferron-Novais and A. Bermejo-Barrera, Column preconcentration of organotin with tropolone-immobilized and their determination by electrothermal atomization absorption spectrometry, *Talanta*, 1998, **46**, 1479-1484.

233. Supelco, *Guide to solid phase extraction*, Supelco, 1998.

234. K. Grob, G. Karrer and M. L. Riekkola, On-column injection of large sample volumes using the retention gap technique in capillary gas-chromatography, *Journal of Chromatography*, 1985, **334**, 129-155.

235. H. G. Janssen, *Inlets for capillary gas chromatography*, http://www.lasersan.com/products_pdf/Inlets_for_Capillary_Gas_Chromatography.pdf, 2008.

236. K. Grob, *On-column injection in capillary gas chromatography: basic technique, retention gaps, solvent effects*, Huethig, Heidelberg, 1987.

237. M. A. Unger, W. G. Macintyre, J. Greaves and R. J. Huggett, GC determination of

butyltins in natural waters by flame photometric detection of hexyl derivatives with mass-spectrometric confirmation, *Chemosphere*, 1986, **15**, 461-470.

238. P. Becher, *Emulsions: theory and practice*, Reinhold Publishing Corporation, USA, 1957.

239. K. C. Molloy, in *Chemistry of tin*, ed. P. G. Harrison, Blackie, Glasgow and London, 1st edn., 1989.

240. ORTEPA, *Method-Butyltin chlorides in air*, http://www.ortepa.org/stabilizers/pages/Butyltinsinair.pdf, 2008.

241. G. J. M. VanderKerk, in *Organotin compounds: new chemistry and applications* ed. R. F. Gould, American Chemical Society, Washington, 1st edn., 1976.

242. M. E. Abdelsalam and P. R. Birkin, A study investigating the sonoelectrochemical degradation of an organic compound employing Fenton's reagent, *Physical Chemistry Chemical Physics*, 2002, **4**, 5340-5345.

243. T. J. Mason and J. P. Lorimer, *Sonochemistry: theory, application and uses of ultrasound in chemistry*, John Wiley & Sons, New York, 1988.

244. K. Makino, M. M. Mossoba and P. Riesz, Chemical effects of ultrasound on aqueous solutions-evidence for *OH and *H by spin trapping, *Journal of the American Chemical Society*, 1982, **104**, 3537-3539.

245. D. Rehorek and E. G. Janzen, Spin trapping of radicals generated by ultrasonic decomposition of organotin compounds, *Journal of Organometallic Chemistry*, 1984, **268**, 135-139.

246. R. T. Morrison and R. N. Boyd, *Organic chemistry*, 4th edn., Allyn & Bacon, Boston, 1983.

247. C. Cornelis, J. Bierkens, I. Joris, P. Nielsen and S. Pensaert, Quality criteria for re-use of organotin-containing sediments on land, *Journal Of Soils And Sediments*, 2006, **6**, 156-162.

248. L. M. Ottosen, E. Arevalo, H. Stichnothe and W. Calmano, Ferric flocks to remove Zn and Cu from dockyard wastewater, *Environmental Chemistry Letters*, 2006, **3**, 164-168.

249. P. Harris, On charcoal, *Interdisciplinary Science Reviews*, 1999, **24**, 301-306.

250. R. E. Franklin, The interpretation of diffuse X-ray diagrams of carbon, *Acta Crystallographica*, 1950, **3**, 107-121.

251. R. A. Kramer, L. Perter and H. S. Valia, *Development of a multipurpose coke plant for synthetic fuel production*, http://www.purdue.edu/dp/energy/pdfs/CokePlantSyntheticFuelProduction-Kramer.pdf, 2008.

252. World Bank Group, *Coke manufacturing*, http://www.ifc.org/ifcext/enviro.nsf/AttachmentsByTitle/gui_coke_WB/$FILE/coke_PPA

H.pdf, 2008.

253. J. C. Crittenden, R. R. Trussell, D. W. Hand, K. J. Howe and G. Tchobanoglous, eds., *Water treatment*, 2nd edn., John Wiley & Sons, New Jersey, 2005.

254. A. Trepte, Montmorillonite structure, with English labels, in *http://commons.wikimedia.org/wiki/File:Montmorillonite-en.svg*, 2007.

255. Industrial Minerals Association, http://www.ima-eu.org/fileadmin/downloads/minerals/Sepiolite_fact_sheet.pdf, 2007.

256. Y. Q. Zhang, J. F. Wang, C. Amrhein and W. T. Frankenberger, Removal of selenate from water by zerovalent iron, *Journal Of Environmental Quality*, 2005, **34**, 487-495.

257. L. B. Hoch, E. J. Mack, B. W. Hydutsky, J. M. Hershman, I. M. Skluzacek and T. E. Mallouk, Carbothermal synthesis of carbon-supported nanoscale zero-valent iron particles for the remediation of hexavalent chromium, *Environmental Science & Technology*, 2008, **42**, 2600-2605.

258. F. D. Coelho, J. D. Ardisson, F. C. C. Moura, R. M. Lago, E. Murad and J. D. Fabris, Potential application of highly reactive Fe(0)/Fe3O4 composites for the reduction of Cr(VI) environmental contaminants, *Chemosphere*, 2008, **71**, 90-96.

259. J. X. Liu, H. Liu, C. Wang, X. Z. Li, Y. X. Tong, X. O. Xuan and G. F. Cui, Synthesis, characterization and re-activation of a Fe-0/Ti system for the reduction of aqueous Cr(VI), *Journal of Hazardous Materials*, 2008, **151**, 761-769.

260. H. L. Lien and W. X. Zhang, Nanoscale Pd/Fe bimetallic particles: Catalytic effects of palladium on hydrodechlorination, *Applied Catalysis B-Environmental*, 2007, **77**, 110-116.

261. A. Gavaskar, L. Tatar and W. Condit, *Cost and performance report for nanoscale zero-valent iron technologies for source remediation*, Naval Facilities Engineering Command,, 2005.

262. Toda Kogyo, *Nano scale iron*, http://www.todaamerica.com/products/eco/rnip/src/RNIP-1M07-05.pdf, 2008.

263. A. M. Neville, *Properties of concrete*, 2nd edn., Pitman, London, 1973.

264. H. F. W. Taylor, *Cement chemistry*, 2nd edn., London, 1997.

265. S. Paria and P. K. Yuet, Solidification-stabilization of organic and inorganic contaminants using portland cement: a literature review, *Environmental Reviews*, 2006, **14**, 217-255.

266. United Kingdom Quality Ash Association, http://www.ukqaa.org.uk/EnvirAndSustain.html, 2008.

267. J. Kumpiene, A. Lagerkvist and C. Maurice, Stabilization of Pb- and Cu-contaminated soil using coal fly ash and peat, *Environmental Pollution*, 2007, **145**, 365-373.

268. V. M. Gun'ko, D. Palijczuk, R. Leboda, J. Skubiszewska-Zieba, R. Smigielski and S. Zietek, Influence of pore structure and pretreatments of activated carbons and water effects

on breakthrough dynamics of tert-butylbenzene, *Journal of Colloid and Interface Science*, 2006, **294**, 53-68.

269. M. Hoch and R. Weerasooriya, New model calculations of pH-depending tributyltin adsorption onto montmorillonite surface and montmorillonite-rich sediment, *Environmental Science & Technology*, 2005, **39**, 844-849.

270. H. L. Bohn, B. L. McNeal and G. A. O'Connor, *Soil chemistry*, 2nd edn., John Wiley & Sons, New York, 1985.

271. M. Hoch and D. Schwesig, Parameters controlling the partitioning of tributyltin (TBT) in aquatic systems, *Applied Geochemistry*, 2004, **19**, 323-334.

272. M. C. Hermosin, P. Martin and J. Cornejo, Adsorption mechanisms of monobutyltin in clay minerals, *Environmental Science & Technology*, 1993, **27**, 2606-2611.

273. D. B. Vance, *Nanoscale Iron Colloids* http://www.pollutionengineering.com/Articles/Feature_Article/9b54a02711e68010VgnVCM100000f932a8c0____, 2008.

274. K. V. Thomas, S. J. Blake and M. J. Waldock, Antifouling paint booster biocide contamination in UK marine sediments, *Marine Pollution Bulletin*, 2000, **40**, 739-745.

275. S. Kan-Atireklap, S. Tanabe and J. Sanguansin, Contamination by butyltin compounds in sediments from Thailand, *Marine Pollution Bulletin*, 1997, **34**, 894-899.

276. *BS EN 12880:2000 Characterisation of sludges-Determination of dry residue and water content*, British Standard, 2000.

277. E. T. Degens, *Geochemistry of the sediments*, Prentice-Hall, New Jersey, 1965.

278. V. M. Hebatpuria, H. A. Arafat, H. S. Rho, P. L. Bishop, N. G. Pinto and R. C. Buchanan, Immobilization of phenol in cement-based solidified/stabilized hazardous wastes using regenerated activated carbon: leaching studies, *Journal of Hazardous Materials*, 1999, **70**, 117-138.

279. X. C. Qiao, C. S. Poon and C. R. Cheeseman, Transfer mechanisms of contaminants in cement-based stabilized/solidified wastes, *Journal of Hazardous Materials*, 2006, **129**, 290-296.

280. M. Hoch and R. Weerasooriya, Modeling interactions at the tributyltin-kaolinite interface, *Chemosphere*, 2005, **59**, 743-752.

281. C. G. Arnold, A. Ciani, S. R. Muller, A. Amirbahman and R. P. Schwarzenbach, Association of triorganotin compounds with dissolved humic acids, *Environmental Science & Technology*, 1998, **32**, 2976-2983.

282. H. A. Arafat, V. M. Hebatpuria, H. S. Rho, N. G. Pinto, P. L. Bishop and R. C. Buchanan, Immobilization of phenol in cement-based solidified/stabilized hazardous wastes using regenerated activated carbon: role of carbon, *Journal of Hazardous Materials*, 1999, **70**, 139-156.

283. A. Neville, *Concrete: Neville's insights and issues*, Thomas Telford, London, 2006.

284. H. Zhang, L. J. Duan, Y. Zhang and F. Wu, The use of ultrasound to enhance the decolorization of the CI Acid Orange 7 by zero-valent iron, *Dyes and Pigments*, 2005, **65**, 39-43.

285. A. Delgado, A. Usobiaga, A. Prieto, O. Zuloaga, A. de Diego and J. M. Madariaga, Optimisation of the headspace-solid phase microextraction for organomercury and organotin compound determination in sediment and biota, *Journal of Separation Science*, 2008, **31**, 768-774.

286. A. Goyal, M. C. Mensinger, S. P. Barone and A. L. Lee, in *Energy and the Environment*, eds. C. A. Brebbia and I. Sakellaris, 2003, vol. 7, pp. 255-265.

287. V. Karius and K. Hamer, pH and grain-size variation in leaching tests with bricks made of harbour sediments compared to commercial bricks, *The Science of The Total Environment*, 2001, **278**, 73-85.

288. P. Gong and P. L. Bishop, Evaluation of organics leaching from solidified/stabilized hazardous wastes using a powder reactivated carbon additive, *Environmental Technology*, 2003, **24**, 445-455.

289. K. M. McDonough, J. L. Fairey and G. V. Lowry, Adsorption of polychlorinated biphenyls to activated carbon: Equilibrium isotherms and a preliminary assessment of the effect of dissolved organic matter and biofilm loadings, *Water Research*, 2008, **42**, 575-584.

290. P. Leglize, A. Saada, J. Berthelin and C. Leyval, Evaluation of matrices for the sorption and biodegradation of phenanthrene, *Water Research*, 2006, **40**, 2397-2404.

291. J. E. Tomaszewski, D. Werner and R. G. Luthy, Activated carbon amendment as a treatment for residual DDT in sediment from a superfund site in San Francisco Bay, Richmond, California, USA, *Environmental Toxicology And Chemistry*, 2007, **26**, 2143-2150.