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Department of Civil Engineering

Tributyltin In The Aquatic Environment

Final Report to the National River Authority
Anglian Region

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SUMMARY.

This report summarises the work undertaken by Imperial College over the past 24 months concerning the fate and distribution of tributyltin and its breakdown products in the aquatic environment.

In 1987 the UK government introduced legislation to control the sale of tributyltin (TBT) based paints. Between 1990-1992, a monitoring program of waters and surficial sediments from five estuarine river systems was undertaken for TBT and its degradation products; dibutyltin (DBT) and monobutyltin (MBT). Despite the retail ban on tributyltin based antifouling paints for use on vessels <25m in length, water concentrations exceeded the Environmental Quality Target (EQT) at certain locations, 3-4 years after its implementation. However, since 1991, water column concentrations have declined significantly and most sites now contain concentrations below analytical detection limits (ng l^{-1}). Butyltin concentrations in surficial sediments displayed high spatial variability. Surficial sediment concentrations have generally decreased since 1990, with highly contaminated sites being confined to marinas and boatyard complexes. A survey of the Norfolk Broads was also undertaken during July 1992, incorporating 12 sites from 3 freshwater river systems which had previously been identified as containing elevated loadings of TBT, to determine whether TBT levels had depreciated since the retail ban. Detectable concentrations of TBT within the water column was only observed at Brundall Marina (site L); all other sites were below the level of analytical detection. Five of the 12 sites, however, contained elevated TBT loadings in the sediment compartment with concentrations ranging from <3-69 ng g^{-1}, the highest concentrations coinciding with boating activity and areas of restricted water exchange. Results from both studies illustrate that controls instituted in 1987 by the UK on the use of TBT based paints have been effective in reducing surface water and surficial sediment concentrations, but over a 5 year time span.

A number of studies were conducted to elucidate the equilibrium and kinetic behaviour of butyltin compounds (including TBT) undergoing water-sediment transfer processes. Partitioning studies revealed that particulate matter concentration, pH and salinity affect the sorption characteristics of TBT and its degradation products. Results indicate that MBT, and to a lesser extent, TBT partition towards the particulate phase in freshwaters, whereas DBT exhibits a 50:50 partitioning between particulate and solution phases. In estuarine waters MBT will almost exclusively sorb onto particulates, TBT will predominantly be in the solid phase fraction but 10-30% may remain in solution. Dibutyltin in contrast is solubilized in estuarine waters. The degree of TBT adsorption onto natural sediment was dependant upon varied with sediment type, with adsorption increasing in the order sandy silt<silty sand<silty clay and was linked to the TOC content of the sediments. Tributyltin

sorption was, however, found to be reversible indicating that contaminated sediments may release TBT to overlying waters following sediment disturbance which may result in water column concentrations in excess of the Environmental Quality standards (EQS[S]) set for UK waters.

Sediment bound TBT does however undergo degradation. A series of laboratory based tank experiments and in-situ studies on freshwater and estuarine sediments revealed in-situ half life values for TBT degradation of between 0.9 to 5.2 years. Dibutyltin ranged from 1.5 - 3.0 years, whilst MBT half lives ranged from 1.8 - 3.7 years. The half life of TBT degradation was not discernible in anaerobic sediments and appears to be in the order of tens of years. The laboratory based degradation data compared favourably with in-situ estimates derived from sediment core data. The results are reviewed in the context of concentrations of TBT determined in marina and boatyard sediments in UK East Coast estuaries. The implications for remedial action and disposal of dredged spoil are discussed.

1. INTRODUCTION.

Tributyltin (TBT) compounds have a broad range of applications, including use as fungicides, bactericides, insecticides and wood preservatives. As a result of its biocidal properties TBT has been increasingly used over the past two decades in antifouling preparations, both as a replacement for organomercury, arsenic and lead boosters in copper based paints and also as the sole biocidal agent (Bryan and Langston, 1992). Due to its extensive use around the world, high concentrations of TBT have frequently been found in waters, sediments and biota in the vicinity of marinas and yacht harbours, implying that antifouling paints applied to boats, ships and docks are a major source of these compounds in the aquatic environment (Clark *et al.*, 1988). Whilst butyltin compounds are exclusively of anthropogenic origin, methyltin compounds may be formed by biological or abiological methylation in the environment (Gilmour *et al.*, 1985 and Thompson *et al.*, 1986).

In the early 1970's the Pacific Oyster (*Crassostrea gigas*) was introduced into Britain for cultivation. Shortly afterwards mariculturists on the East coast of England reported an increase in growth abnormalities, in particular shell thickening (Waldock *et al.*, 1987a). The increase in abnormal shell growth coincided with the increased use of organotin based antifouling paints, which had become more widespread with the development of self-polishing copolymer paints (Waite *et al.*, 1991). Toxicity studies have revealed acute effects of TBT for aquatic organisms at concentrations as low as 1 $\mu g\ l^{-1}$, whilst sublethal effects of TBT on the Dog Whelk (*Nucillus lapillus*) occur at concentrations <10 ng l^{-1}, with imposex being initiated at a TBT water concentration of <0.5 ng l^{-1}. Thus TBT has been shown to be damaging at levels far below those recorded for other marine pollutants (Bryan and Gibbs, 1990).

During the 1980's the UK Government introduced a number of measures to reduce the environmental impact of TBT from antifouling paints. In 1986, under the Control of Pollution Act (1974), the retail sale of organotin paints was restricted to co-polymer paints containing <7.5% tin and free-association paints containing <2.5% tin in the dry film. An environmental quality target (EQT) for TBT of 20 ng l^{-1} was set for estuarine and coastal waters. However, work undertaken by the Ministry of Agriculture, Food and Fisheries (MAFF) and the Department of the Environment (DoE) in 1987 revealed that the EQT of 20 ng l^{-1} was exceeded at more than half of the 40 locations sampled (Waldock *et al.*, 1987a), including the majority of sites where oysters were cultivated. In the River Crouch, Essex, for example, oysters accumulated TBT to levels exceeding 1 $\mu g\ g^{-1}$ wet weight and growth was poor in terms of both meat weight and shell thickening (Waldock *et al.*, 1987b). High TBT water column concentrations usually coincided with the presence of small boats and it

was concluded that the UK Government's measures had been ineffective in reducing environmental levels of TBT to meet the EQT of 20 ng l^{-1}.

In 1987, the UK Government implemented further controls, under the Food and Environment Protection Act (1985), to limit the sale and use of TBT-based antifouling paints. Firstly, all products containing triorganotins were banned for use on vessels less than 25 m in length and on fish-farming equipment. Secondly, all antifoulants were to be treated as pesticides, and so could only be sold after approval by the Advisory Committee on Pesticides. Finally, triorganotin paints could only be sold wholesale and in drums containing 20 l or more. In 1988 the Government set an environmental quality standard (EQS) for TBT in seawater of 2 ng l^{-1} to further safeguard marine life (Water Research Centre, 1988).

The toxicity, bioaccumulation and fate of xenobiotic compounds in the aquatic environment is closely linked to their partitioning between aqueous media and particulate matter. Organic pollutants can either be sorbed onto particulate matter or exist in solution. The dominant processes that affect the distribution of contaminants between dissolved and particulate phases are adsorption onto particulate matter and flocculation in which the species are trapped by newly formed particulate matter. Because the two mechanisms are not easily distinguishable, the term 'sorption' is generally used to describe the cumulative effect of both processes. Sorption is considered one of the most important processes responsible for reducing the concentration and toxicity of butyltin compounds in the water column and is also the principal pathway for TBT accumulation in sediments (De Mora *et al.*, 1989). Soluble pollutants are more mobile and available than particulate bound compounds and are consequently more likely to undergo bioaccumulation (Knezovich and Harrison, 1987). Hydrophobic organic contaminants, such as butyltins have a high affinity for particulates and tend to readily adsorb onto sediment (Unger *et al.*, 1988). Most suspended and dissolved materials accumulate hydrophobic organic chemicals that upon deposition, contribute to the build up of contaminants in sediment (Bedding *et al.*, 1983). It is generally acknowledged that the adsorption of organic pollutants onto sediments can inhibit biodegradation. This is especially true for TBT compounds whose persistence in sediment is much greater than in water (Maguire *et al.*, 1986).

Numerous studies indicate that TBT degrades by a stepwise debutylation pathway to the less toxic breakdown products; dibutyltin (DBT), monobutyltin (MBT) and finally inorganic tin (Maguire and Tkacz, 1985, Stang and Seligman, 1986 and De Mora *et al.*, 1989). Laboratory studies have shown that a wide variety of agents are capable of cleaving the tin-carbon bond (Blunden and Chapman, 1982 and Stewart and De Mora, 1989). In the aquatic environment, the most relevant processes are likely to be photochemical and

biological cleavage by micro-organisms, the latter being the most dominant (Maguire *et al.*, 1986). The relatively high proportions of TBT breakdown products, di- and monobutyltin measured in sediments (Maguire *et al.*, 1986 and Stewart and De Mora, 1989), suggests that degradation processes limit the persistence of TBT in the aquatic environment. Previous assessments of TBT degradation have indicated that the compound had a low persistence in the water column (Unger *et al.*, 1988). However, as TBT exhibits a tendency to accumulate in sediments, TBT degradation processes in sediments are more likely to control the overall persistence of TBT in the environment (Stewart and De Mora, 1989).

Physico-chemical properties of organic-micropollutants determine their persistence, distribution, behaviour, bioavailability and toxicity within the environment, but their ultimate fate is also dependent upon complex interactions with their external environment. Differences in water and sediment chemistry could have a marked effect upon the fate of xenobiotic compounds. It is therefore necessary to determine the principal factors dictating the behaviour of tributyltin and its degradation products in the aquatic environment.

2. OBJECTIVES.

1. Investigate the seasonal trends in the partitioning and magnitude of TBT enrichment in waters and sediments of the main Suffolk and Essex river estuaries.

2. Assess the effectiveness of the retail ban on TBT antifouling paints for use on vessels <25 m in length, in the Norfolk Broads and the river estuaries of Suffolk and Essex.

3. Elucidate the equilibrium and kinetic behaviour of butyltins (including TBT) undergoing sediment-water transfer processes and assess the effect of pH, particulate matter concentration, salinity and sediment type upon the transfer of butyltin compounds from the soluble to particulate phase.

4. Determine the ability of sediments to re-release sorbed butyltin compounds back to the water column following sediment disturbances due to dredging operations or other forms of physical agitation.

5. Estimate the potential bioavailability of TBT from the partitioning of butyltin compounds within the sediment compartment.

6. Establish the persistance of TBT in freshwater and estuarine sediments through the study of contaminated sediment cores and laboratory based degradation experiments.

7. Review the results in the context of the concentrations of TBT determined in marinas and boatyards from sediments in East Coast estuaries of the UK and discuss implications for remedial action and disposal of dredged spoil.

3. MATERIALS AND METHODS.

3.1. Seasonal variability of butyltin concentrations in Essex and Suffolk estuaries

3.1.1. Sampling procedure

This study was designed to examine the temporal distribution of a range of butyltin compounds including TBT, from 6 contaminated estuarine systems, (previously identified by Dowson *et al.*, 1992a) incorporating the Rivers Alde, Deben, Blackwater, Roach, Orwell and Walton Backwaters (Figure 1). Water column and sediment surveys were undertaken between November 1990 and April 1992, on a 3 monthly basis, designed to coincide with seasonal boating activities. For all site locations, average percentage grain size fractions and percentage volatile solids loadings (% VS) were determined to characterize the sediemnt (Table 1). An additional spatial survey of water column and sediments was also undertaken during July 1992 in the Norfolk Broads at sites previously found to be contaminated with TBT (Dowson *et al.*, 1992b). Sample site locations are displayed in Fig. 2.

Water samples were taken by immersing 500 ml polyethylene containers approximately 20 cm under the surface to prevent the inclusion of any of the surface microlayer, as high concentrations of organotins have been found in the surface microlayer, and its inclusion may exaggerate organotin concentrations in the water column (Cleary and Stebbing, 1987). The acid clean containers were rinsed with river water three times before sample acquistion. Surficial sediment samples were taken with disposable polypropylene scoops. The top 5 cm (approximately) of sediment was collected to ensure that only the most recent deposits were sampled. Sediments were placed in acid washed glass sample jars and stored in cool boxes during transport. On returning to the laboratory, all water samples were stored in a refrigerator at 12°C, whilst all sediment samples were either extracted for analysis immediately or frozen.

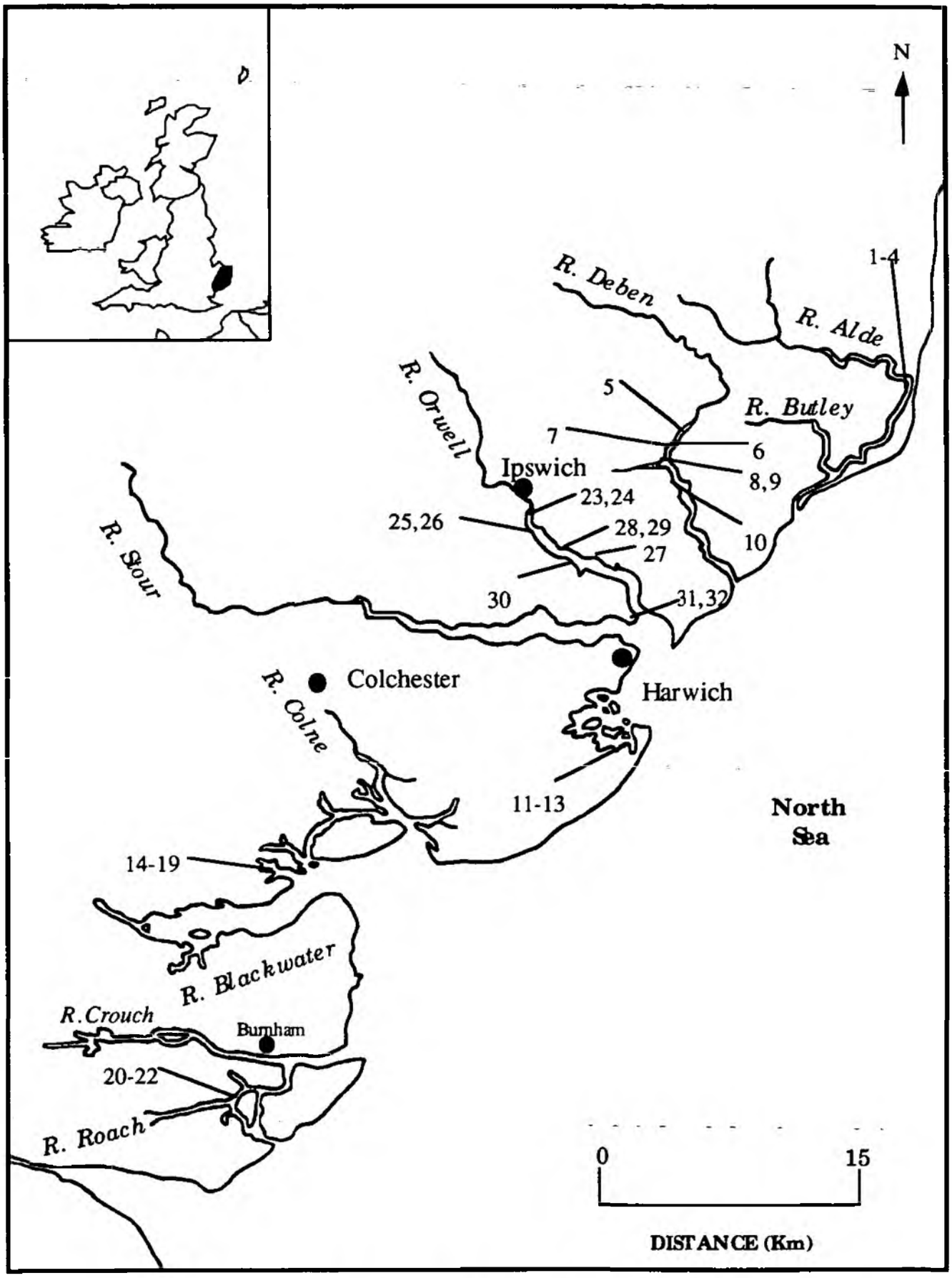


Fig.1. Locations in Essex and Suffolk for the temporal survey

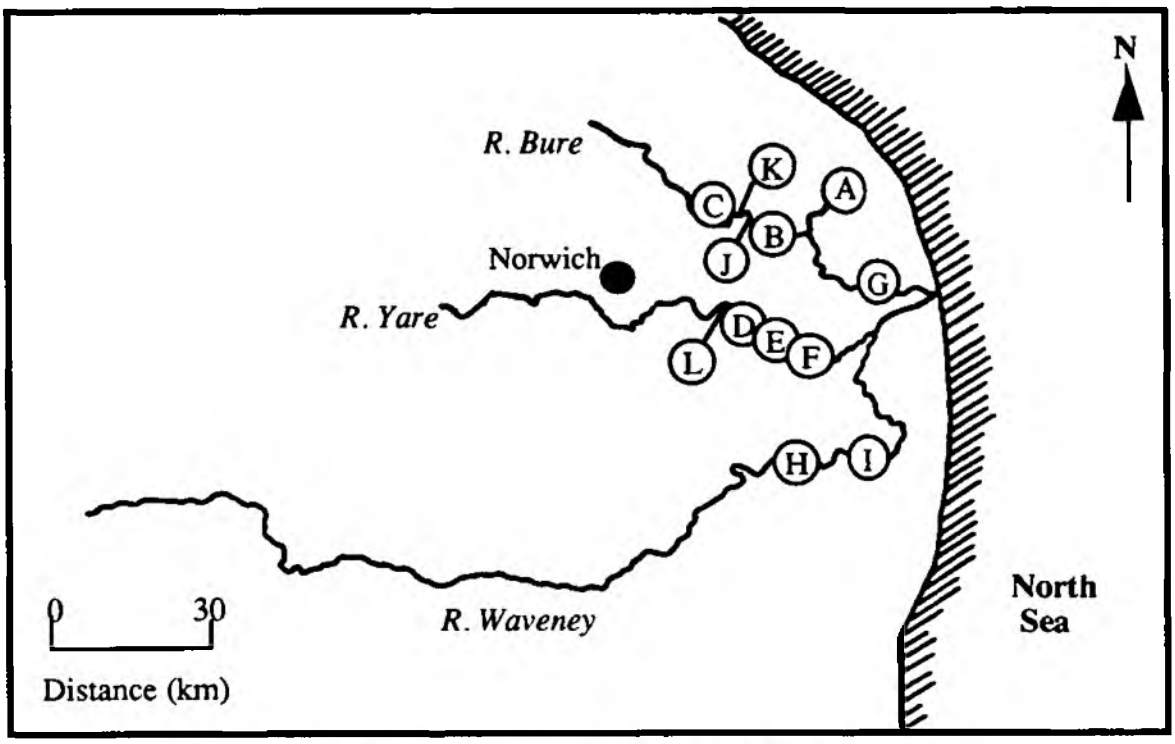


Fig. 2. Sampling sites in the Norfolk Broads

Key to sample sites

A - Hickling Broad
B - Horning Ferry
C - Wroxham Rail Bridge
D - Fishers Dyke
E - Coldham Hall
F - Reedham Quay
G - Acle Bridge
H - Beccles Town Quay
I - Oulton Broad
J - Norfolk Broads Yacht Club
K - Landamores Boatyard
L - Brundall Marina

Table 1

Temporal site locations and physical sediment properties

Site	Location	Sediment particle distribution			% VS	Water
		% Sand	% Silt	% Clay		
	River Alde (Aldeburgh)					
1	Aldeburgh Yacht Club	20	66	14	6.6	√
2	Slaugden Sailing club (250 m d/s)	15	72	13	8.6	
3	Slaugden (between Y.C and Quay)	17	66	19	5.5	
4	Martello Tower	14	70	16	8.1	
	River Deben (Woodbridge)					
5	Robertsons Boatyard	23	65	12	6.3	√
6	Tidemill Marina	44	52	4	10.4	√
7	Whisstocks Boatyard	26	58	16	7.8	√
8	Deben Yacht Club	21	70	9	5.6	√
9	Deben Yacht Club (250 m d/s)	18	74	8	9.1	
10	Waldringfield Quay	32	67	1	4.2	√
	WaltonBackwaters (Titchmarsh)					
11	Titchmarsh Marina (slipway)	27	66	7	6.7	√
12	200 m seaward of marina	11	73	16	9.9	
13	Below Marina office	17	62	21	14.7	
	River Blackwater (Tollesbury)					
14	Tollesbury Marina (north entrance)	21	69	10	13.8	
15	Slipway by cruising club	28	64	8	9.5	√
16	Along sea wall (0.75 km)	16	71	13	7.3	
17	Along sea wall (1.5 km)	18	65	17	6.1	
18	Seaward of marina (100 m)	14	58	28	7.5	
19	Seaward of marina (200 m)	17	62	21	16.2	
	River Roach (Paglesham)					
20	Downstream of slipway (400 m)	72	19	9	4.9	
21	Upstream of slipway (25 m)	86	14	0	3.9	√
22	Upstream of slipway (400 m)	75	22	3	4.5	
	River Orwell					
23	Ipwich Lock Gates	-	-	-	-	√
24	Ipswich Wet Docks	-	-	-	-	√
25	Bourne Creek	-	-	-	-	√
26	Foxes Marina	-	-	-	-	√
27	Levington Marina	-	-	-	-	√
28	Woolverstone Marina	-	-	-	-	√
29	Orwell at Woolversone	-	-	-	-	√
30	Pin Mill	-	-	-	-	√
31	Shotley Marina	-	-	-	-	√
32	Shotley Point	-	-	-	-	√

N.B d/s = downstream YC = yacht club % VS = Average % volatile solids loadings
% sand = >60µm % silt = 30-60µm % clay = <30µm

3.2. Partitioning and sorptive behaviour of butyltins

3.2.1. Factorial experiments

A factorial experimental design enables the simultaneous investigation into the individual and synergistic effects that a number of physico-chemical parameters exert on the removal of butyltin compounds from the solution phase[1]. The advantages and disadvantages of factorial experiments have been summarised by Box *et al.* (1978) and their application to the study of methyltin sorption has been undertaken by Donard and Weber (1985). Due to

1 Solution phase defined as that portion which passes through a 0.45µm filter.

the complexity of environmental processes and interactions during river transport, this design is most appropriate. The use of the factorial design is however, slightly limiting, in that it only reports data for the high and low points of each parameter range and as such is used as an exploratory tool to assess the significance of both single and multiple parameters which affect the removal of butyltin compounds at any confidence level (Randall and Weber, 1986). Associations between these parameters can subsequently be investigated further using detailed batch isotherm studies.

The factorial experiments focussed on 3 parameters which have been shown to be important in determining the partitioning of butyltins in fresh and estuarine waters. The pH of water determines the association and dissociation of functional groups (eg. carboxyl groups) which affects the degree of solubility. Salinity was used as a reference scale to define estuarine processes, while an artificial sorbent, in the form of hydrous iron oxide (BDH Ltd., Dagenham, UK), was used to represent suspended particulate matter. Hydrous iron oxide is a major constituent of most riverine sediments and is an important binding and complexing agent. Lee (1975), proposed that the hydrous metal oxides of iron and manganese are the principal control mechanism for a number of heavy metals in sediments. The common occurrence of these oxides as coatings allows them to exert a chemical activity far in excess of their concentrations. Various concentrations of iron oxide were used in this present study as it is known to be a very important scavenger for heavy metals (Salomons and Förstner, 1984).

3.2.1.1. Partitioning of butyltins in freshwaters

Two parameters were used to investigate the partitioning of butyltin compounds in freshwater river systems; a pH range representative of freshwater areas (pH 6-8) and a particulate matter concentration ranging from 10-1000 mg l^{-1}. A large volume of freshwater was collected from the River Ore in Suffolk, which has been found to be uncontaminated by organotin compounds (Dowson *et al.*, 1992a). Average values for chemical parameters at this site are included in Table 2 along with those for Orford Haven the saline site, during the week of sampling (NRA water register, 1992). The water was filtered through 0.45 µm cellulose nitrate filters (Whatman Ltd., Watford, UK) to remove all suspended matter. Water volumes of 200 ml were placed in amber glass bottles (Fisons Ltd., Loughborough, UK) adjusted to the various pH values under study and hydrous iron oxide was added at the required concentrations. The pH was determined using a portable pH probe (ELE International, Hemel Hempstead, UK) according to the manufacturers instructions. Acidic solutions were obtained by adding 0.1 M HCl (Aristar) and alkaline solutions by adding 0.1 M Na_2CO_3 (BDH Ltd., Dagenham, UK). Solutions were subsequently shaken for 12 h to equilibrate and the pH rechecked and adjusted if neccesary (Randall and Weber, 1986), although very little change in pH was found to occur over this 12 h equilibration period.

Table 2

Average chemical parameters for water utilised in factorial experiments

Parameter	Snape Quay (Freshwater)	Orford Haven (Saline)
pH	7.95	7.93
Temperature (°C)	14.0	14.0
Conductivity (μS cm^{-1})	1825	48990
BOD (mg l^{-1})	2.29	1.19
Chloride (mg l^{-1})	372	19657
Ammonia (mg l^{-1})	0.11	0.034
Salinity (ppt)	0.67	35.6
DO (Field %)	94	92
DOC (mg C l^{-1})	5.26	1.41

NRA Water Register Archive (1992)

Butyltin chloride spikes (181 ng l^{-1} for TBT, 97 ng l^{-1} for DBT and 209 ng l^{-1} for MBT) were subsequently introduced and the pH re-checked. The samples were shaken for a further 12 h. Dooley and Homer (1983), in similar sorption experiments, found that butyltins rapidly sorb to sediment from aqueous solution, so a 12 h period was considered sufficient for equilibrium to be attained. Each sample was filtered through 0.45 μm nucleopore polycarbonate filters (Millipore Ltd., Watford, UK) and the filtrate collected in amber glass bottles and analysed. The adsorption of butyltin compounds onto polycarbonate filters has been found to be negligible (Valkirs *et al.*, 1991). One set of 7 factorial experiments was performed in duplicate for TBT, DBT and MBT in the freshwater partitioning experiments along with experimental blanks for each butyltin compound.

3.2.1.2. Partitioning of butyltins in estuarine waters

A large volume of estuarine water was collected from the saline reach of the River Ore at Orford Haven (this was at the upper end of the salinity range (ie. 35 parts per thousand) and filtered through 0.45 μm filters to remove suspended matter. Dilutions of saline water were made with the freshwater obtained further upstream to give the salinity values of 5, 17.5 and 35 ppt. Hydrous iron oxide was added to these solutions at the required concentrations (10 and 1000 mg l^{-1}), equilibrated for 12 h, spiked with butyltin compounds and shaken for a further 12 h. Samples were filtered through 0.45 μm nucleopore polycarbonate filters and analysed for butyltin compounds. For the estuarine experiments 12 factorial experiments were undertaken in duplicate for the 3 butyltin compounds (TBT, DBT and MBT) along with experimental blanks.

3.2.1.3. Background losses and decomposition

Adsorption of butyltin compounds to container walls was measured on random sample bottles by first rinsing the test bottles with 25 ml of distilled water and shaking for 12 h with 100 ml of 10% Aristar nitric acid/deionised water (v/v) (Randall and Weber, 1986). The leaching solutions were analysed for butyltin compounds. Sorptive losses to container walls, were less than 7% for all compounds. Limited degradation of butyltin compounds occurred during the factorial experiments. However, degradative losses were less than 5% in TBT solutions and 4% in DBT and MBT solutions. Adsorptive losses of TBT to container walls in batch isotherm experiments were less than 3%. No degradation appeared to occur during these experiments.

3.2.2. TBT isotherm adsorption experiments

The sorption of tributyltin chloride by selected East Anglian sediments was studied using a batch isotherm technique similar to the concentration difference method used by MacIntyre and deFur (1985) and Unger *et al.* (1988). Solutions were analyzed for TBT, DBT and MBT, to confirm that degradation did not occur during the course of the experiments.

Freshwater sediments with varying sand, silt and clay composition were collected from different areas of the River Yare in Norfolk. The physical and chemical properties of the sediments are included in Table 3.

Table 3

Physical and chemical properties of sediments used for batch isotherm adsorption studies

Site & grid reference	% Grain size			Parameters		
	Sand %	Silt %	Clay %	TOC %	pH	S^{2-} mg kg^{-1}
Trowse Mill (243 068)	62.8	37.2	0	1.4	7.6	n.d
Rockland (340 053)	39.7	60.3	0	12.5	7.2	180
Cantley (384 033)	15.0	84.0	1.0	6.9	7.8	108

n.d = not detectable

Water from the River Yare uncontaminated by butyltins was filtered through 0.45 µm cellulose nitrate filters (Whatman Ltd., Watford, UK) to remove all suspended matter in the water and stored in the dark at 12 °C. A tributyltin chloride spike was made up from a 10 mg l^{-1} stock solution and added to filtered water to achieve a water column concentration of 3.6 µg l^{-1} (as Sn). Water volumes of 200 ml (containing 0.72 µg TBT as Sn) were placed in teflon centrifuge bottles (BDH Ltd., Dagenham, UK). For each isotherm experiment, five different weighed amounts of sediment were used, ranging from 0-2 g dry weight. The

bottles were shaken for 24 h at 14 °C in the dark. A sixth tube (tube 6) containing just water and a TBT spike was also run with each batch to account for any TBT adsorption losses to the tube walls. After the 24 h equilibration period the tubes were centrifuged at 2000 g for 10 min at 20 °C. The supernatant was filtered through <0.45 µm nucleopore polycarbonate filters (Millipore Ltd, Watford, UK) and analyzed for TBT and its degradation products to determine concentrations in the aqueous phase. Particulate bound TBT were calculated by subtracting the aqueous TBT concentration from the total available TBT (tube 6) as described by Unger *et al.* (1988).

3.2.3. Investigation into butyltin desorption from contaminated sediments

A number of freshwater and estuarine TBT contaminated sediments including Robertsons Boatyard, Tidemill, Woolverstone, Titchmarsh and Tollesbury Marinas were utilized in the desorption experiments to determine if sediments act as permanent sinks or re-release butyltins back into the water column following physical perturbations. Sediments containing between 59 and 696 ng g^{-1} TBT (per 20g wet wt), together with 200 ml of uncontaminated overlying water, were placed in teflon centrifuge bottles and shaken for 12 h. All water was filtered through 0.45 µm cellulose nitrate filters (Whatman Ltd., Watford, UK) prior to use to remove suspended matter. Samples were stored in the dark at 12 °C. Each experiment was undertaken in triplicate using the same shaking and filtering procedure as described previously. Filtered solutions were analyzed for TBT, DBT and MBT and percentage desorption for each compound was calculated.

3.2.4. Butyltin partitioning between sediment and interstitial water

Partitioning studies were undertaken to give an insight into the distribution of butyltin compounds between solid and interstitial water phases in the sediment compartment. Sediment samples were obtained from a number of East Anglian rivers and estuaries. The samples were subdivided and one set was extracted for TBT as described in Section 3.5. to determine total butyltin concentrations in the sediment. The other subsamples were centrifuged at 6000 g at 20 °C for 20 min to separate interstitial water from the sediment. The centrifugate was filtered through <0.45 µm nucleopore polycarbonate filters (Millipore Ltd, Watford, UK) and analysed for butyltin compounds.

3.3. In-situ field and laboratory studies of TBT degradation in sediments

3.3.1. In-situ studies of TBT degradation in sediment cores.

The vertical distribution and historic loadings of organotins has been determined from sediment cores obtained from eight 'hot spot' regions, which were previously identified in the 1990 summer spatial survey (Dowson *et al.*, 1992a) and are listed in Table 4. Sediment

cores were obtained by means of a modified drainpipe sampler. This was used in preference to the Jenkins surface mud sampler since it only sampled a limited depth and only operated effectively in fine silty deposits. The drainpipe in contrast allowed the acquistion of deeper cores, extending to a depth of 60 cm, and proved operationally viable in a wide variety of sediments. The cores were subdivided into discrete units (2-5 cm depending upon the depth and nature of the core).

Table 4
Sediment core sampling sites

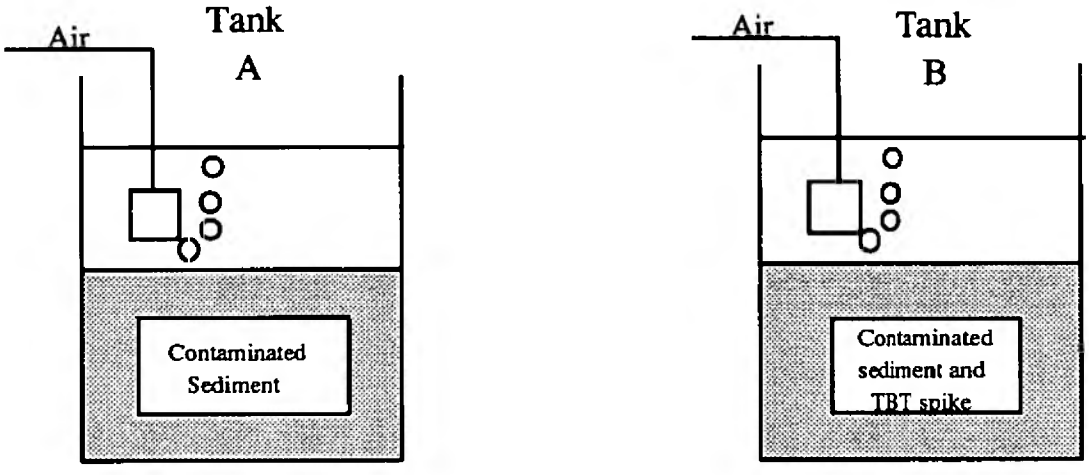
Core No.	Location	Sedimentation rate (cm a^{-1}) *	Comments
1	Tollesbury Marina	13	Near main slipway, disturbed
2	Tollesbury Marina	-	50m from marina sill
3	Titchmarsh Marina	13	Near main slipway, disturbed
4	Robertsons Boatyard	5	Upstream of slipway
5	Waldringfield Quay	4	Next to boating pontoon
6	Paglesham	2	Near scrubbing posts
7	Oulton Broad	2	Near boat moorings, disturbed
8	Ipswich Docks	-	Near to ship repair yard, disturbed

*Sedimentation rates were estimated from local knowledge of dredging activities.

3.3.2. Laboratory studies of TBT degradation in sediments

The TBT sediment degradation experiments were undertaken in a series of 60 l polyethylene cylindrical tanks containing contaminated sediments from Robertsons Boatyard on the River Deben, (freshwater) and from Tollesbury Marina on the River Blackwater (estuarine). Four TBT contaminated tanks were set up in the manner illustrated in Fig. 3. All sediments were collected with the aid of a Birke-Ekman grab sampler, placed in reinforced polyethylene bags and returned to the laboratory on the day of collection. Bulk samples were sieved through a 2000 µm mesh and stored at 14°C. All tanks were set up within 24 h. Both silt sediments were thoroughly homogenised before being placed in the tanks to ensure that TBT was uniformly distributed throughout the sediment. The sediment was covered with water from the respective freshwater and estuarine sites to minimise desorption processes between sediment and overlying water. Additional replenishment of overlying water was undertaken periodically to replace water lost through evaporation. All tanks were aerated in alternate 12 h light and dark cycles, at 14°C to give constant conditions that approximate to those encountered in the environment.

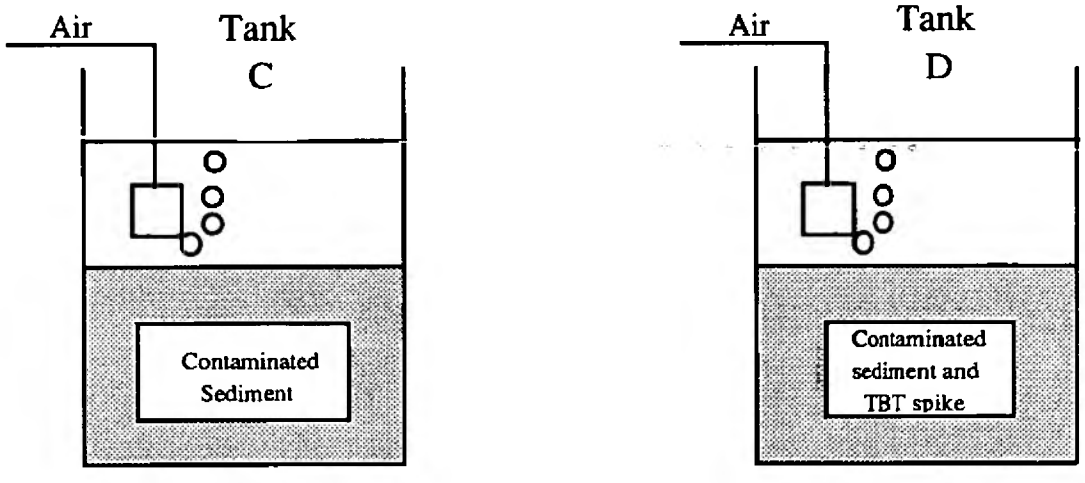
Freshwater sediments



Robertsons Boatyard

Robertsons Boatyard

Estuarine sediments



Tollesbury Marina

Tollesbury Marina

Fig. 3

Determination of TBT degradation in freshwater and estuarine sediments

3.3.2.1. Sampling procedure

Cored samples were taken on a predesignated grid pattern after 15 days and subsequently at monthly intervals. The coring apparatus was designed to minimise sample disturbance. The corer comprised of two close fitting concentric tubes (the outer constructed of durapipe and the inner of perspex). The inner tube (o.d. 38 mm, i.d. 32 mm) was split along almost its entire length to facilitate core extraction, the samples being taped during sample extraction. The outer core (o.d. 45 mm, i.d. 39 mm) remained in place following core acquisition, to prevent sediment collapse within the tank. The cores were subdivided into 5 segments (0-5, 5-15, 15-25, 25-35 and 35-45 cm intervals) to highlight any depth trends in the degradation, in particular between aerobic and anaerobic sediment zones. The samples were analysed for TBT, DBT and MBT along with percentage volatile solids (%VS). Additional monitoring of pH and redox potential in the sediments was undertaken as descibed in Section 3.6.

3.3.4. Influence of freezing and sterilisation on degradation of TBT in sediments

A series of frozen and sterilised sediment controls were set up to run in parallel with the tank degradation experiments to assess the viability of freezing as a storage technique for contaminated sediment prior to analysis and to evaluate the significance of chemical against biological degradation of TBT. Analysis was performed in conjunction with the tank samples. Homogenised sediment aliquots (50 g) were taken from both Robertsons Boatyard and Tollesbury Marina on day 1 of the experiment and frozen in polyethylene containers. Static sterilised controls were set up in triplicate in a series of MaCartney bottles utilising mercuric chloride as the sterilising agent (400 ng g^{-1} dry weight concentration) and aseptically sealed. This agent has previously been shown to prevent microbial degradation by acting as a metabolic inhibitor. All glassware was sterilised with dry heat prior to use in a 'Hot Box' oven for 4 hours at 180°C (Gallenkamp, London, UK). Phosphate buffer diluent and Plate Count Agar media (Millipore Ltd., Watford, UK) was steam sterilised in a gas autoclave (121°C for 15 min). Analysis was performed in triplicate at monthly intervals in conjunction with the tank samples and under the same environmental conditions. Bacterial counts were measured at 3 monthly intervals to determine if sterile conditions were maintained in the abiotic experiments.

3.4. Organotin Determination

The sediment extraction procedure for organotins was initiated on the day of collection, immediately on return to the laboratory. Bulk sediment samples were homogenised by vigorously shaking for 1 min. Sediment (10 g) was placed into a preweighed centrifuge tube with 20 ml of Aristar acetic acid and shaken for 15 h at room temperature in the dark. Samples were then centrifuged at 2000g for 20 min. A 2 ml volume of the supernatant was

subsequently diluted with 200 ml of deionised water and 6 ml of concentrated Aristar acetic acid in the reaction flask prior to analysis. Water samples were analysed without pretreatment. Samples (200 ml) were acidified with 8 ml of concentrated Aristar acetic acid in the reaction flask. Organotins were speciated using the 'purge and trap' boiling point separation method with modifications described by Dowson *et al.* (1992a). Detection was performed by a Perkin-Elmer 1100 B atomic absorption spectrometer operating at a wavelengh of 224.6 nm, using an electrothermally heated (900°C) quartz furnace and a tin EDL lamp (Perkin-Elmer Ltd., Beaconsfield, UK).

3.4.1. Evaluation of analytical procedure for determination of organotins

The analytical characteristics of the 'purge and trap' technique for the determination of organotin compounds are summarised in Table 5. All detection limits were calculated on the basis of a peak height twice that of background noise. The recovery of organotin compounds has been calculated for both water and sediment samples as follows. Spiked organotin standards were added to sediment (10 g) and water (200 ml) and extracted as described in Section 3.4.

Table 5.
Characteristics of the 'Purge and Trap' method for organotin determination

Parameter	TBT	DBT	MBT	MMT	DMT	TMT
Water						
Recovery (%)	95	80	81	66	91	76
Detection Limit (ng l^{-1})	<3	<1	<1	<0.8	<0.6	<0.7
Sediment						
Recovery (%)	68	77	76	65	82	75
Detection Limit (ng g^{-1})	<3	<1	<1	<0.2	<0.2	<0.2
Repeatability (%)	±10.0	±9.20	±5.40	±8.90	±1.20	±18.4
Reproduceability (%)	±14.8	±11.1	±18.3	±9.30	±13.1	±14.4

Note: TBT - Tributyltin, DBT - Dibutyltin, MBT- Monobutyltin, MMT- Monomethyltin, DMT - Dimethyltin, TMT - Trimethyltin
-Repeatability assessed on 5 analyses of one extraction.
-Reproduceability assessed on 5 extractions of the same sediment.

3.4.1.1. Quality control and assurance

One set of spiked sediment and water samples were undertaken with each batch of environmental samples along with distilled water blanks. Additionally, a standard reference material 'PACS 1' marine sediment (National Water Research Institute, Canada) has been analysed. The analytical results along with the certified values in the sediment are displayed in Table 6. Results for all butyltin compounds displayed concentrations within acceptable ranges of the certified material.

Table 6

Results of the analysis of PACS 1 certified marine sediment

Parameter	TBT	DBT	MBT
Butyltin levels found (ng g^{-1})	1152±165	1064±126	361±108
Certified values (ng g^{-1})	1270±220	1160±180	280±170

3.5. Routine chemical analysis

3.5.1. Total and volatile solids determination

Duplicate subsamples of each sample were analysed for total and volatile solids according to the standard method (Standing Committee of Analysts, 1980). The procedure used was as follows; 10g of homogenised sediment was placed in a preweighed muffled crucible (500°C for 30 min.) and dried at 105°C to constant weight. After drying the subsample was placed in a dessicator to cool and subsequently reweighed. The total solids were then calculated as a percentage of the wet weight. The measurement of organic content by 'loss on ignition' has its limitations, but a good relationship has been observed for organic carbon measured in this way and by total organic carbon analysis (Luoma and Bryan, 1981).

3.5.2. Redox potential and pH

Redox and pH were determined using a portable proble (ELE International, Hemel Hempstead, UK) according to the manufacturers procedures.

3.5.3. Total organic carbon analysis

Sediment total organic carbon (TOC) was achieved by dry combustion and infrared detection (Dohrmann Carbon Analyser, Santa Clara, USA) of air dried sediment, according to the procedures described by Unger *et al.* (1988).

3.5.4. Particle size distribution

Sediment particle size determination was undertaken using the Malvern 2600/3600 Particle Sizer (Malvern Instruments Ltd, Worcester, UK) with a 300 mm lens on wet sediment samples. Reverse osmosis water was used as the sediment carrying medium in the cell. Each sample was analysed in triplicate and the analysis undertaken according to the manufacturers methods.

3.6. Cleaning of glassware and equipment

All glassware was of borosilicate glass to minimise adsorptive loss of organotin compounds. Glassware and teflon centrifuge tubes were cleaned by soaking for 24 h in 5% v/v Decon 90 detergent (BDH Ltd., Dagenham, UK) to remove organic contamination, rinsed in distilled water, and then transferred to 10% (v/v) Analar HNO_3 for a further 24 h to reduce metallic contamination (Thornes and Nickless, 1981). Items were then rinsed three times with distilled water and dried.

4. RESULTS.

4.1. Seasonal distribution of organotins in estuarine sediments in Essex and Suffolk

Six seasonal surveys were undertaken between November 1990 and April 1992 to assess temporal changes in the distribution of butyltins within surficial sediments and waters in Essex and Suffolk river estuaries. The results are presented in Table 7 and have been categorised according to the degree of contamination in Table 8. Temporal changes in butyltin concentrations and percentage butyltin composition for selected sites are illustrated in Figs. 4a and b respectively.

Table 7
Temporal distribution of TBT in Essex and Suffolk estuarine sediments

Site	Location	TBT concentration (ng g^{-1})					
		autumn 1990	winter 1991	spring 1991	summer 1991	autumn 1991	spring 1992
	River Aide (Aldeburgh)						
1	Aldeburgh Yacht Club	49	20	22	<3	<3	<3
2	Slaugden Sailing club (250 m d/s)	<3	<3	466	<3	<3	<3
3	Slaugden (between Y.C and Quay)	36	<3	106	<3	<3	-
4	Martello Tower	<3	<3	<3	<3	<3	<3
	River Deben (Woodbridge)						
5	Robertsons Boatyard	343	203	653	1036	202	186
6	Tidemill Marina	<3	260	647	461	97	112
7	Whisstocks Boatyard	61	57	293	123	35	45
8	Deben Yacht Club	49	<3	241	<3	38	<3
9	Deben Yacht Club (250 m d/s)	-	<3	<3	<3	<3	<3
10	Waldringfield Quay	-	-	163	52	49	24
	Walton Backwater (Titchmarsh)						
11	Titchmarsh Marina (slipway)	2668	1394	1272	554	386	520
12	200 m seaward of marina	1019	512	663	317	499	88
13	Below Marina office	1785	1701	747	1047	734	512
	River Blackwater (Tollesbury)						
14	Tollesbury Marina (north entrance)	1528	4207	1135	591	571	568
15	Slipway by cruising club	3097	409	2112	288	676	416
16	Along sea wall (0.75 km)	954	243	20	87	<3	<3
17	Along sea wall (1.5 km)	1253	119	350	<3	<3	<3
18	Seaward of marina (100 m)	707	1628	218	<3	<3	68
19	Seaward of marina (200 m)	376	2056	249	228	<3	22
	River Roach (Paglesham)						
20	Downstream of slipway (400 m)	294	<3	23	<3	<3	<3
21	Upstream of slipway (25 m)	128	24	90	67	40	35
22	Upstream of slipway (400 m)	66	<3	19	<3	<3	<3

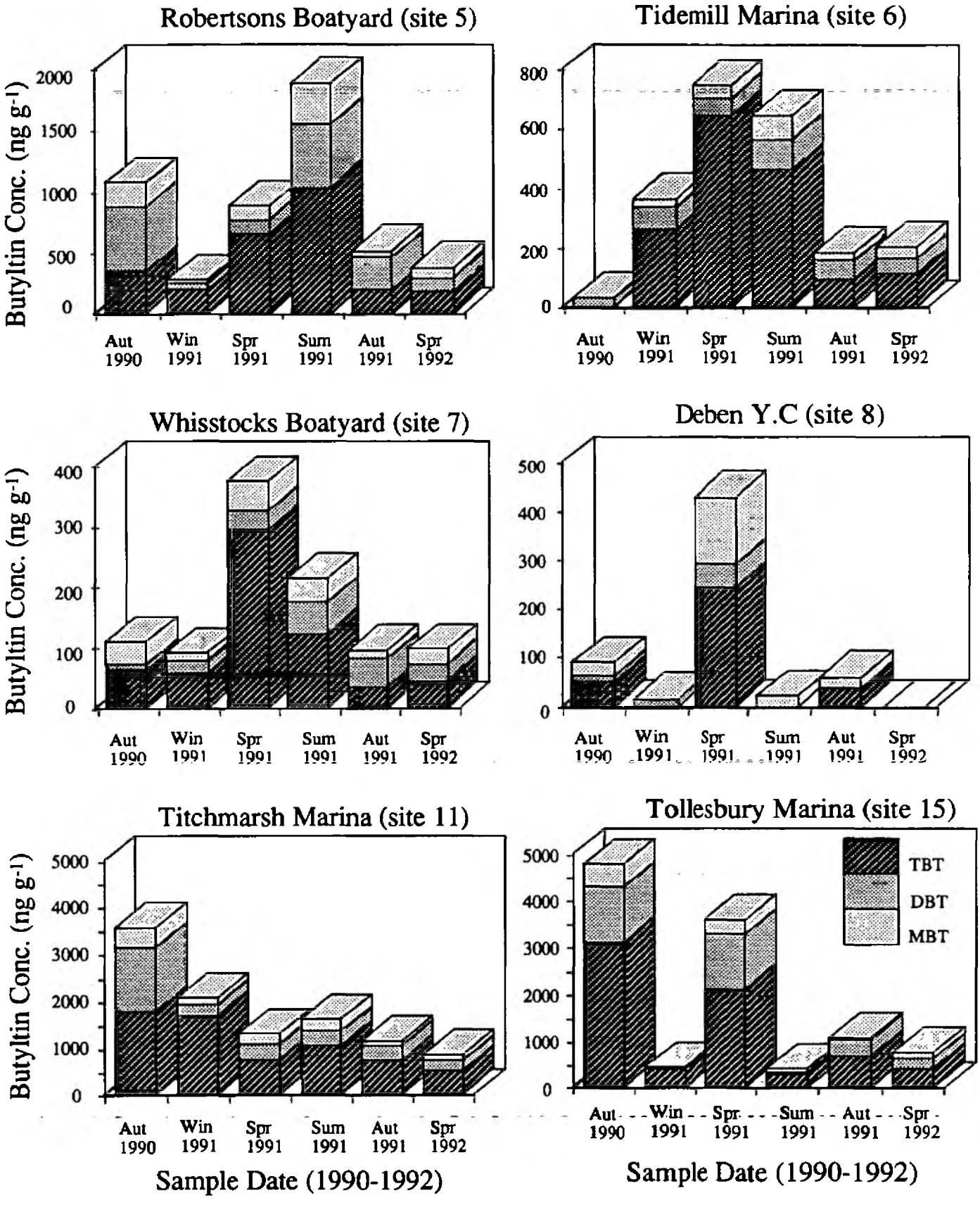


Fig. 4a
Mean temporal butyltin concentrations in sediments at six sites in Essex and Suffolk

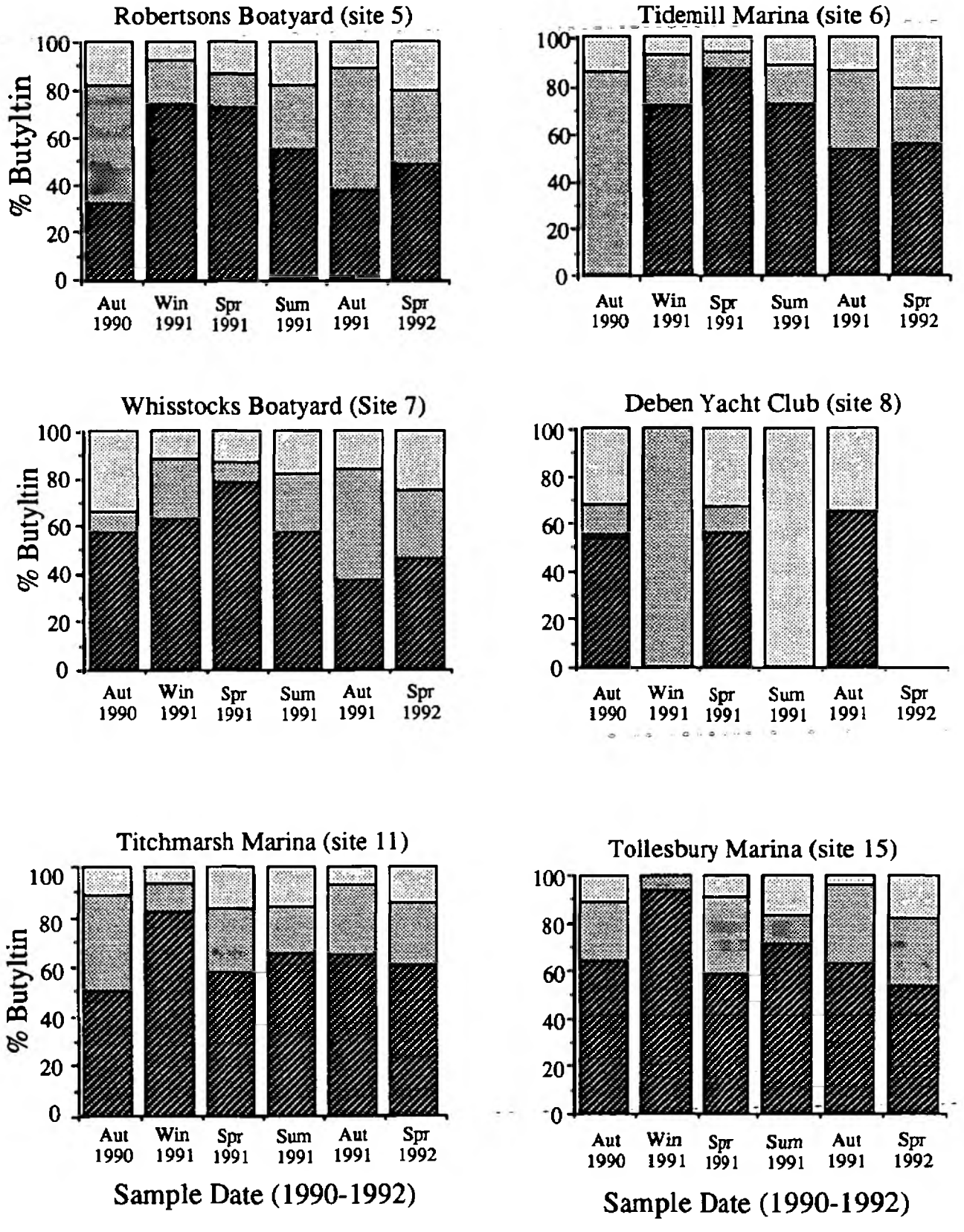


Fig. 4b

Mean temporal percentage butyltin distribution in sediments at six sites in Essex and Suffolk

Table 8
TBT Site classification for temporal sediment and water column surveys in Essex and Suffolk

			Number of sites in each category					
Site Classification	Conc. Range	Sample Type	aut 1990	win 1991	spr 1991	sum 1991	aut 1991	spr 1992
Uncontaminated	<3 ng l^{-1}	water	9	13	17	19	21	21
	<3 ng g^{-1}	sediment	4	7	2	11	10	10
Light contamination	3-20 ng l^{-1}	water	1	1	0	2	0	0
	3-20 ng g^{-1}	sediment	0	0	1	0	0	0
Moderate contamination	20-100 ng l^{-1}	water	0	5	3	0	0	0
	20-100 ng g^{-1}	sediment	5	3	4	2	7	5
High contamination	100-500 ng l^{-1}	water	0	0	1	0	0	0
	100-500 ng g^{-1}	sediment	5	6	8	5	2	3
Gross contamination	>500 ng l^{-1}	water	0	0	0	0	0	0
	>500 ng g^{-1}	sediment	8	6	7	4	3	3

Two types of seasonal distribution were apparent. The first was characterized by elevated organotin concentrations during the spring and summer months. Robertsons Boatyard (site 5) consistently displayed the highest levels of TBT contamination on the River Deben with sediment concentrations ranging from a high of 1036 ng g^{-1} in summer 1991 to 186 ng g^{-1} in spring 1992. Although all sites on the Deben displayed a high degree of spatial variability, the spring-summer seasonal maxima was quite distinct at all 4 sites in 1991, giving way to a successive decline in the autumn and winter. This was not however repeated in the following year (April 1992) spring maxima pattern displayed the previous year. This finding coupled with the fact that the River Deben sites exhibited lower sediment concentrations in the spring of 1992 than in the initial autumn 1990 survey implies that a decrease in TBT loadings in surficial sediments had occurred over time. This is backed up by the occurrence of higher proportions of DBT and MBT in the latter surveys, implying that degradation of TBT to DBT and MBT was occurring. No apparent degradation patterns were evident at Deben Yacht Club (site 8).

The second seasonal trend was one of maximum enrichment in the autumn and winter, as is generally the case at Titchmarsh Marina (sites 11-13) and Tollesbury Marina (sites 14-19). Titchmarsh and Tollesbury exhibited TBT maxima of 3097 and 2668 ng g^{-1} respectively in November 1990. At Titchmarsh the maximum TBT concentrations progressively decreased at all 3 sites to a low of 512 ng g^{-1} in April 1992, whilst Tollesbury displayed greater temporal variability. Outside the marina and along the sea wall at Tollesbury, TBT concentrations declined considerably and were generally below analytical detection in the autumn 1991 and spring 1992 surveys. Sites on the River Alde (sites 1-4) and at Paglesham, (sites 20-22) displayed either light

contamination or were uncontaminated throughout the study period. In the autumn 1991 and spring 1992 surveys only site 21, at Paglesham displayed detectable TBT concentrations. Paired correlation observations between percentage volatile solids loadings and temporal TBT concentrations did not reveal any statistically significant relationships. Similarly no significant relationships between grain size partitioning and temporal TBT concentrations were identified.

From Table 8 it can be seen that the number of high and grossly contaminated sites has decreased over the 2 year study period, with a subsequent increase in the number of uncontaminated sites. This infers that TBT contamination over the Suffolk and Essex region is generally declining. In most cases TBT appeared to be the dominant butyltin form in contaminated sediments and large increases in butyltin concentrations from one season to the next were principally attributed to increases in TBT rather than its derivatives.

Concentrations of methyltins were low compared to their butyltin counterparts ranging from <0.2 ng g^{-1} (the analytical detection limits) to a maximum of 14 ng g^{-1}, the emphasis being firmly placed at <0.2 ng g^{-1}. No seasonal relationships were found to occur with any of the methyltin compounds studied.

4.2. Seasonal variations in organotin concentrations in the water column of Suffolk and Essex estuarine river systems

The temporal changes in butyltin concentrations have been categorised for each river system according to the criteria laid out in Table 8. The most evident trend throughout the study was the increase in the number of sites displaying undetectable TBT concentrations in later surveys. In the winter 1991 survey, 13 out of 19 sites contained undetectable TBT water column concentrations, whereas in the autumn 1991 and spring 1992 all sites surveyed displayed TBT concentrations below the detection limits. There were, however, temporal variations in butyltin concentrations in water column samples, examples of which are illustrated in Figure 5, whilst actual concentrations are displayed in Appendix 2.

On the River Deben at Robertsons Boatyard (site 5), Whisstocks Boatyard (site 7) and Titchmarsh Marina (site 13) maximum TBT concentrations were evident in the spring 1991 survey, whilst Tidemill Marina (site 6), Deben Yacht Club (site 8) and Tollesbury Marina (site 15) all displayed maximum concentrations in winter 1991. After spring 1991, TBT was only detectable at 2 of the sample sites; Titchmarsh (site 13) and Shotley marina on the River Orwell (site 31) during the summer 1991 survey.

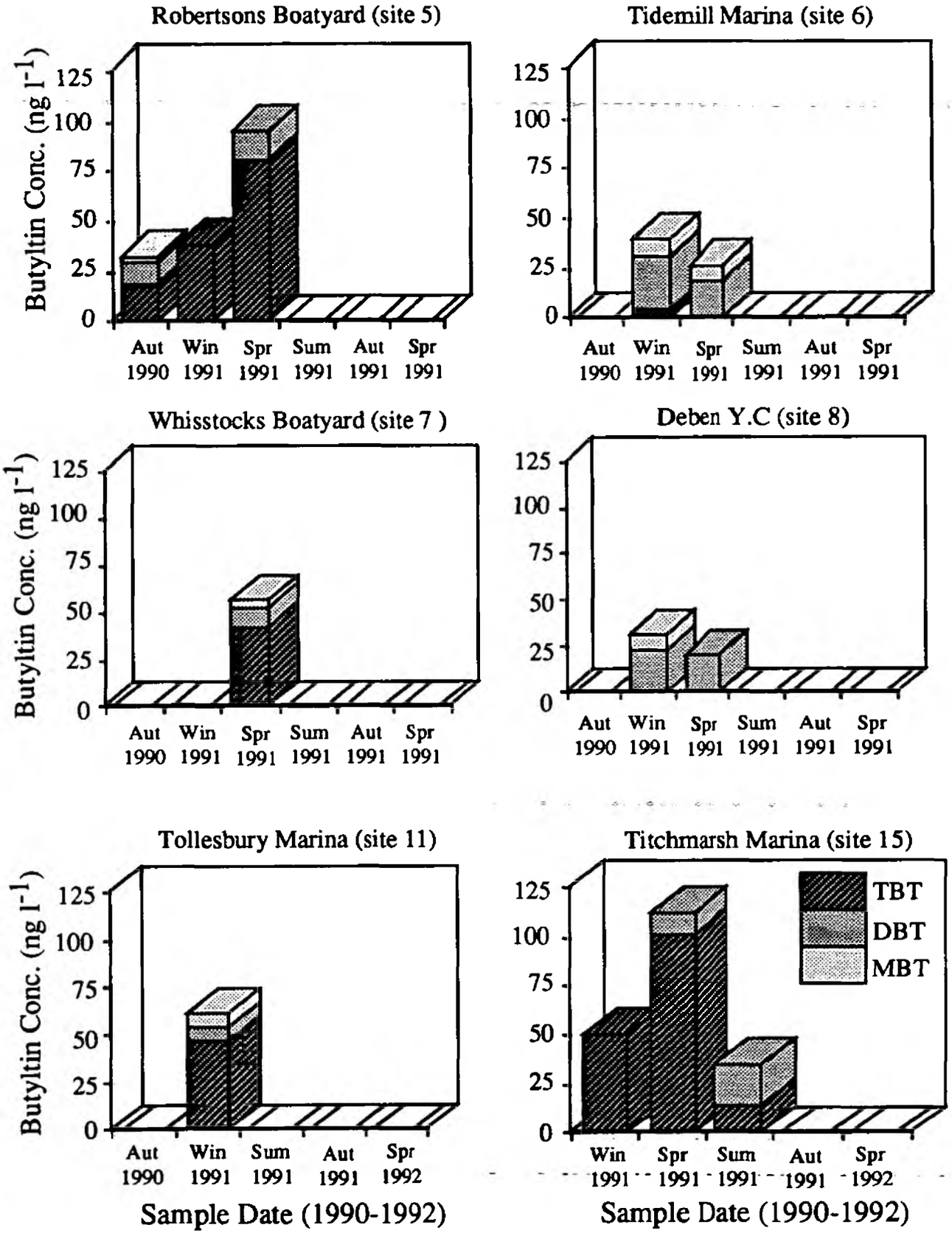


Fig. 5
Mean temporal butyltin distribution in waters at six sites in Essex and Suffolk

No detectable levels of TBT, DBT or MBT were observed in subsequent surveys (autumn 1991 and spring 1992) indicating that TBT inputs from antifouling paints were either no longer occurring or were sufficiently small to be analytically undetectable. No TBT was detected from sites on the River Alde (sites 1) and at Paglesham (site 21).

4.3. Spatial distribution of organotins in the Norfolk Broads

Butyltin concentrations in surficial sediments from the 1989 and 1992 sediment surveys are included in Table 9 along with % TBT/Total butyltin values. The spatial sediment survey conducted in 1992 found 5 out of the 12 sites to be contaminated with TBT ranging from <3-69 ng g^{-1}, with the highest concentrations coinciding with boating activity and areas of restricted water exchange, for example Brundall Marina (site L) and Fishers Dyke (site D). In open channel sites such as Coldham Hall, TBT contamination was less marked and generally below detection limits. The 1992 water column survey only revealed detectable concentrations of TBT at Brundall marina (14.8 ng l^{-1}) all others were below the level of analytical detection. In all cases butyltin concentrations, notably TBT, had decreased considerably over the 3 year period seperating the two surveys indicating that the 1987 retail ban has been successful in reducing TBT contamination in the East Anglian region.

Table 9
Butyltin concentrations in surficial river sediments in East Anglia in 1989 and 1992

		1989 Sediment Conc. (ng g^{-1})				1992 Sediment Conc.(ng g^{-1})			
Site	Location	%TBT	TBT	DBT	MBT	%TBT	TBT	DBT	MBT
A	Hickling Broad	**78**	467	117	13	**39**	19	21	9
B	Horning Ferry	**67**	10	5	<1	-	<3	<1	<1
C	Wroxham Rail Bridge	**49**	69	53	20	-	<3	<1	<1
D	Fishers Dyke	**92**	769	64	4	**40**	69	49	56
E	Coldham Hall	**84**	499	58	35	**0**	<3	10	<1
F	Reedham Quay	**45**	33	39	2	-	<3	<1	<1
G	Acle Bridge	**49**	70	27	45	-	<3	<1	<1
H	Beccles Town Quay	**67**	168	68	16	**0**	<3	15	29
I	Oulton Broad	**94**	1291	83	4	**57**	28	8	13
J	Norfolk Broads Y.C	N.S	N.S	N.S	N.S	-	<3	<1	<1
K	Landamores Boatyard	N.S	N.S	N.S	N.S	47	22	16	9
L	Brundall Marina	N.S	N.S	N.S	N.S	**64**	56	21	10

NB % TBT = % TBT/total butyltin N.S = Not sampled

4.4. Partitioning and sorption of butyltins in the aquatic environment

4.4.1. Influence of pH and particulate matter concentrations on the partitioning behaviour of butyltin compounds

In factorial experiments when there are n parameters to consider, 2^n experiments are neccesary to measure the effects of all combinations of parameters when testing at high and low levels. The n+1 centre point experiments (ie. experiments 5-7 in the

freshwater experiments listed in Table 10 and experiments 9-12 in the estuarine experiments listed in Table 12) detect any deviation from linearity in the experimental response and allow random error determination. Standard deviations, calculated from these centre points, display the degree of experimental variability.

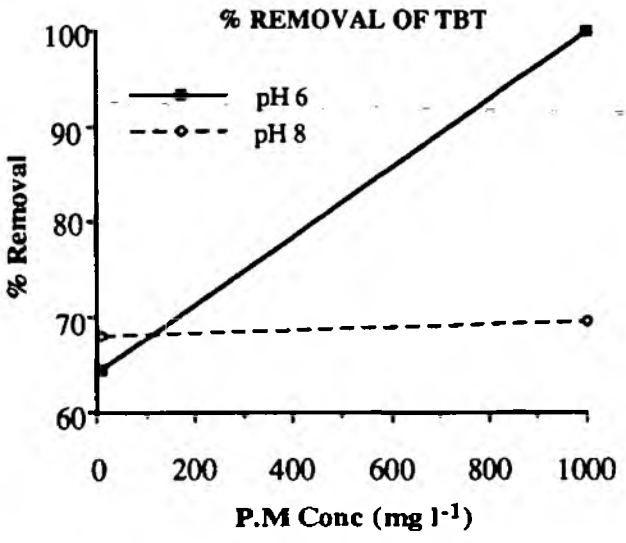
4.4.1.1. Freshwater

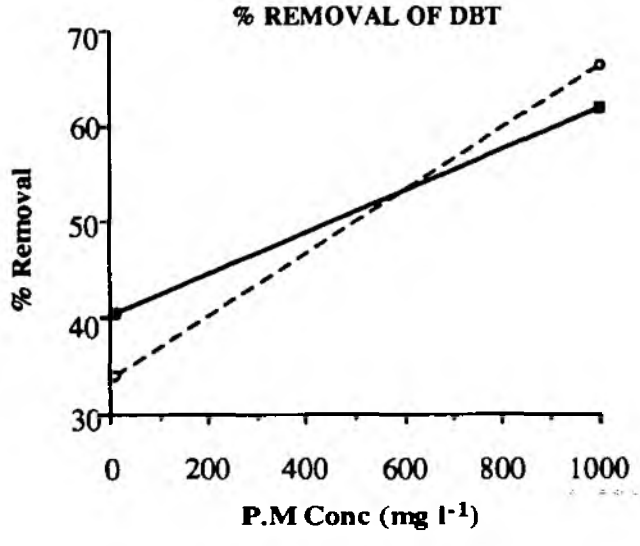
The percentage removal of TBT, DBT and MBT from the aqueous to sediment phase under freshwater conditions at different pH and particulate matter concentrations is given in Table 10. The results indicate different patterns of sorption for each butyltin compound as controlled by the physico-chemical environment, but in general terms TBT exhibited a tendency toward solid phase partitioning, accounting for between 65-100% of the TBT available, whilst DBT displayed a much lower level of sorption (34-67%), and MBT was almost completely sorbed to particulate matter in all experiments (89-100%).

The partitioning of TBT in freshwater samples was dictated by both pH and particulate matter concentration (Fig. 6). At low pH (6.0) sorption was enhanced by increased suspended matter; increasing from 65 to 100% as the total suspended solid concentration increased from 10 to 1000 mg l^{-1}. At higher water pH, TBT removal was independent of particulate matter concentration. Sorption of DBT appeared to be influenced more by particulate matter concentration than water pH. Removal of DBT was about 40% at low particulate matter concentrations (10 mg l^{-1}) but increased to ≈ 62% at 1000 mg l^{-1} suspended matter, irrespective of pH. MBT revealed a very strong affinity for hydrous iron oxide which was independent of pH. Sorption of MBT was enhanced by increased suspended matter; increasing from 90-100% as the total suspended solid concentration increased from 10 to 1000 mg l^{-1} respectively, but generally displayed a very strong affinity for solid phase partitioning at all particulate matter concentrations between pH 6-8.

Table 10
Mean percentage removal of butyltins from freshwaters under differing environmental conditions

Experiment	Particulate matter (mg l^{-1})	pH	% Butyltin Removal		
			TBT	DBT	MBT
1	1000	8	69.5	66.5	100
2	10	8	68	34	92.5
3	1000	6	100	62	100
4	10	6	64.5	40.5	89
5	100	7	70.5	50.5	96.5
6	100	7	73	38	100
7	100	7	71	38	100
Mean value of centre points			71.5	42.2	98.8
Standard deviation of centre points			±3.6	±8.9	±2.9





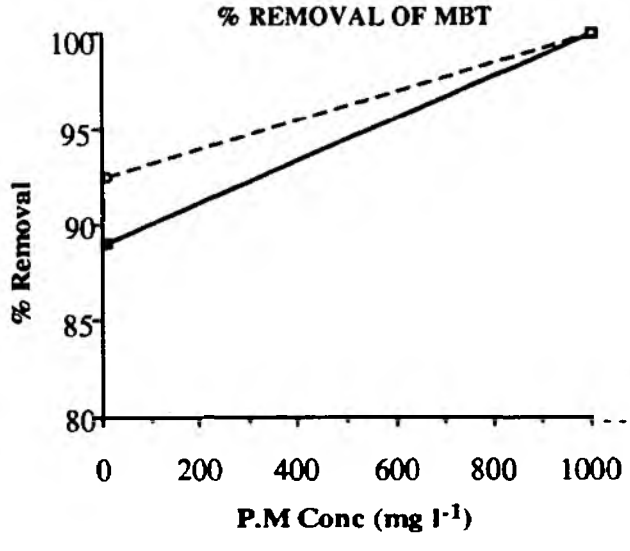


Fig. 6
Relationships between butyltin sorption and particulate matter concentration derived from factorial experiments

Batch isotherm experiments were subsequently undertaken to further elucidate the behaviour of butyltin sorption by the use of natural particulate matter rather than a model substrate in freshwater sediments. In order to compare the different adsorptive capacities of the sediment types under study and to allow a direct comparison of TBT adsorptive properties with other compounds, the Freundlich adsorption model was used. The aqueous and sorbed equilibrium data from each experiment are presented in Table 11. Aqueous and sorbed equilibrium data were then logged and plotted by linear regression according to the linearised form of the Freundlich equation illustrated below.

$$\log qe = \log K + \frac{1}{n} \log Ce \qquad \text{(iii)}$$

where: n and K = Freundlich constants
qe = amount of TBT adsorbed per unit mass of sediment ($\mu g\ g^{-1}$)
Ce = aqueous residual concentration of TBT ($mg\ l^{-1}$)

Freundlich adsorption isotherms for TBT on sandy silt, silty sand and silty clay sediments are displayed in Figure 7. All experiments produced linear isotherms. The isotherms illustrate that the finer grained silty clay sediment exhibited a larger capacity for TBT adsorption than an equivalent mass of a silty sand. In all 3 cases an increase in particulate matter concentration led to an increase in TBT removal. However, the percentage TBT removal from the dissolved phase at equivalent concentrations is lower in the isotherm experiments than in both the freshwater and estuarine factorial studies conducted with iron oxide as a model substrate.

Table 11
TBT adsorption isotherm data for freshwater sediments

Sediment type	Suspended Dry wt (g)	Dissolved TBT (µg)	Sorbed TBT (µg)	% sorbed	Kp
Silty clay	0.319	0.209	0.511	70.97 ±1.4	1464±136
sorption data	0.638	0.112	0.606	84.17 ±2.0	1677±265
	0.957	0.047	0.671	93.19 ±0.9	2929±414
	1.276	0.022	0.698	96.94 ±0.8	4973±1643
	1.595	0.016	0.704	97.78 ±0.5	4900±1765
Silty sand	0.370	0.251	0.469	65.14 ±2.2	960±97
sorption data	0.740	0.136	0.584	81.11 ±0.77	1096±57
	1.110	0.060	0.660	91.67 ±1.25	1863±335
	1.480	0.041	0.679	94.30 ±1.30	2195±605
	1.850	0.029	0.691	95.97 ±0.96	2493±760
sandy silt	0.626	0.313	0.405	56.25±1.34	400±5
sorption data	1.252	0.197	0.523	72.69±1.06	398±40
	1.878	0.104	0.616	85.56±0.77	607±55
	2.504	0.057	0.663	92.08±0.64	883±76
	3.130	0.046	0.674	93.57±0.63	896±75

Note: All analyses were performed in triplicate TBT spike in each experiment = 0.72 µg TBT as Sn

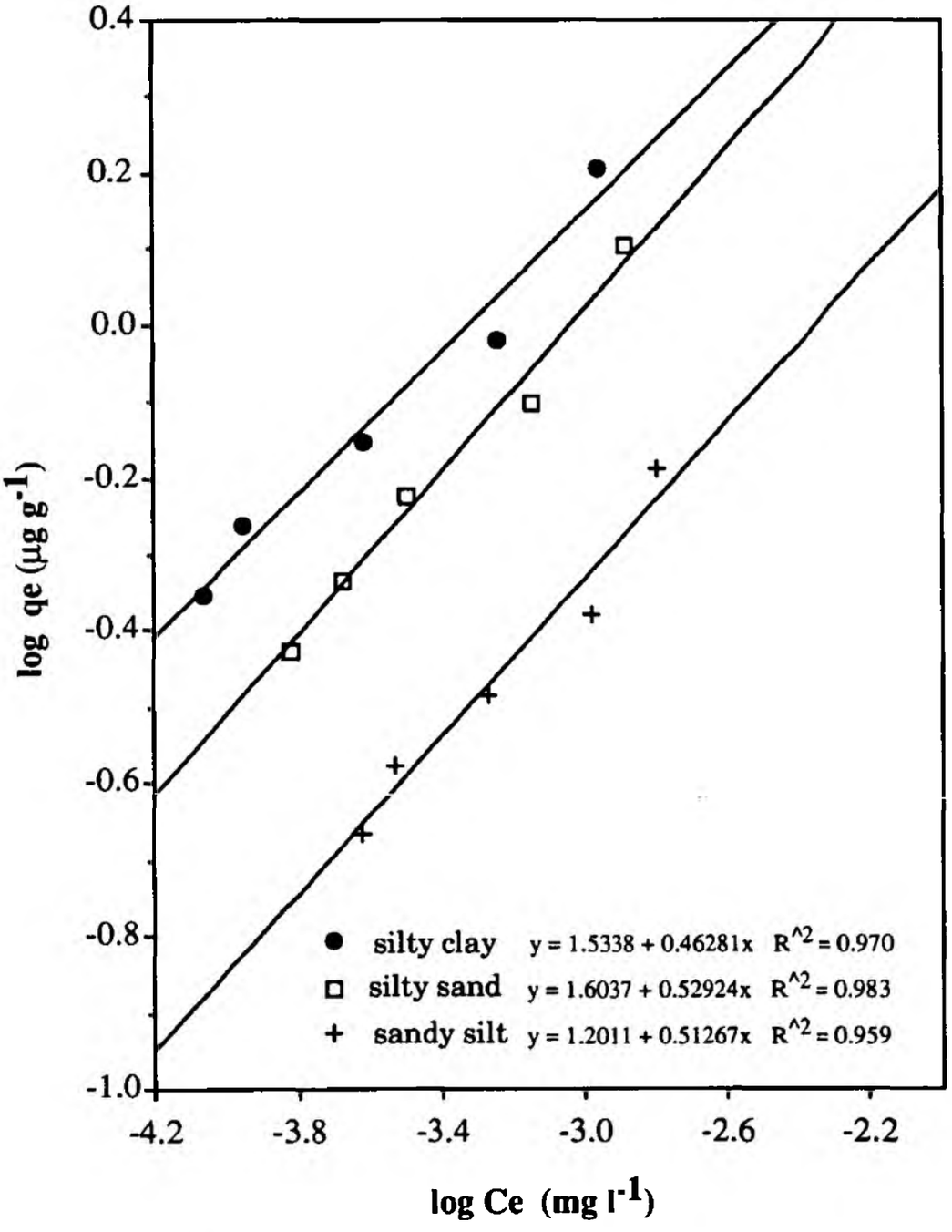


Fig. 7

Adsorption isotherms of TBT on freshwater sediments

4.4.1.2. Estuarine waters

The relationships between pH, particulate matter concentration, salinity and their respective influences on butyltin partitioning are included in Table 12 for a simulated estuarine environment. The estuarine experiments revealed different patterns of adsorption for each butyltin compound. These ranged from 67-100% for TBT, 15-47% removal for DBT, whilst MBT was almost completely removed in all experiments (71-100%) which was similar to the freshwater partitioning behaviour. However, sorption of TBT was dictated, to some degree by salinity. An increase in salinity caused a slight increase in TBT adsorption (>16%) in experiments where pH was low (6.0), irrespective of particulate matter concentration, but at high pH (8.0), no significant increase in adsorption occurred as particulate matter concentration increased. Dibutyltin however, appeared to be influenced more by pH than either particulate matter concentration or salinity, with the greatest adsorption (47%) occurring at a lower pH (6.0) and high salinity, irrespective of particulate matter concentration. An increase in particulate matter concentration at pH 6.0 resulted in a 13% increase in DBT sorption. Monobutyltin displayed a very strong affinity for particulate matter which was independant of pH and salinity. In all but one experiment, MBT was completely sorbed onto the particulates regardless of the suspended matter concentration or any other factorial combinations. The only experiment to display <100% sorption of MBT was at high pH, low particulate matter and low salinity.

Table 12
Mean percentage removal of butyltin from estuarine waters under differing environmental conditions

Experiment	pH	Particulate matter ($mg\ l^{-1}$)	Salinity (ppt)	% Butyltin Removal		
				TBT	DBT	MBT
1	8	1000	35	72	20	100
2	8	1000	5	75	25	100
3	8	10	35	80	15	100
4	8	10	5	76	18	71
5	6	1000	35	100	47	100
6	6	1000	5	84	35	100
7	6	10	35	89	34	100
8	6	10	5	67	38	100
9	7	100	17.5	80	25	100
10	7	100	17.5	76	29	100
11	7	100	17.5	70	32	100
12	7	100	17.5	83	35	100
Mean value of centre points				77.3	30.3	97.8
Standard deviation of centre points				±5.6	±4.3	±8.4

ppt=parts per thousand

4.4.2. Butyltin desorption from contaminated sediments

Experiments designed to assess the release of butyltin compounds from contaminated sediments following sediment disturbance revealed that desorption of TBT, DBT and MBT occurred as a result of physical agitation. Table 13 illustrates the total butyltin concentration in 20g of sediment (μg) and the resulting percentage butyltin release to overlying water after a 12 h shaking period. Results revealed that desorption occurred to varying degrees in all 5 contaminated sediments. The general order of desorption was DBT>MBT>TBT indicating that TBT is most strongly bound and DBT the least strongly bound to sediments. Although this only amounts to a TBT release of <1% from contaminated sediments it resulted in equivalent TBT water concentrations of between 30-170 ng l^{-1}, which is still significant. Desorption of DBT predominated at 3 out of 5 sites, accounting for between 1.4-6% of the DBT available, whilst MBT desorption was most predominant at the remaining 2 sites, accounting for between 0.8-2.5%.

Table 13
Availability and percentage desorption of butyltins in sediment

	Butyltin concentration in sediment (ng g^{-1})				Butyltin desorption (%)		
Location	Total Butyltin	TBT	DBT	MBT	TBT	DBT	MBT
Robertsons Boatyard (F)	522	202	265	55	0.57	1.30	2.43
Tidemill Marina (F)	182	96.8	59	26.1	0.85	6.08	0.81
Woolverstone Marina (E)	108	59.3	26.9	21.8	0.85	5.86	2.31
Titchmarsh Marina (E)	767	385	178	204	0.70	1.43	0.79
Tollesbury Marina (E)	1082	676	357	49.1	0.56	0.74	1.63

(F) = freshwater site, (E) = estuarine site

4.4.3. Butyltin Partitioning between sediment and Interstitial water

Butyltin partition coefficients (Kp) between sediment and interstitial water were calculated from the equation below. Partition coefficient values are displayed in Table 14 along with the total organic carbon and percentage grain size distribution.

$$Kp = \frac{\text{Butyltin concentration in sediment } (\mu g\ kg^{-1})}{\text{Butyltin concentration in interstitial water } (\mu g\ l^{-1})} \qquad \text{(iv)}$$

From Table 14 it can be seen that the Kp values fall within the range 1.59×10^3 - 4.55×10^4 for TBT, 4.32×10^2 - 5.71×10^2 for DBT and 1.71×10^2 - 4.43×10^3 for MBT. Values for Kp are generally in the order of TBT > MBT > DBT, although in certain cases for example, Oulton Broad and Brundall Marina, DBT had the highest Kp value. In order to investigate the possible relationships between butyltin partitioning and

organic matter content Spearmans Rank correlation analysis was undertaken. Paired observations between sediment TOC and TBT gave significant correlation (0.88) at the 99.5% confidence level, whilst slightly less significant relationships were observed for DBT (R^2 = 0.77 at 95% confidence level). No statistically significant relationship was observed between MBT and TOC at any confidence level.

Table 14
Butyltin partition coefficients (kp) in sediment and interstitial water

	Sediment Type				Partition coefficients (kp)		
Location	% Sand	% Silt	% Clay	(%) TOC	TBT	DBT	MBT
Fishers Dyke (F)	13	60	27	7.4	4.55×10^4	1.49×10^3	9.15×10^2
Brundall Marina (F)	17	56	28	9.8	5.55×10^3	5.71×10^3	9.47×10^2
Hickling Broad (F)	82	18	0	0.9	1.48×10^3	4.32×10^2	1.71×10^2
Oulton Broad (F)	11	70	29	4.1	2.24×10^3	4.07×10^3	2.56×10^2
Robertsons Boatyard (F)	23	65	12	3.3	2.89×10^3	2.70×10^3	2.17×10^3
Whisstocks Boatyard (F)	26	58	16	3.3	1.62×10^3	1.36×10^3	2.25×10^3
Tidemill Marina (E)	44	52	4	3.3	2.87×10^3	1.15×10^3	3.80×10^3
Woolverstone Marina (E)	29	57	14	3.4	1.59×10^3	1.06×10^3	1.26×10^3
Titchmarsh Marina(E)	27	66	7	3.7	6.20×10^3	2.50×10^3	4.43×10^3
Tollesbury Marina (E)	28	64	8	3.3	6.69×10^3	3.00×10^3	3.99×10^3

TOC - Total organic carbon, (F) - Freshwater sediment (E) - Estuarine sediment

4.5. Degradation of TBT in sediments

4.5.1. In situ studies of TBT degradation in sediment cores

The depth distribution of butyltin partitioning between the tri-, di- and monobutyltin forms is presented in Figures 8(a-c), as both absolute concentrations and as a percentage of the total butyl concentration. These cored profiles revealed a gradual decline in TBT concentrations with depth. Core 1 (Tollesbury Marina A) and core 3 (Titchmarsh Marina) sediments displayed a systematic reduction in organotin concentrations from surficial to subsurface layers. Most of the vertical profiles exhibited maximum TBT enrichment just below the surface, which subsequently declined with depth. The maximum concentrations occurred at a depth of 4-8 cm in core 5 (Waldringfield Quay), core 6 (Paglesham), and core 7 (Oulton Broad), but extended to depths of 10-15 cm in core 4 (Robertsons Boatyard) and core 8 (Ipswich Docks).

Sediment cores obtained from Tollesbury Marina B (core 2) and Robertson's Boatyard (core 4) were deep enough to reveal the historical loadings of TBT. Elevated concentrations of TBT extended to depths of 48 cm and 40 cm, respectively, before levels could no longer be detected. Despite the absence of TBT at these depths low concentrations of DBT and MBT were evident over a limited depth interval of 4-6 cm

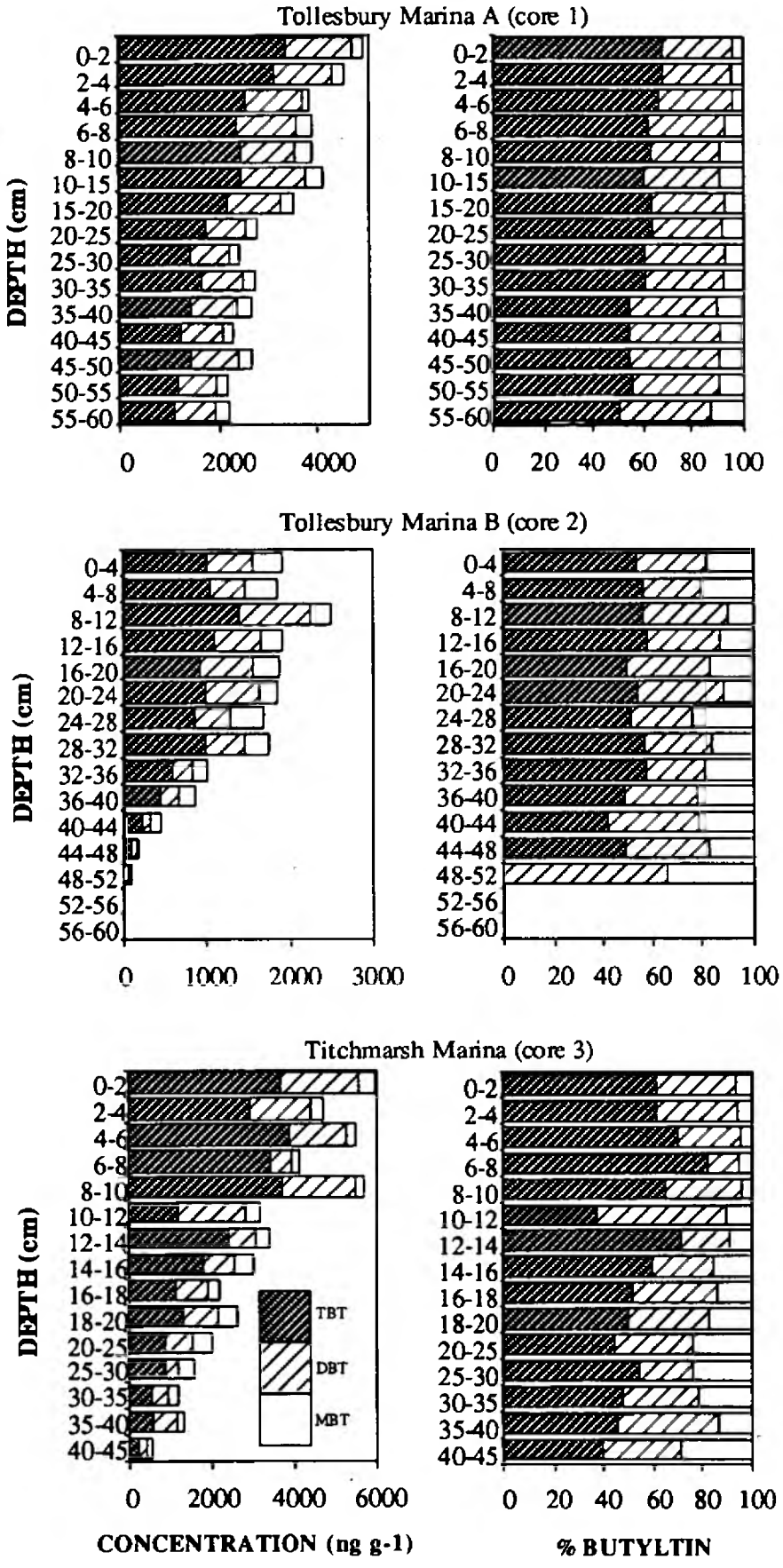


Fig. 8a
Vertical distribution and percentage composition
of butyltin compounds in sediment cores

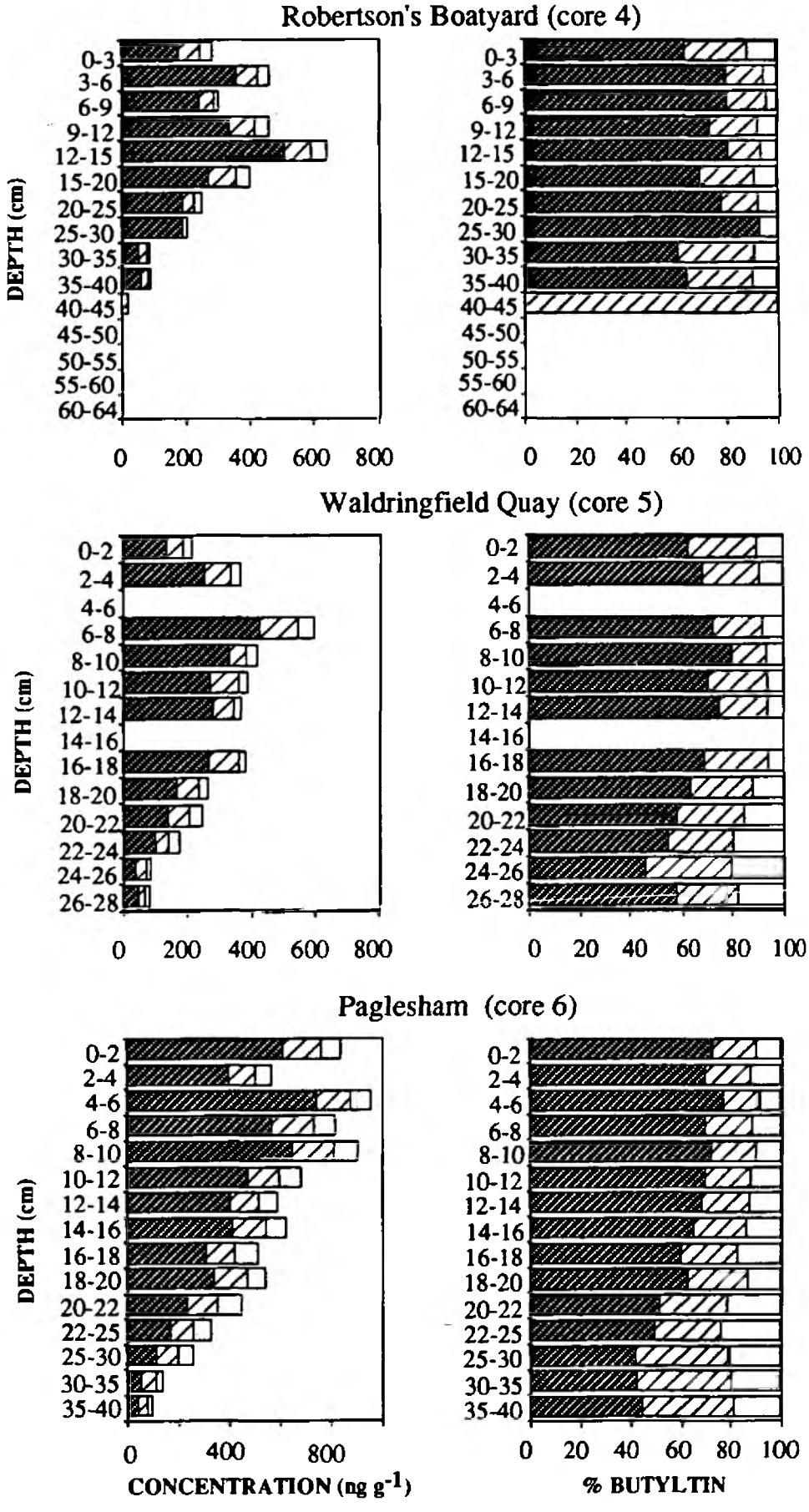


Fig. 8b.
Vertical distribution and percentage composition of butyltin compounds in sediment cores

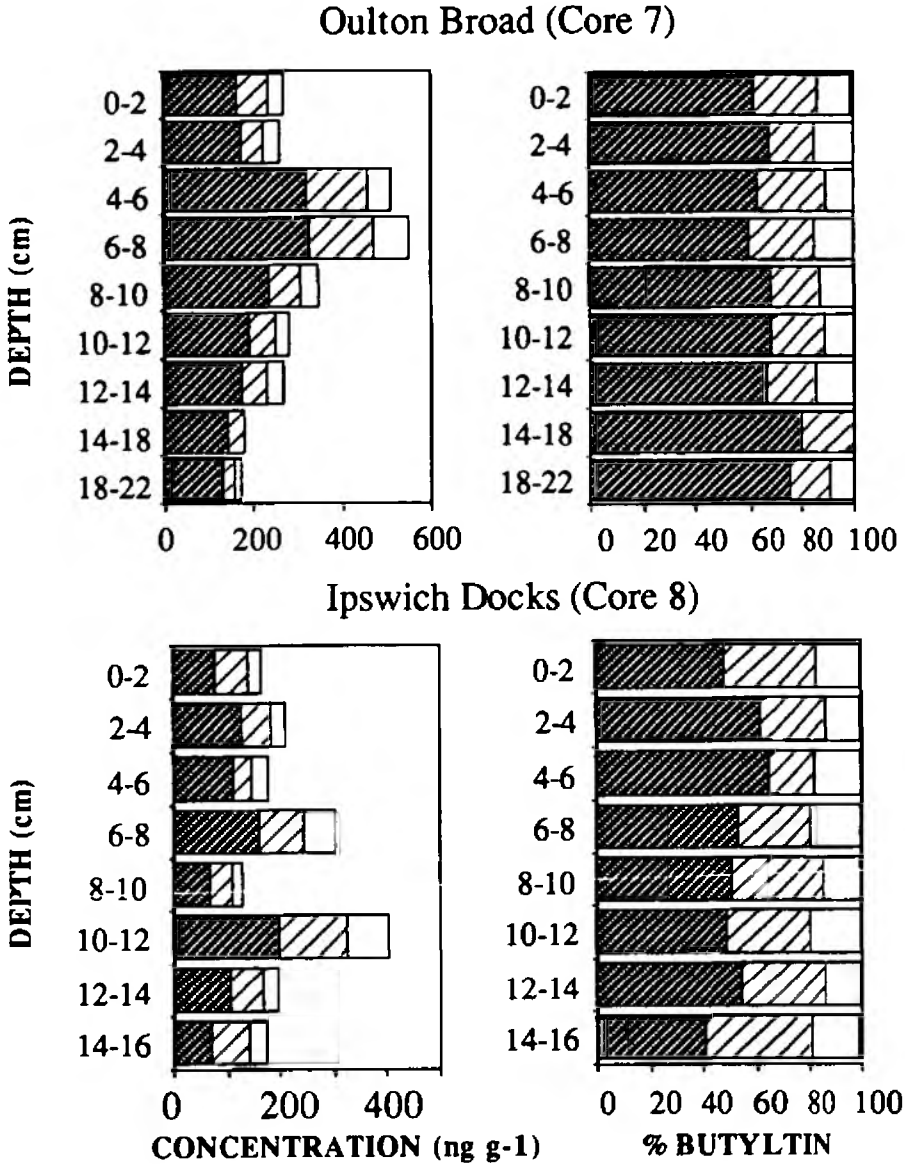


Fig. 8c.
Vertical distribution and percentage composition of butyltin compounds in sediment cores

before undetectable levels of all butyltin compounds were observed at the base of the cores (below 52 and 45 cm, respectively). Not all the cores were deep enough to elucidate the boundary between TBT enriched and uncontaminated strata.

The vertical distribution of organotins in some of the cores was unsystematic and implied some degree of sediment disturbance. This was particularly evident at core 8, where concentrations varied randomly with depth. An investigation of the vertical partitioning of organotins revealed that tributyl forms were the dominant Sn species, accounting for ≈60-80% of the total butyltins. The percentage distribution profiles of total butyltin in Figures 8(a-c) indicate that at most sites the proportion of TBT tended to remain constant with depth. However, at core 1, core 4 and core 5, a slight decline in the proportion of TBT with increased sediment depth was matched by an increase in the proportions of DBT and MBT, whilst in the remaining cores the proportions of DBT and MBT remained fairly constant.

The degradation rate of TBT in sediment was determined from the sediment profiles using the regression model described by De Mora *et al.* (1989). The model was applied to six of the sediment cores at sites where TBT concentrations decreased markedly with depth. The model was based upon the following assumptions:

i). Sedimentation rates were derived from local knowledge of previous dredging activities within individual marinas and boatyards. These ranged from 2 cm a^{-1}, at Oulton Broad, up to 13 cm a^{-1} at Tollesbury Marina A (Table 4). Although average sedimentation rates displayed a high spatial variability between sites, consistant estimates were obtained at each site (ie from at least 2 sources) apart from Ipswich Docks and Tollesbury Marina B where no information was available. It is assumed that sedimentation rates remained constant over the 30 year time span that TBT based paints have been in widespread use.

ii). Sediment age was calculated from this average sedimentation rate.

iii). The flux of TBT to the sediments was assumed to be constant over the 30 year period of usage. However, the UK retail ban came into force in 1987, and coring evidence has shown a decline in TBT accumulation in surface sediments in subsequent years. To take this into account and the fact that TBT paints have an average of 2 year antifouling ability, data points corresponding to deposits later than 1989 were omitted.

iv). It was assumed that the decline in TBT concentration with depth occurred as a result of decomposition mechanisms.

v). No account has been taken of mixing effects such as bioturbation or diffusion out of the sediments.

Butyltin data from six sites was used to determine the apparent degradation rate of TBT, DBT and MBT in sediment cores. In the case of TBT, for example, the natural log (ln) of each TBT data point was attained and plotted against the estimated sediment age in years (determined from estimated sedimentation rates) in the form of a scatterplot. Regression analyses subsequently derived the lines of best fit for each core using linear least squares approximation methods (see Fig. 9). The estimated half lives for TBT are calculated from the following standard half life equation (Atkins, 1986):

$$t^{1/2} = (^{1}/_{k})\ \ln 2 \qquad (v)$$

where $t^{1/2}$ = half life (years)
k = decay rate constant (years)
ln = natural log

All regression coefficients, rate constants (represented by the slope of the line of best fit) and half life values are presented in Table 15. Plots of TBT concentrations against estimated sediment age revealed straight line fits in all cases indicating that TBT degradation occurs via a first order kinetic process. Half life values obtained for TBT degradation ranged from 0.9 years (core 3, Titchmarsh Marina) to 5.2 years (core 7, Oulton Broad).

Subsequent modelling of DBT and MBT data revealed poorer regression plots than were derived for TBT. A number of cores did however reveal straight line fits for both species, once again indicating a first order kinetic degradation process. Half life values for DBT ranged from 1.5 - 3.0 years, whilst MBT half lives ranged from 1.8 - 3.7 years, although the latter was derived from a poor regression line. An examination of regression data from the sediment cores revealed that half lives were of the same order of magnitude for TBT, DBT and MBT indicating that the degradation sequence TBT>DBT>MBT occurs. However, the existance of all 3 butyltin compounds at depth within the sediment cores implies that in all 3 cases debutylation can be a very slow process.

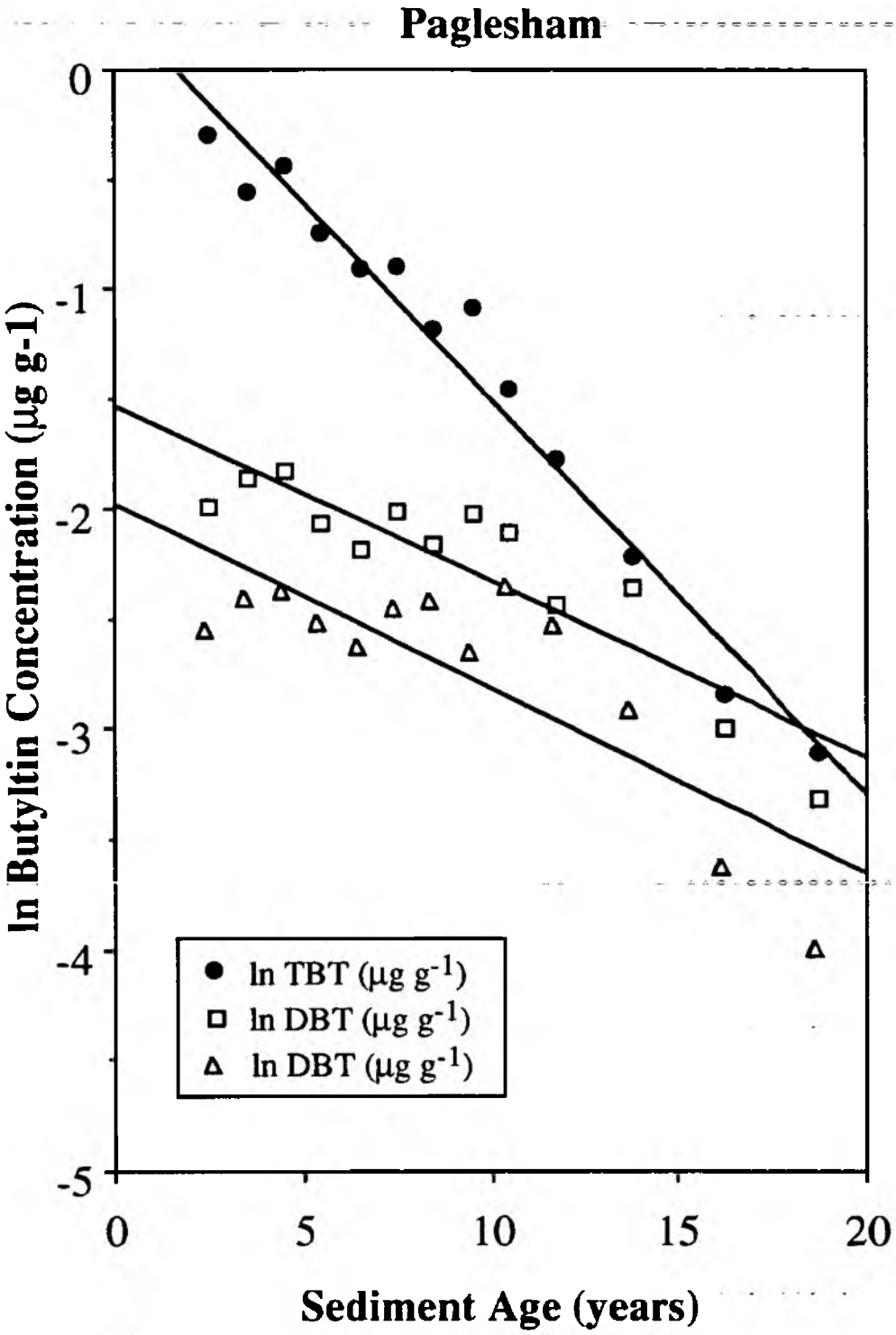


Fig. 9

Estimation of the half lives of butyltins in sediment cores taken at Paglesham

Table 15
Estimation of butyltin half lives in sediment cores

Compound	Site	n	Regression Coefficient	Decay Constant (yrs)	Half Life (yrs)
TBT	Tollesbury Marina (Core 1)	9	0.814*	0.177	3.92
	Titchmarsh Marina (Core 3)	9	0.896*	0.759	0.91
	Robertsons Boatyard (Core 4)	7	0.856*	0.398	1.74
	Waldringfield Quay (Core 5)	10	0.874*	0.437	1.59
	Paglesham (Core 6)	11	0.978*	0.480	1.44
	Oulton Broad (Core 7)	7	0.924*	0.133	5.21
	Mean		0.890	0.397	2.47
	S.D (%)		0.057	0.227	1.70
DBT	Tollesbury Marina (Core 1)	9	0.083	-	
	Titchmarsh Marina (Core 3)	9	0.678*	0.461	1.50
	Robertsons Boatyard (Core 4)	7	0.905*	0.250	2.77
	Waldringfield Quay (Core 5)	10	0.614*	0.240	2.89
	Paglesham (Core 6)	11	0.837*	0.228	3.04
	Oulton Broad (Core 7)	7	0.919*	0.232	2.99
	Mean		0.791	0.282	2.64
	S.D (%)		0.137	0.100	0.64
MBT	Tollesbury Marina (Core 1)	15	0.078	-	-
	Titchmarsh Marina (Core 3)	15	0.654*	0.381	1.82
	Robertsons Boatyard (Core 4)	17	0.906*	0.325	2.13
	Waldringfield Quay (Core 5)	10	0.321	-	-
	Paglesham (Core 6)	11	0.745*	0.260	2.67
	Oulton Broad (Core 7)	7	0.812*	0.188	3.69
	Mean		0.779	0.289	2.58
	S.D (%)		0.106	0.083	0.82

* = Significant regression at the 95% confidence level

4.5.2. Laboratory based TBT degradation experiments

4.5.2.1 TBT degradation in freshwater and estuarine sediments

A series of tank degradation experiments were undertaken on freshwater and estuarine sediments under controlled experimental conditions described previously in Section 3.3. Results for all experiments are included in Appendices 4(a-m). Initial TBT concentrations in contaminated sediments varied from 449 ng g^{-1} in Robertsons Boatyard (freshwater sediment) to 1290 ng g^{-1} in Tollesbury Marina (estuarine spiked sediment). All 4 tanks illustrated similar trends in that only the aerobic sediment zone (0-5 cm sections) displayed any decline in TBT concentrations over a 330 day period. The decline in TBT concentrations in aerobic surface sediments (0-5 cm) are displayed in Figure 10. In all cases there is a decline in TBT concentrations and a concomitant increase in DBT and MBT over time. However, in anoxic sediments (below 5 cm) no decrease in TBT concentration was evident in any of the experiments. Similarly, no concomitant increase in DBT or MBT occurred.

The degradation rate of TBT in aerobic sediments was determined using first order regression coefficient methods described earlier in Section 4.5.1. The natural log (ln) of each TBT data point was obtained and plotted against the number of days which the

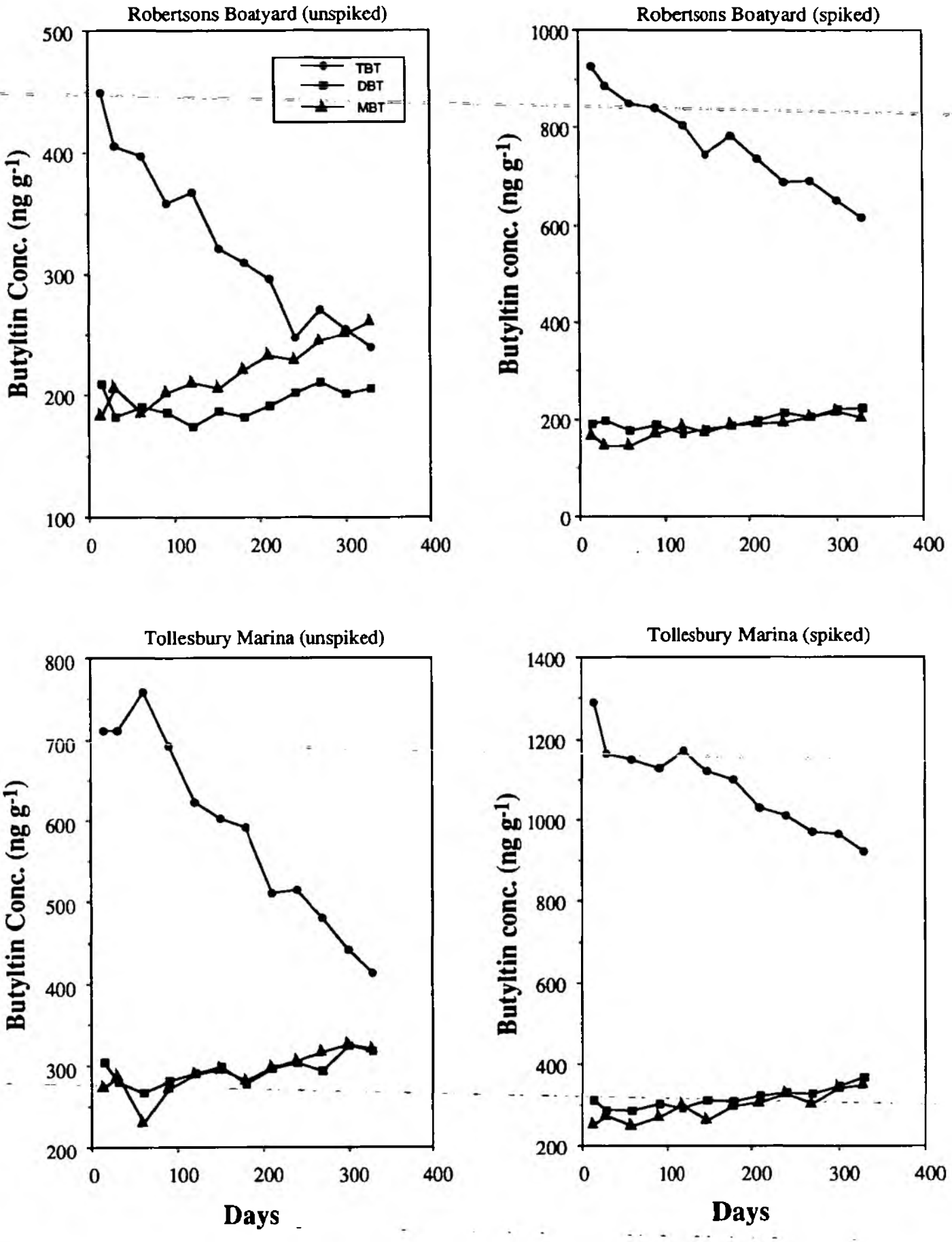


Fig. 10
Trends in the degradation of butyltins in contaminated surficial sediments in laboratory tank experiments

experiment had run. Regression analyses subsequently derived the lines of best fit for each core using linear least squares approximation methods and estimated half lives for TBT were calculated as described previously in Section 4.5.1. and are presented in Table 16.

Table 16
Degradation of TBT in contaminated surficial sediments in laboratory tank experiments.

Tank	Conditions	Depth (cm)	Regression Coefficient	Initial TBT Conc. (ng g^{-1})	Half life (days)
A	Freshwater (unspiked)	0-5	0.952	449	360
B	Freshwater (spiked)	0-5	0.967	926	587
C	Estuarine (unspiked)	0-5	0.953	711	374
D	Estuarine (spiked)	0-5	0.980	1290	775

n=12

The shortest TBT half life of 360 days was found in the freshwater sediment from Robertsons Boatyard (initial concentration of 449 ng g^{-1}). There appears to be very little difference in freshwater and estuarine sediments, although a notable increase in TBT half life was evident in spiked sediment from both Robertsons Boatyard and Tollesbury Marina, whose TBT half life values (587 and 775 days respectively) were almost double the values obtained from unspiked sediment from the same sites. Overall total butyltin values revealed a slight decrease throughout the duration of the experiments indicating that TBT decreases were not only attributable to debutylation to DBT and MBT in the sediment. In anaerobic sediment the half life of TBT was not discernible in the experimental time span and appears to be in the order of tens of years.

4.5.2.2. Butyltin desorption to overlying water

Analysis of overlying water was also undertaken during the tank experiments to determine whether desorptive processes could also be responsible for the decline in butyltin concentrations in surficial sediment samples. The results revealed that desorption of all 3 butyltin compounds occurred throughout the experimental period in all 4 tanks (Figure 11). Although there appeared to be no temporal trends in butyltin desorption, the order of desorption was generally DBT>TBT>MBT, indicating that DBT is lost to overlying waters more easily than the other butyltin compounds where it could then undergo more rapid degradation to MBT and inorganic tin. This could explain why mass butyltin mass balance was not maintained in aerobic sediments.

4.5.2.3. Effects of freezing and sterilisation on sediment TBT degradation

Analysis of frozen sediment was undertaken in conjunction with the tank experiments to determine whether degradative processes could occur at sub zero temperatures. Figure 12 displays butyltin sediment concentrations in both freshwater and estuarine

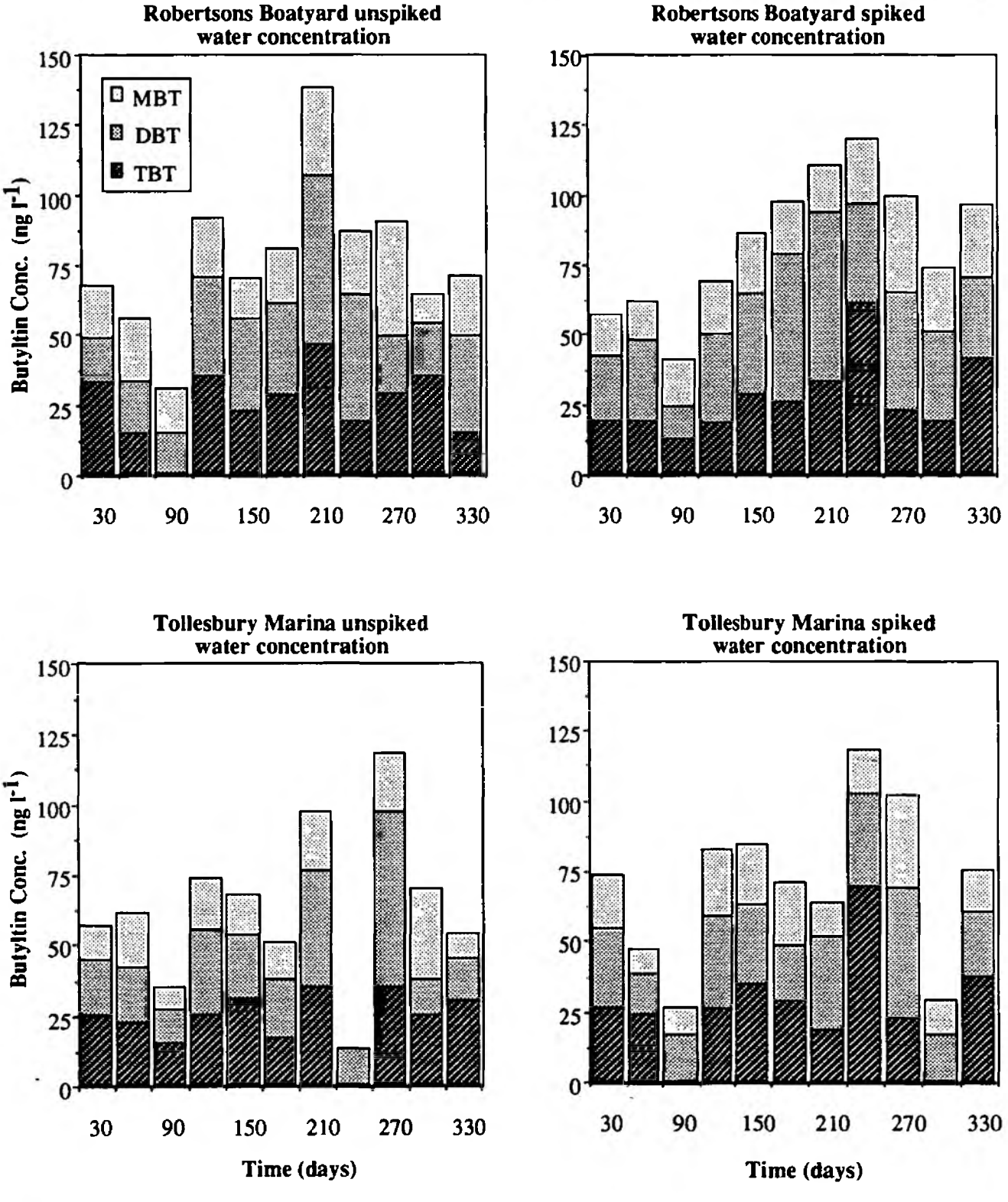


Fig. 11
Butyltin water column concentrations in Tank experiments

sediments frozen on the same day as the tank experiments were initiated. No significant losses of TBT were evident in either freshwater or estuarine sediment after 330 days indicating that samples of butyltin contaminated sediment can be frozen and maintained for upto a year and still yield reproduceable results.

Triplicate analysis of sterilised sediment was undertaken in conjunction with the tank experiments to determine whether abiotic degradative processes could occur in freshwater and estuarine sediments. Figure 13 displays butyltin sediment concentrations for freshwater and estuarine sediments over a 330 day period. No statistically significant change in TBT, DBT or MBT compounds was evident in freshwater or estuarine sediment samples, implying that abiotic degradation was not an effective process under these experimental conditions. Concentrations of TBT remained constant throughout the study although some variability was evident. Sterilised sediments were assayed for bacteria on a 3 monthly basis to determine the effectiveness of the sterilisation. Bacterial counts were determined on diluted sediment samples and results indicate that sterility was effectively achieved in both freshwater and estuarine sediments. Prior to sterilisation, the bacterial cell counts were in the order of $3x10^9$ CFU g^{-1}, and after sterilisation, bacterial cells were not observed (<10 CFU g^{-1}). Therefore the use of mercuric chloride as a sterilising agent appears to have been successful in destroying all microorganisms in the sediment for a 1 year period.

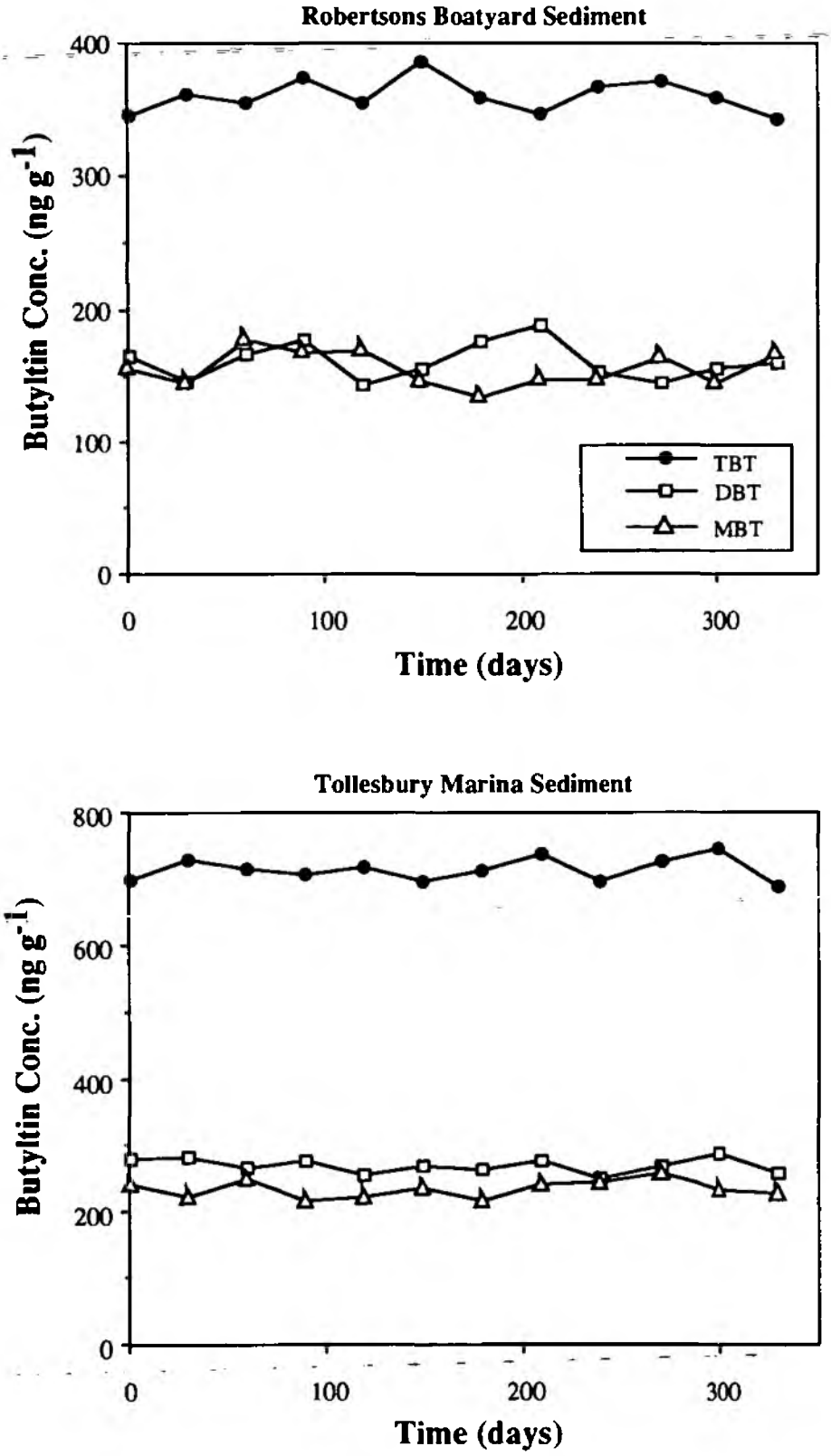
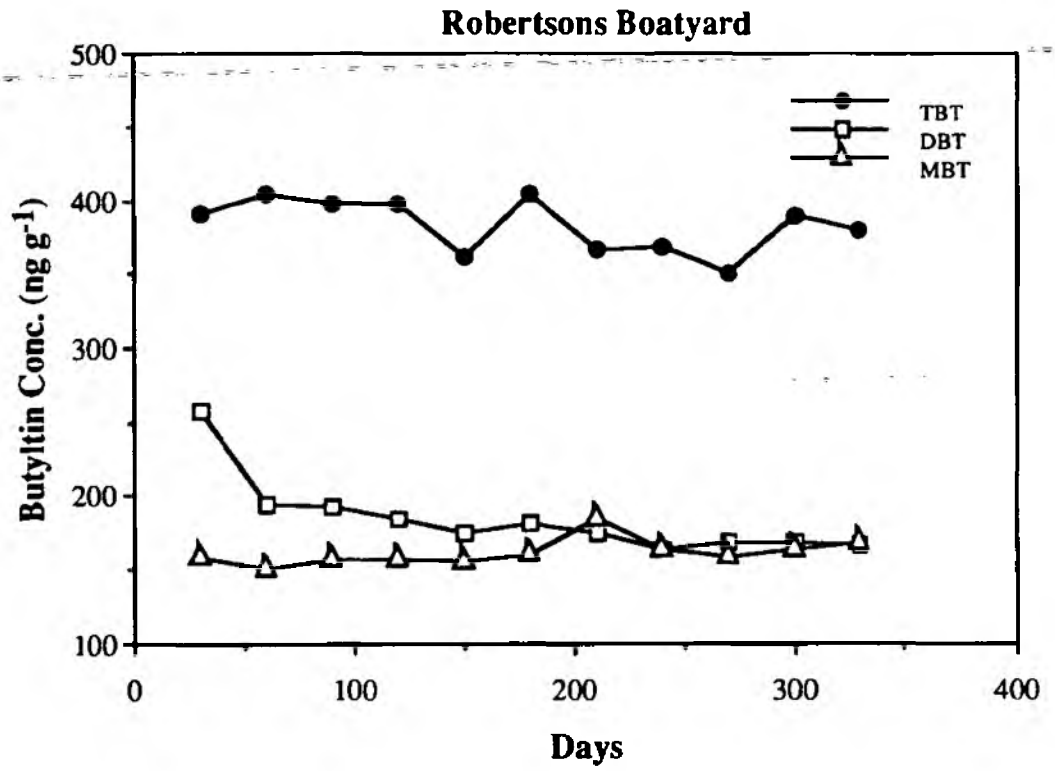


Fig. 12
Trends in the degradation of butyltins in frozen sediments



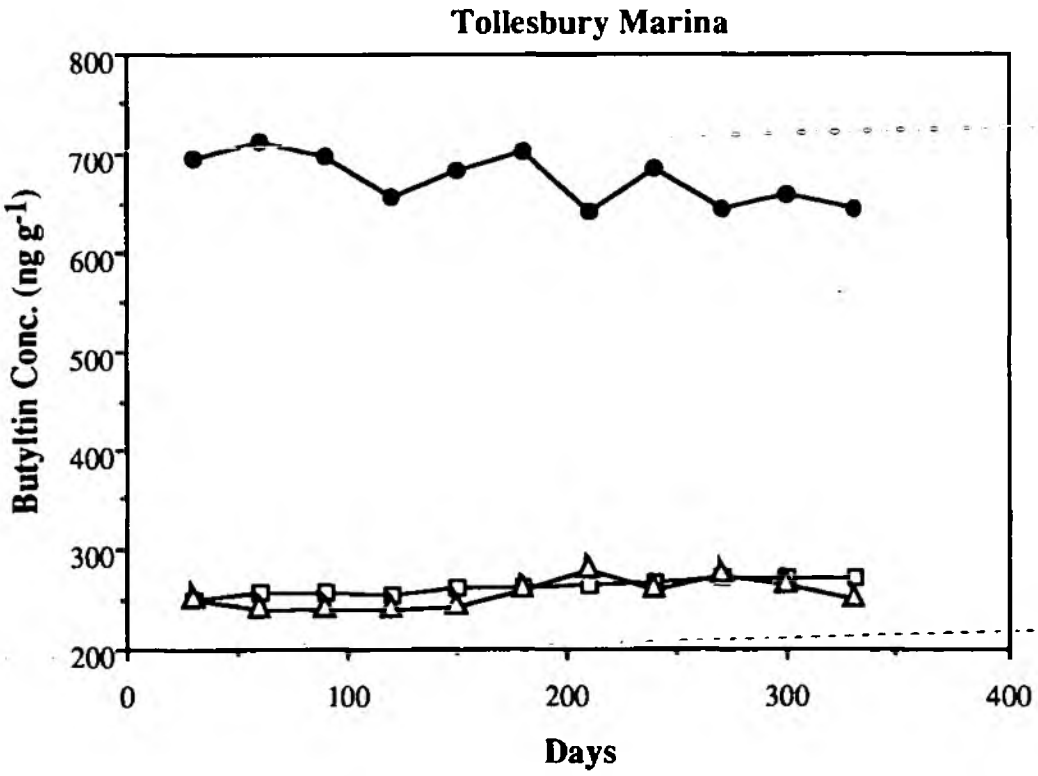


Fig. 13
Trends in the degradation of butyltins in sterilised sediment

5. DISCUSSION.

Elevated concentrations of tributyl-, dibutyl- and monobutyltin were detected in a number of estuarine systems within Essex and Suffolk. The distribution of TBT reflected boat usage with enrichment occurring at marinas, boatyards and mooring sites. This implies that antifouling paints were a major source of these compounds in the aquatic environment.

There appeared to be no universal rule pertaining to the seasonal behaviour of butyltin levels in water column or surficial sediment samples during the temporal study in Essex and Suffolk estuaries. However, a number of seasonal trends were evident and can be linked with the boating activities described in Table 17. On the River Deben, for example, high sediment and water concentrations in the spring and summer give way to a successive decline in concentration in the autumn and winter. This pattern coincides with boating activity, from the influx of freshly painted boats in the spring, their extensive use in the summer and boat scrubbing in the autumn.

Table 17
Seasonal boating activities in the East Anglian region

Season	Seasonal boating activities
Spring	Antifouling paint application and initial boating activity
Summer	Peak boating season
Autumn	Boating season ends, boat scrubbing and high pressure hosing activities
Winter	Very little boating activity

Different seasonal trends in butyltin contamination were displayed in sediments at Titchmarsh (site 21) and Tollesbury (site 25) where peak TBT concentrations occurred during autumn-winter, 1990. Initial high TBT levels in autumn, 1990, could be related boat scrubbing and high pressure hosing which are used to remove old layers of paint and could result in TBT paint flakes been flushed into the sediment, where they may form a nucleus for long term release to overlying waters and surficial sediments. Wet sieving of contaminated sediments has revealed visible paint flakes in the past (Dowson *et al.*, 1992a and Waite *et al.*, 1991). Trends in TBT sediment concentrations exhibited at Titchmarsh (sites 11-13) could also be due to antifoulant ageing. Antifouling paints containing TBT have been shown to exhibit initially high release rates during the first 1-2 months after a freshly painted hull has been placed in the water. This could be responsible for the increase in water column concentrations in the spring, whilst sorption onto particulates and

subsequent degradation effects would act to reduce water concentrations, whilst enriching bottom sediments.

Seasonal variation in boating activities could also account for patterns in TBT water column concentrations. Water samples at Robertsons Boatyard (site 5), Whisstocks Boatyard (site 7) and Titchmarsh Marina (site 13) contained detectable levels of TBT during the spring and summer months, despite the retail ban implemented in 1987. A number of samples exceeded the Environmental Quality Standard (EQS) set for inland waters and implies that TBT may still have been in use during the 1990-1992 period. This confirms reports by Waite *et al.* (1991), who found that water samples taken from Hythe Marina in 1988 had a mean TBT concentration of approximately 2000 ng l^{-1}. This marina only opened in 1988 and contained no boatyard facilities, so TBT contamination in the water column could not have originated from the hosing down of boats coated with old layers of TBT paint, or from TBT desorption from contaminated sediments. The TBT concentrations thus appear to be due to the presence of boats which had recently been painted with TBT based antifoulants in 1988. Similarly, in France, several years after the French ban on the use of TBT based paints for small boats in 1982, Alzieu *et al.* (1989) reported that abnormally high inputs of TBT to the environment were occurring. This was especially noticeable in Boyardville Marina on the Atlantic coast, where TBT concentrations up to 1500 ng l^{-1} were recorded.

Tidemill Marina (site 6), Deben Yacht Club (site 8) and Tollesbury Marina (site 15) displayed elevated TBT levels in the water column during the winter months when boating activity is at a minimum. This could be due to dredging activities which may have resulted in TBT desorption from the sediment compartment back into the water column. The desorption studies revealed that TBT sorption is reversible, with all three butyltin compounds desorbing to differing degrees. Although only 1% of TBT appeared to be desorbed from contaminated sediments, this amount may be significant, releasing between 30-170 ng l^{-1} to the overlying water, which is well in excess of the (EQS) for fresh and saline waters (20 ng l^{-1} and 2 ng l^{-1} respectively), which can be detrimental to aquatic life. Dredging activities have been undertaken at the above sites during the past few years (Pers. Comm. from NRA, 1992) and surveys undertaken in this study have revealed TBT compounds in water column samples of the same order of magnitude as the desorption experiments. This indicates that desorption of butyltin compounds from TBT contaminated sediments in the sample areas could be responsible for TBT levels still being found in water column. However in the freshwater sites at Robertsons Boatyard and Tidemill Marina, water column concentrations from the desorption studies yielded higher butyltin concentrations than the 1990 water column surveys. Water column concentrations could however depend on the degree of sediment disturbance and the time lag since sediment

disturbance. Sorption of butyltin compounds back onto particulate matter would also occur and should be taken into account when estimating butyltin concentrations in the water column resulting from desorption. However it cannot be conclusively proved whether TBT levels still detected in the water column are the result of continued TBT antifouling paint use or as a result of sediment desorption.

A number of study sites in Essex and Suffolk are open to commercial shipping and Thames barges (>25m in length) which are not covered by the 1987 ban on the use of TBT antifouling paints. These could be releasing TBT into the water column, although the highest levels of TBT have generally been found where small boats were abundant, not in areas of commercial shipping, confirming reports by Cleary and Stebbing (1987). The fact that there appeared to be no substantial difference between the levels of TBT detected in waters used by ocean going vessels, such as on the River Orwell, and waters utilized exclusively by pleasure boats, implies that commercial sea shipping has little effect on the level of organotins.

The degree of TBT contamination may also be enhanced in the surface microlayer where TBT is known to concentrate in films containing alcohols and fatty acids which tend to concentrate lipophillic pollutants, such as organotins (Cleary and Stebbing, 1987). This can increase TBT concentrations by factors of between two and ten compared to average water column loadings. This has major implications for intertidal areas where deposition on the shore occurs at low tide (Quevauviller *et al.*, 1990). The occurrence of high water column concentrations below the surface microlayer at some of the sampling locations implies that further enrichment of these toxic compounds may occur within the microlayer (Cleary and Stebbing, 1987).

In general, concentrations of TBT have declined with time indicating that the 1987 retail ban has been effective in reducing water and sediment concentrations in the majority of east coast estuaries. This trend is further supported by the fact that there has also been a concomitant improvement in Oyster growth on the east coast. A *C. gigas* fishery on the River Blackwater, UK, which had been closed since the 1970s, was reopened in late 1987 and was producing oysters of nearly marketable size by the end of 1988 (Waite *et al.*, 1991). Cleary (1991) also reports significant reductions in TBT water concentrations since 1987 at coastal and estuarine sites in south-west England. Legislation in other countries has also been effective in reducing TBT contamination of the aquatic environment. In the oyster growing areas of France, the concentrations of TBT in water have decreased since 1982 and are now generally <5 ng l^{-1}, (Michel and Alzieu, 1990) and as a result TBT contamination of oysters (*Crassostrea gigas*), has decreased and spatfall has greatly improved (Alzieu, 1991). Further evidence of a decline in TBT in the aquatic environment

has been described by Valkirs *et al.* (1991) who found a reduction in the levels of TBT in yacht harbours in San Diego Bay, USA, which they attributed to the restriction of TBT based paints on small boats.

Methyltin concentrations in sediments were low compared to butyltin species but compared favourably with other published work (Tugrul *et al.*, 1983; Maguire *et al.*, 1986 and Dowson *et al.*, 1992a, b). The source of methyltins remains elusive; anthropogenic discharges, abiotic methylation reactions and biotic methylation have all been demonstrated (Thompson *et al.*, 1985). Gilmour *et al.* (1985) found that mixed cultures from Chesapeake Bay sediments were capable of methylating tin under anaerobic as well as aerobic conditions and anaerobes of the genus *Desulfovibrio* are capable of accomplishing methylation. It is most likely that the relatively low concentrations of methyltins found in this survey arise through the *in-situ* methylation of inorganic tin.

A very important factor which affects the fate of xenobiotic compounds in the aquatic environment is their partitioning between the aqueous phase and particulate matter. The degree of sorption is generally influenced by the surface area available for contaminant binding, the presence of other organic and inorganic compounds competing for those adsorption sites and the structure and charge of butyltin compounds in the water (Randall and Weber, 1986). The removal of butyltin compounds from the soluble to particulate phase in both the freshwater and estuarine experiments could be accounted for by sorption onto glassware. However, leaching experiments demonstrated that there were no major losses of TBT, DBT and MBT due to adsorption onto container walls, so it can therefore be assumed that sorption onto particulate matter was the removal mechanism responsible for the reduction in soluble water column concentrations.

The partitioning experiments undertaken in freshwater samples highlighted the importance of particulate matter concentration in dictating the sorption characteristics of TBT and its degradation products in both estuarine and freshwater environments. Batch isotherm experiments utilising natural sediment for TBT sorption studies, however, revealed that an increase in particulate matter results in increased TBT sorption in all sediment types. Results obtained for the relationship between pH and adsorption were not as clear as those discussed for particulate matter and no statistically significant relationships were apparent between pH and any of the butyltin compounds. The effect of different particulate matter loadings and pH in estuarine waters revealed different trends to those conducted in freshwater. A definite trend was revealed for DBT where a decrease in removal occurred with increasing pH. Tributyltin exhibits a similar behaviour to DBT but is statistically less significant, whilst no significant conclusions can be drawn from the MBT experiments.

The order of affinity (sorption) of the butyltins for iron oxide (MBT>TBT>DBT) may be attributed to differences in the chemistry of these compounds. The hydrophobicity of alkyltin compounds increases with an increasing number of carbon atoms and the number of alkyl groups bonded to the tin. The observed mixed adsorption trend for butyltin compounds results from tributyltin adsorption favoured by hydrophobicity and monobutyltin adsorption favoured by polarity. Randall and Weber (1986), suggested that the polarity of the butyltins could be an important factor influencing sorptive behaviour with the more polar MBT being more strongly attracted to the dissolved phase. However, in the freshwater factorial experiments presented here, MBT was almost totally associated with the particulate phase which appears to contradict Randall and Weber's findings.

A major factor to consider which may be responsible for the different sorptive behaviour of TBT between the factorial and isotherm experiments is the different nature and age of adsorbent used. The ageing of the precipitate reduces the sorption capacity of the iron oxide as a result of molecular rearrangements which improve the crystalline structure of the precipitate (Lee, 1975). The hydrous iron oxide precipitate used in the factorial studies was only aged for one week and this could have played a major role in the ability of these precipitates to interact with heavy metals and other chemical contaminants (Stumm and Morgan, 1981). This could explain why the hydrous iron oxide displayed a greater sorptive capacity than the natural sediment used in the isotherm experiments. The difference in sorption between sediment types may be explained by the significantly greater surface area and more active sites for adsorption of TBT by sediments with a finer silt and clay content. Silts and clays contain charged minerals such as montmorillonite which impart a negative charge and therefore attract cationinic species thus resulting in a higher degree of sorption. Sands in contrast, have a lower specific surface area and a lower organic carbon content, which reduces their binding capacity. Sands are also composed of inert minerals such as quartz and feldspar which are neutrally charged which will result in decreased sorption (Förstner and Wittmann, 1979).

The estuarine partitioning experiments assessed the additional effect of salinity upon butyltin removal from solution and revealed salting out effects of TBT but an apparent decrease in DBT sorption with increasing salinities. Salinity appeared not to influence the sorptive behaviour of MBT. This agrees favourably with work undertaken by Randall and Weber (1986) and by Harris and Cleary (1987), who also reported a salting-out effect for TBT. This effect has been attributed to the increased salinities accentuating the importance of nonpolar interactions by neutralization of the carboxyl groups of the adsorbed fulvic acid by positively charged sodium ions (Randall and Weber, 1986). It is however in disagreement with Unger *et al.* (1988), who found that TBT sorption coefficients decreased with increasing salinity and varied by a factor of 2 over the salinity range. They suggest

that the strongly linear decrease of the TBT sorption coefficient with increasing salinity may result from ion exchange competition of seawater cations with sorbed TBT species, or from changes in the nature of TBT species in solution due to formation of chloro-TBT complexes. At high salinities less adsorption is expected due to competition of chloride ions with the particulate matter for the butyltin species and competition of sodium ions with the butyltin compound for carboxylate sites on the particulate matter. Thus sodium ions partially neutralize the carboxyl groups of organic acids bound to the particulate matter leading to a less negative particulate matter charge (Donard and Weber, 1985). This explanation could be valid for DBT, where sorption appears to decrease with increasing salinity, but in the case of TBT an increase in salinity seems to enhance adsorption. Changes in the salinity effect over the estuarine range cannot be inferred from the results obtained in this study or by Randall and Weber (1986), because the factorial design only reports data for the high and low end of the salinity range (ie 5 and 35 ppt.).

The work reported by others such as Randall and Weber (1986) and Unger *et al.* (1988), utilizes artificial seawater devoid of organic compounds and complexing agents which are known to be important for contaminant binding (Förstner and Wittmann, 1979), whereas in all the experiments undertaken in this study natural fresh and estuarine water has been used. It is possible that adsorption differences between artificial and natural waters may be considerable. Natural fresh and estuarine waters contain dissolved organic compounds such as humic and fulvic acids that may associate in some unknown manner with butyltin species in solution. It is therefore possible that butyltin adsorption may be specific to the particular estuary considered. This has been suggested by Unger *et al.* (1988) who felt that adsorption characteristics should be determined for each individual river system.

Experimental work to determine the partitioning of butyltin compounds between sediment and interstitial water illustrated that TBT was principally associated with the particulate phase. At Robertsons Boatyard, for example, solid and dissolved phase TBT concentrations were 202 ng g^{-1} and 70 ng l^{-1}, respectively. This can be accounted for by the hydrophobic nature of TBT which displays a higher affinity for particulate interactions than the more polar DBT and MBT. The partition coefficients for TBT ranged from 1.07 x 10^2 - 4.55 x 10^4 which is in general agreement with other published work (Maguire and Tkacz, 1985; Randall and Weber, 1986 and Unger *et al.*, 1988). Sediment TOC appeared to be an important control upon TBT partitioning with the highest partition coefficients coinciding with high organic loadings. This would indicate that the binding capacity for TBT increases in highly organic sediments. There appears to be no systematic relationship between the partition coefficients of TBT, DBT and MBT in freshwater or estuarine sediments, but in general MBT appeared to display slightly less affinity for the particulate phase in freshwater sediments compared to DBT and TBT. However, in estuarine

sediments (Woolverstone, Titchmarsh and Tollesbury) MBT partition coefficients are higher than for DBT. This indicates that the more polar MBT has a higher affinity for the particulate phase in saline areas than DBT and as a result is less bioavailable. In all cases, significant amounts of TBT are potentially available for uptake by aquatic biota despite the degree of solid phase partitioning.

It is evident that TBT sorbs readily to sediments. It is important therefore to determine if degradation is a major process in reducing TBT concentrations within the sediment compartment. Only a limited number of studies have been undertaken on TBT degradation in sediments (Table 18). Two types of study have been attempted to determine TBT degradation rates. The first involves analysis of sediment cores, followed by subsequent regression modelling to determine the TBT half life. The other technique utilises laboratory based tank experiments and half life modelling to monitor degradation trends. This allowed the determination of TBT degradation rates in freshwater and estuarine sediments to be fully assessed.

Table 18
Comparison of TBT half lives in sediment degradation studies

Study and date	Comments	Half life
Tank experiments		
Waldock *et al.* (1990)	TBT degradation in harbour and marina sediments	28-76 weeks
Maguire and Tkacz (1985)	TBT degradation in Toronto lake sediments	16±2 weeks
Stang and Seligman (1986)	Degradation of TBT in San Diego bay sediments	23 weeks
In-situ core studies		
De Mora *et al.* (1989)	TBT profiles in sediment cores from a marina	1.85 years
Astruc *et al.* (1989)	TBT profiles in sediment cores from Arcachon Bay	>8-15 years

Cored sediment profiles obtained for 8 TBT hot spot sites in Essex and Suffolk provide an historic perspective on TBT contamination and also give an indication of the main degradation pathways. Sediment butyltin concentrations generally declined with depth, reaching undetectable levels at >40 cm. Antifouling paints containing TBT as a biocide were first introduced in Europe in 1959-61 (Clark *et al.*, 1988) and it has been estimated that by 1985, 20-30% of vessels world wide utilised TBT antifouling formulas (Valkirs *et al.*, 1986). This time scale of events fits well with the TBT profiles obtained from Tollesbury Marina B and Robertsons Boatyard which exhibited maximum organotin

loadings at 12 cm and baseline levels at 48 and 40 cm, respectively. Assuming an average sedimentation rate of 5.0 cm a^{-1} at Robertsons Boatyard, maximum usage of TBT occurred here around the time of the retail ban in 1987. It is evident from the cored profiles that organotin accumulation in surface sediments is on the decline and this coincides approximately with the implementation of the 1987 ban.

Degradation trends supporting debutylation are evident in the sediment core profiles from Tollesbury Marina B (core 2) and Robertsons Boatyard (core 4). Degradation is indicated by the absence of TBT at the core base and the presence of DBT and MBT. Additionally, in core 1 (Tollesbury Marina 1), core 6 (Paglesham) and core 5 (Waldringfield Quay) the decline in percentage TBT with depth is matched with an increase in DBT and MBT, thereby indicating a stepwise degradation pathway for TBT. In the other cores sediment TBT degradation trends were identified from statistical analysis, through the occurrence of exponential decay curves. However, no significant increase in DBT or MBT was observed to compensate for the degradation or loss of TBT. This exponential relationship with depth may in fact represent temporal variability in TBT accumulations since its introduction, rather than degradation trends. In all cases if degradation of TBT in contaminated sediments was occurring it appeared to be slow confirming reports by De Mora *et al.* (1989) and Astruc *et al.* (1989).

The sediment core approach revealed a TBT half life ranging from 0.91-5.2 years, which agrees favourably with the 1.85 year half life in marine sediments, calculated by De Mora *et al.* (1989). The authors suggest that the presence of TBT in 10-year-old sediments indicates that TBT has considerable persistence in the environment. Similarly, Astruc *et al.* (1989), in a study of Arcachon Bay sediments, reported that TBT was the major butyltin species in sediments deposited between 8-15 years ago. The authors concluded that the half-life of TBT in these heavily contaminated sediments must be measured in years or even decades, although no half life values were presented. Stang and Seligman (1986) obtained profiles of TBT and its breakdown products within sediment cores from San Diego Bay. In several of the cores, TBT was the major butyltin species at depths of over 20 cm, although no chronology was provided. However, these authors attribute the presence of TBT at depth to sediment mixing processes, rather than to slow degradation (Stewart and De Mora, 1989).

The core profile approach used in this study is confounded by a number of limitations originating from the model assumptions. Firstly, it is very difficult to obtain accurate sedimentation rates for an estuarine river system. Even if an accurate rate can be ascertained, it is constantly fluctuating due to differing storm patterns, dredging and boat disturbance. To obtain accurate sedimentation rates, it is possible to date the sediment with

^{210}Pb (Evans and Wrigler, 1983) or with ^{137}Cs (Bennett, 1987). Although this has been undertaken on static systems (eg; lakes) the dynamics of an estuary create major problems, since sediment is being continually mixed, disturbed and redeposited. These factors combined with the considerable expense of sediment dating techniques prevented accurate sediment dating in this instance. Secondly, TBT is a non point source pollutant and will not provide a constant influx to the sediments; thirdly, a significant degree of bioturbation was found to occur in a number of sediment cores at depths of up to 40 cm. Definitive, unambiguous information can therefore only be obtained from cores where reworking of sediment has not caused the excessive mixing of TBT (De Mora *et al.*, 1989).

The tank experiments undertaken over 330 days offer an alternative approach to determine degradation rates in sediments. Results indicated that the shortest TBT half life (0.98 years) was found in freshwater sediment (Robertsons Boatyard). Although this value is greater than values cited in studies undertaken by Maguire and Tkacz (1985) and Stang and Seligman (1986), who determined that TBT degrades in surficial sediment/water mixtures with half-lives of 0.31 and 0.44 years respectively, which agrees favourably with Waldock *et al.* (1990) who found TBT half-lives of 0.54-1.46 years in estuarine marina sediments in the UK. In some instances, half lives obtained from tank experiments are shorter than in the core studies, although laboratory experiments undertaken by by Imperial College and Waldock *et al.* (1990) are of similar magnitude to half lives obtained from *in-situ* sediment studies.

It is difficult to explain the apparent difference between laboratory and *in-situ* TBT half life values. In the laboratory tank degradation experiments, sediments are aerobically maintained in surface sediments in a controlled environment with no additional sedimentation throughout the course of the experiments. However, in eutrophic systems anaerobic conditions prevail which may result in slower degradation rates (Waldock *et al.*, 1990). Similarly at marinas with high sedimentation rates, surficial sediments may quickly become buried and exposed to anaerobic conditions, thus resulting in slower TBT degradation rates. As TBT tends to accumulate in sediments it is possible that biodegradation of TBT will be inhibited if sufficiently high concentrations are present due to the extreme toxicity of TBT to the butyltin degrading bacteria. The few studies made of TBT persistence in sediments appear to support this possibility (Stewart and De Mora, 1989). Seasonal changes in temperature within the sediment compartment may also affect the rate of TBT degradation. In all the tank experiments temperatures were constantly maintained at 14 °C, whilst in the real environment temperatures may drop below 10°C for 3-4 months of the year. This could result in slower metabolic rates for butyltin degrading bacteria which in turn could produce slower degradation rates.

Very little difference between degradation rates in contaminated freshwater and estuarine sediments was evident, although a notable increase in TBT half life was apparent in Robertsons Boatyard and Tollesbury Marina elevated spiked sediments, whose TBT half life values (1.61 and 2.12 years respectively) were almost double the values obtained from unspiked sediment from the same sites. This further supports the hypothesis that slower degradation rates may be caused by the inhibition of microbial activity at higher TBT sediment concentrations. Similar inhibition to TBT degradation has been found in studies conducted with water containing higher TBT concentrations (Clark *et al.*, 1988).

Degradation trends supporting a stepwise debutylation sequence are not apparrent from the tank studies. If stepwise debutylation had occurred, the DBT slope should have also decayed at a rate proportional to the tributyltin decay slope. As Figure 10 illustrates, this is not the case and in most of the tanks the MBT increases slightly more than the DBT slope indicating debutylation straight through to MBT. Another possibility is that the rate of debutylation from TBT to DBT is nearly identical to the rate from DBT to MBT which would result in a similar effect to that observed. The limited published data concerning TBT degradation products from sediment experiments has given variable results. Dibutyltin was the primary initial degradation product in Toronto Harbour sediment (Maguire and Tkacz, 1985), whilst MBT was the principal initial degradation product in San Diego Bay sediments (Stang and Seligman, 1986).

Overall total butyltin values revealed a slight decrease throughout the duration of the experiments indicating that TBT decreases were not only attributable to debutylation to DBT and MBT in the sediment. It may be possible that TBT degrades to DBT in the aerobic sediment layer where it subsequently desorbs to the overlying water column. This trend is further supported by the elevated DBT concentrations in the tank waters and the results of the desorption experiments. *In-situ* mesocosm studies undertaken by Stang and Seligman (1987) at the sediment-water interface also indicate a potential for DBT desorption from the sediment.

In anoxic sediment the half life of TBT was not discernible in the experimental time span and appears to be in the order of tens of years. Surficial sediments are not a significant area in terms of mass balance of the whole sediment and the presence of elevated loadings of TBT at depth coupled with low rates of degradation in contaminated areas, implies that aquatic sediments may form a reservoir for TBT a number of years after inputs have ceased.

The important environmental issue regarding TBT is to ensure that the steady state concentration remains below levels where significant chronic or population effects can

occur, particularly in areas of important ecological and economic resources. Future monitoring programs should be directed towards this goal, keeping in focus the large spatial, temporal and vertical variability that has been documented. The sporadic nature of point source discharges must also be considered. To date, many of the monitoring efforts have focused primarily in source regions, particularly in marinas and areas of boating activity. More work is needed to evaluate accurately the scope of the TBT problem.

6. CONCLUSIONS.

1. The major pathway for the input of TBT to the aquatic environment is via boat servicing facilities such as boatyards, marinas and mooring sites. High water column concentrations in boating areas coincided with summer boat usage patterns implying that TBT was either being leached from boat hulls, four years after the implementation of the retail ban or that desorption of TBT from contaminated sediments as a result of dredging activities was releasing organotins back into the water column.

2. In general, TBT concentrations have declined with time indicating that the 1987 retail ban has been effective in reducing concentrations in the water column and the majority of surficial sediment samples analysed from UK East Coast river and estuarine systems.

3. It is probable that aquatic sediments act as both a sink and a potential source of TBT to the aquatic environment, despite a reduction in direct TBT inputs.

4. Tributyltin appeared to be the dominant butyltin form in contaminated sediments and large increases in butyltin concentrations from one season to the next were principally attributed to increases in TBT rather than its derivatives.

5. The partitioning and sorptive behaviour of butyltin compounds is dictated by a number of physico-chemical parameters in the aquatic environment. In freshwaters MBT, and to a lesser extent, TBT will be present mainly in the adsorbed phase whereas DBT will be present in both the dissolved and particulate phases. In estuarine waters MBT and TBT will almost exclusively adsorb onto particulates although 10-30% of TBT could be retained in solution. Dibutyltin in contrast is solubilized in estuarine waters. The order of adsorption to particulate matter for butyltins is MBT>TBT>DBT. However these adsorption characteristics probably differ between catchments and should be determined for individual river systems. Interstitial water partitioning studies indicate that TBT is predominantly associated with the particulate phase. Partition coefficients in sediments appeared to be related to total organic carbon loadings with the highest partition coefficients coinciding with the highest organic carbon content.

6. Tributyltin sorption is dependent on sediment type with finer grained clay and silt compounds been more receptive to TBT adsorption than coarser grained sand particles.

7 Degradation of organotin compounds within the sediment compartment is comparatively slow. Butyltin compounds are found in significant quantities at depths of up to 45 cm within the sediments of marina and boatyard complexes. This dates back to the introduction of TBT antifouling paints in the early 1960's.

8. *In-situ* half life values obtained for TBT degradation ranged from 0.9 to 5.2 years and compared favourably with laboratory based degradation studies. Dibutyltin half lives ranged from 1.5 - 3.0 years, whilst those of MBT ranged from 1.8 - 3.7 years. In anaerobic sediment the half life of TBT was not discernible and appears to be in the order of tens of years.

9. There appears to be no significant difference in TBT degradation rates between freshwater and estuarine sediments.

10. Biotic processes are the most important mechanisms for the decomposition of TBT in freshwater and estuarine sediments. Biodegradation of TBT appears to be inhibited if high concentrations of TBT accumulate in sediments

11. The occurrence of high TBT levels in aquatic sediments could potentially serve as a long term threat to aquatic habitats in the immediate vicinity of marina complexes. Sediment dredging operations should be kept to a minimum and executed carefully to minimise TBT desorption from sediments into overlying waters and disposal of TBT contaminated dredged sediment should be undertaken with care to minimise leaching of TBT back into the water column.

12. Given that TBT has been detected in surface waters and still exists in elevated concentrations in bottom sediments, further monitoring of specific sites may be desirable, particularly given the relatively slow degradation kinetics of TBT in anoxic sediments.

7. REFERENCES.

Alzieu, C. (1991). Environmental problems caused by the TBT in France: assessment, regulations, prospects. *Mar. Environ. Res.*, **32**, 65-89.

Alzieu, C., Sanjuan, J., Michel, P., Borel, M. and Dreno, J.P. (1989). Monitoring and assessment of butyltins in Atlantic coastal waters. *Mar. Pollut. Bull.*, **20**, 22-26.

Astruc, M., Lavigne, R., Pinel, R., Desauziers, V., Quevauviller, Ph. and Donard (1989). Speciation of trace tin in sediments of Arcachon Bay, In: *Metal Speciation, Seperation and Recovery*, J.W. Patterson and R. Passino (eds.) Lewis Publishers, Rome, **2**, pp. 263-281.

Bedding, N.D., McIntyre, A.E. and Lester, J.N. (1983). Organic contaminants in the aquatic environment, II: Behaviour and fate in the hydrological cycle. *Sci. Total Environ.*, **26**, 255-312.

Bennett, J. (1987). The physics of sediment transport, resuspension and deposition. *Hydrobiologia*, **149**, 5-12.

Blunden, S.J. and Chapman, A.H. (1982). A review of the degradation of organotin compounds in the environment and their determination in water. *Environ. Technol. Letts.*, **3**, 267-274.

Box, G.E.P., Hunter, W.G. and Hunter, J.S. (1978). *Statistics for Experiments;* John Wiley and Sons (eds.), New York, USA. pp. 111-114.

Bryan, G.W. and Gibbs, P.E. (1990). Impact of low concentrations of TBT on marine organisms: A review. In: *Metal Ecotoxicology: Concepts and Applications*, Newman M.C. and McIntosh A.W. (eds.) Ann Arbor, Boca Raton, Boston, pp. 323-361.

Bryan, G.W. and Langston, W.(1992). Bioavailability of heavy metals in the UK estuaries: a review. *Environ. Pollut.*, **84**, 267-285.

Clark, E.A., Sterritt, R.M. and Lester, J.N. (1988). Fate and distribution of TBT in the aquatic environment. *Environ. Sci. Technol.*, **22**, 600-605.

Cleary, J.J. (1991). Organotin in the marine surface microlayer and sub-surface waters of southwest England: relation to toxicity thresholds and the UK environmental quality standard. *Mar. Environ. Res.*, **32**, 86-95.

Cleary, J.J. and Stebbing, A.R.D. (1987). Organotin in the surface microlayer and subsurface waters of south west England. *Mar. Pollut. Bull.*, **18**, 238-245.

De Mora, S.J., King N.G. and Miller M.C. (1989). TBT and total tin in marine sediments. *Environ. Technol.*, **10**, 901-908.

Donard, O.F.X and Weber, J.H. (1985). Behaviour of methyltin compounds under simulated estuarine conditions. *Environ. Sci. Technol.*, **19**, 1104-1110.

Dooley, C.A. and Homer, V. (1983). Organotin compounds on the marine environment. Uptake and sorption behaviour. Naval Ocean Systems Technical Report No. 917. U.S. Navy, San Diego, CA.

Dowson P.H., Bubb J.M. and Lester, J.N. (1991a). Organotin distribution in waters and sediments of selected east coast UK estuaries. *Mar. Pollut. Bull.*, **24**, 492-498.

Dowson, P.H., Pershke D, Bubb J.M. and Lester, J.N. (1991b). Spatial distribution of organotin compounds in sediments of a lowland river catchment. *Environ. Pollut.*, **76**, 259-265.

Evans, R.B. and Wrigler, F.H. (1983). A test of lead ^{210} dating for the measurement of whole lake soft sediment accumulation. *Can. J. Fish. Aquat. Sci.*, **37**, 817-822.

Förstner, U. and Wittmann, F. (1979). *Metal Pollution in the Aquatic Environment.* Springer-Verlag, New York, NY. pp. 265-285.

Gilmour, C., Tuttle, J. and Means, J. (1985). Tin methylation in sulphide bearing sediments. In: *Marine and Estuarine Geochemistry,* Sigleo, A. and Mattori, A. (eds.), Lewis Pub. Inc., Chelsea, MI, p. 239.

Harris, J.R.W. and Cleary, J.J. (1987). Particle-water partitioning and organotin dispersal in an estuary. *Proceedings,* Oceans '87 Organotin Symposium, Vol. 4. IEEE Serve Center, Piscataway, NJ, pp. 1370-1374.

Knezovich, J.P. and Harrison, F.L. (1987). The bioavailability of sediment sorbed organic chemicals: a review. *Water, Air, Soil Pollut.*, **32**, 233-245.

Lee, G.F. (1975). Role of hydrous metal oxides in the transport of heavy metals in the environment. *Proc. Int. Conf.* 'Heavy Metals In The Aquatic Environment', Nashville, Tenessee, Krendell P.A. (eds.). Pergamon Press, Oxford. pp. 137-149.

Luoma, S.N. and Bryan, G.W. (1981). A statistical assessment of the form of trace metals in oxidised sediments employing chemical extractants. *Sci. Tot. Environ.*, **17**, 165-196.

MacIntyre, W.G. and deFur, P.O. (1985). The effect of hydrocarbon mixtures on adsorption of substituted Naphthalenes by clay and sediment from water. *Chemosphere,* **14**, 103-111.

Maguire, R.J. and R.J. Tkacz (1985). Degradation of the Tri-n-butyltin species in water and sediment from Toronto Harbour. *J. Agric. Food Chem.*, **33**, 947-953.

Maguire, R.J., Tkacz, J.R., Chau, Y.K., Bengeot, G.A. and Wong, P.T.S. (1986). Occurrence of organotin compounds in water and sediment in Canada. *Chemosphere,* **15**, 253-274.

Personal Communication (1992) from National Rivers Authority, Anglian Region, 11 March, 1992.

Quevauviller, P. and Donard, O.F.X. (1990). Variability of butyltin determination in water and sediment samples from European coastal environments. *Appl. Organometal. Chem.*, **4**, 353-367.

Randall, L. and Weber, J.H. (1986). Adsorptive behaviour of butyltin compounds under simulated estuarine conditions. *Sci. Total. Environ.*, **57**, 191-203.

Salomons, W. and Förstner, U. (1984). *Metals in the Hydrocycle.* Springer-Verlag, New York, NY. pp. 343-350.

Standing Committee of Analysts (1980). Methods for the determination of total, total dissolved and total suspended solids in waters and wastewaters. Her Majestys Stationary Office.

Stang, P.M. and Seligman, P.F. (1986). Distribution and fate of butyltin compounds in the sediment of San Diego Bay, CA. Proc. Organotin Symposium. Marine Technology Society. Washington DC. USA, IEEE, NJ, USA. pp. 1256-1261.

Stang, P.M. and Seligman, P.F. (1987). In situ adsorption and desorption of butyltin compounds from Pearl Harbour, Hawaii, sediment. *Proceedings,* Oceans '87 Organotin Symposium, Vol. 4. IEEE Service Center, Piscataway, NJ, pp. 1386-1391.

Stumm, W and Morgan, J.J. (1981). *Aquatic Chemistry.* John Wiley and Sons, USA. pp. 156.

Stewart, C.J and De Mora, S.J. (1989). A review of the degradation of tributyltin in the marine environment. *Environ. Technol.,* **11**, 565-570.

Thorne, L.T. and Nickless, G. (1981). The relation between heavy metals and particle size fractions within the Severn Estuary (UK) inter-tidal sediments. *Sci. Tot. Environ.,* 207-213.

Thompson, J.A.J., Sheffer, M.G., Pierce, R.C., Chau, Y.K., Cooney, J.J., Cullen, W.R. and Maguire, R.J. (1985). National Research Council Canada Publ. N.R.C.C. 22494, Ottawa, 1-284.

Tugrul, S., Balkas, T. and Goldberg, E. (1983). Methyltins in the marine environment. *Mar. Pollut. Bull.,* **14**, 297-303.

Unger, M.A., MacIntyre, W.G. and Huggett, R.J. (1988). Sorption behaviour of tributyltin on estuarine and freshwater Sediments. *Environ. Toxicol. Chem.,* **7**, 907-915.

Valkirs, A.O., Davidson, B., Fransham, R.L., Grovhough, J.G. and Seligman, P.F. (1991). Long-term monitoring of tributyltin in San Diego Bay, California. *Mar. Environ. Res.,* **32**, 111-126.

Waite, M.E., Waldock M.J., Thain, J.E., Smith, D.J. and Milton, S.M. (1991). Reductions in TBT concentrations in UK estuaries following legislation in 1986 and 1987. *Mar. Environ. Res.,* **32**, 89-111.

Waldock, M.J., Thain, J.E. and Waite, M.E. (1987a). The distribution and potential toxic effects of TBT in UK estuaries during 1986. *Appl. Organometal. Chem.,* **1**, 287-301.

Waldock, M.J., Waite, M.E. and Thain, J.E. (1987b). Changes in concentrations of organotins in UK rivers and estuaries following legislation in 1986. In: *Proceedings of the Organotin Symposium of the Oceans '87 Conference, Halifax, Canada, September 29-October 1, 1987, Vol. 4.* IEEE, Piscataway, NJ., pp. 1352-1356.

Waldock, M.J., Thain, J.E., Smith, D and Milton, S. (1990). The degradation of TBT in estuarine sediments. In: *3rd International Organotin Symposium Proceedings, Monaco, 17-20 April, 1990.* IAEA, pp. 176-177.

Water Research Centre. (1988). Proposed Envirionmental Quality Standards for List II subsances in Water (Organotins). TR 255, Zabel T.F., Seager, J and Oakley S.D. (eds.). Water Research Centre (WRC), Medmenham, UK.

8. APPENDICES.

Appendix 1. Organotin sediment data for the seasonal surveys conducted on Essex and Suffolk river estuaries

(a): Autumn 1990

Site	Sample Location	Organotin Concentration (ng g^{-1} as Sn) Total butyltin	TBT	DBT	MBT	TMT	DMT	MMT
	River Alde (Aldeburgh)							
1	Aldeburgh Yacht Club	136	49.3	69.0	17.2	1.41	3.50	<0.20
2	Slaugden Sailing club (250 m d/s)	30.0	<3	21.4	8.55	<0.20	2.12	<0.20
3	Slaugden (between Y.C and Quay)	78.5	36.1	31.9	10.5	<0.20	1.98	6.40
4	Martello Tower	5.37	<3.0	<1	5.37	<0.20	<0.20	<0.20
	River Deben (Woodbridge)							
5	Robertsons Boatyard	898	343	535	200	1.55	1.33	4.81
6	Tidemill Marina	33.5	<3.0	28.2	5.33	<0.20	<0.20	<0.20
7	Whisstocks Boatyard	108	61.2	10.0	37.2	<0.20	<0.20	<0.20
8	Deben Yacht Club	89.1	49.1	12.0	28.0	<0.20	<0.20	<0.20
9	Deben Yacht Club (250 m d/s)	-	-	-	-	-	-	-
10	Waldringfield Quay	-	-	-	-	-	-	-
	WaltonBackwaters (Titchmarsh)							
11	Titchmarsh Marina (slipway)	4050	2668	1458	324	2.52	<0.20	25.5
12	200 m seaward of marina	2567	1019	1272	276	2.12	<0.20	4.11
13	Below Marina office	3571	1785	1357	429	2.49	2.68	5.95
	River Blackwater (Tollesbury)							
14	Tollesbury Marina (north entrance)	2768	1528	904	336	<0.20	<0.20	<0.20
15	Slipway by cruising club	4782	3097	1182	503	5.88	2.71	4.75
16	Along sea wall (0.75 km)	1924	954	596	374	<0.20	<0.20	6.40
17	Along sea wall (1.5 km)	2468	1253	908	307	<0.20	2.57	4.71
18	Seaward of marina (100 m)	919	707	138	73.7	<0.20	<0.20	<0.20
19	Seaward of marina (200 m)	882	376	290	216	<0.20	<0.20	4.86
	River Roach (Paglesham)							
20	Downstream of slipway (400 m)	415	294	81.6	39.3	<0.20	2.20	1.54
21	Upstream of slipway (25 m)	180	128	50.8	1.32	<0.20	1.22	1.54
22	Upstream of slipway (400 m)	88.1	66.2	13.6	8.29	<0.20	<0.20	<0.20

(b): Winter 1991

Site	Sample Location	Organotin Concentration (ng g^{-1} as Sn) Total butyltin	TBT	DBT	MBT	TMT	DMT	MMT
	River Alde (Aldeburgh)							
1	Aldeburgh Yacht Club	50.0	20.1	20.6	9.33	<0.20	<0.20	<0.20
2	Slaugden Sailing club (250 m d/s)	<5.0	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
3	Slaugden (between Y.C and Quay)	27.8	<3.0	15.6	12.2	<0.20	<0.20	<0.20
4	Martello Tower	<5.0	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
	River Deben (Woodbridge)							
5	Robertsons Boatyard	275	203	49.2	22.4	<0.20	<0.20	3.38
6	Tidemill Marina	89.5	56.8	22.2	10.5	<0.20	<0.20	<0.20
7	Whisstocks Boatyard	366	260	76.0	30.2	<0.20	<0.20	<0.20
8	Deben Yacht Club	16.9	<3.0	16.9	<1.0	<0.20	<0.20	<0.20
9	Deben Yacht Club (250 m d/s)	32.5	<3.0	32.5	<1.0	<0.20	<0.20	<0.20
10	Waldringfield Quay	-	-	-	-	-	-	-
	WaltonBackwaters (Titchmarsh)							
11	Titchmarsh Marina (slipway)	1585	1272	187	126	<0.20	<0.20	<0.20
12	200 m seaward of marina	676	512	108	55.7	<0.20	1.91	3.32
13	Below Marina office	2084	1701	230	153	<0.20	<0.20	<0.20
	River Blackwater (Tollesbury)							
14	Tollesbury Marina (north entrance)		4207	1848	407	<0.20	<0.20	<0.20
15	Slipway by cruising club	438	409	28.6	<1.0	<0.20	<0.20	<0.20
16	Along sea wall (0.75 km)	321	243	78.4	<1.0	<0.20	<0.20	<0.20
17	Along sea wall (1.5 km)		119	70.9	24.3	<0.20	<0.20	<0.20
18	Seaward of marina (100 m)	2041	1628	297	116	<0.20	<0.20	<0.20
19	Seaward of marina (200 m)	2414	2056	255	103	<0.20	<0.20	<0.20
	River Roach (Paglesham)							
20	Downstream of slipway (400 m)	38.5	<3.0	27.7	10.8	<0.20	<0.20	<0.20
21	Upstream of slipway (25 m)	51.3	23.7	17.2	10.4	<0.20	<0.20	<0.20
22	Upstream of slipway (400 m)	30.1	<3.0	17.1	13.0	<0.20	<0.20	<0.20

(c): Spring 1991

Site	Sample Location	Organotin Concentration (ng g^{-1} as Sn) Total butyltin	TBT	DBT	MBT	TMT	DMT	MMT
	River Alde (Aldeburgh)							
1	Aldeburgh Yacht Club	44.7	22.2	6.58	15.9	<0.20	<0.20	<0.20
2	Slaugden Sailing club (250 m d/s)	584	466	65.5	52.6	<0.20	<0.20	<0.20
3	Slaugden (between Y.C and Quay)	201	106	57.6	37.4	<0.20	<0.20	3.38
4	Martello Tower	<5.0	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
	River Deben (Woodbridge)							
5	Robertsons Boatyard	891	653	120	118	1.95	6.05	<0.20
6	Tidemill Marina	747	647	55.1	44.5	2.73	2.76	4.02
7	Whisstocks Boatyard	375	293	31.6	50.2	<0.20	<0.20	<0.20
8	Deben Yacht Club	427	241	48.2	138	<0.20	14.0	3.48
9	Deben Yacht Club (250 m d/s)	104	<3.0	79.5	24.1	2.15	<0.20	<0.20
10	Waldringfield Quay	259	163	60.5	35.1	<0.20	<0.20	<0.20
	WaltonBackwaters (Titchmarsh)							
11	Titchmarsh Marina (slipway)	1921	1394	384	143	<0.20	<0.20	<0.20
12	200 m seaward of marina	1194	663	340	191	<0.20	<0.20	<0.20
13	Below Marina office	1311	747	342	222	5.59	<0.20	3.69
	River Blackwater (Tollesbury)							
14	Tollesbury Marina (north entrance)	2315	1135	412	221	5.15	<0.20	4.55
15	Slipway by cruising club	3586	2112	1163	311	17.1	25.1	3.32
16	Along sea wall (0.75 km)	61.9	20.2	37.9	3.82	3.82	<0.20	<0.20
17	Along sea wall (1.5 km)	419	350	59.5	9.94	4.21	<0.20	7.48
18	Seaward of marina (100 m)	278	218	45.6	14.8	<0.20	<0.20	4.12
19	Seaward of marina (200 m)	410	249	89.0	71.9	<0.20	<0.20	<0.20
	River Roach (Paglesham)							
20	Downstream of slipway (400 m)	38.2	22.9	15.3	<1.0	<0.20	<0.20	<0.20
21	Upstream of slipway (25 m)	180	89.9	30.0	22.6	<0.20	2.67	<0.20
22	Upstream of slipway (400 m)	62.4	18.8	24.7	18.9	<0.20	<0.20	<0.20

(d): Summer 1991

Site	Sample Location	Organotin Concentration (ng g^{-1} as Sn)						
		Total butyltin	TBT	DBT	MBT	TMT	DMT	MMT
	River Alde (Aldeburgh)							
1	Aldeburgh Yacht Club	3.6	<3.0	<1.0	3.60	<0.20	<0.20	<0.20
2	Slaugden Sailing club (250 m d/s)	57.6	<3.0	42.9	14.7	<0.20	<0.20	<0.20
3	Slaugden (between Y.C and Quay)	15.8	<3.0	15.8	<1.0	<0.20	6.71	<0.20
4	Martello Tower	<5.0	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
	River Deben (Woodbridge)							
5	Robertsons Boatyard	1881	1036	513	332	13.88	<0.20	<0.20
6	Tidemill Marina	214	123	52.3	39.1	<0.20	<0.20	<0.20
7	Whisstocks Boatyard	643	461	105	76.9	0.20	<0.20	<0.20
8	Deben Yacht Club	23.3	<3.0	<1.0	23.3	<0.20	0.20	<0.20
9	Deben Yacht Club (250 m d/s)	16.0	<3.0	16.0	<1.0	<0.20	<0.20	0.20
10	Waldringfield Quay	64.2	<3.0	51.6	126	<0.20	<0.20	<0.20
	WaltonBackwaters (Titchmarsh)							
11	Titchmarsh Marina (slipway)	1145	554	276	315	<0.20	<4.23	<0.20
12	200 m seaward of marina	729	317	183	229	<0.20	<0.20	<0.20
13	Below Marina office	1613	1047	306	260	5.59	<0.20	3.69
	River Blackwater (Tollesbury)							
14	Tollesbury Marina (north entrance)	909	591	202	116	3.91	<0.20	<0.20
15	Slipway by cruising club	328	208	48.8	71.0	<0.20	<0.20	<0.20
16	Along sea wall (0.75 km)	105	86.6	<1.0	18.6	<0.20	<0.20	<0.20
17	Along sea wall (1.5 km)	96.1	<3.0	43.9	52.2	<0.20	<0.20	<0.20
18	Seaward of marina (100 m)	42.1	<3.0	<1.0	42.1	<0.20	<0.20	<0.20
19	Seaward of marina (200 m)	263	228	55.4	29.2	<0.20	<0.20	<0.20
	River Roach (Paglesham)							
20	Downstream of slipway (400 m)	<5.0	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
21	Upstream of slipway (25 m)	78.2	67.0	<1.0	11.2	4.55	4.21	<0.20
22	Upstream of slipway (400 m)	50.5	<3.0	26.0	24.5	<0.20	<0.20	<0.20

(e): Autumn 1991

Site	Sample Location	Organotin Concentration (ng g^{-1} as Sn) Total butyltin	TBT	DBT	MBT	TMT	DMT	MMT
	River Alde (Aldeburgh)							
1	Aldeburgh Yacht Club	14.4	<3	<1	14.4	<0.20	<0.20	<0.20
2	Slaugden Sailing club (250 m d/s)	17.2	<3	<1	17.2	<0.20	<0.20	<0.20
3	Slaugden (between Y.C and Quay)	14.5	<3	14.5	<1	<0.20	<3.77	<0.20
4	Martello Tower	<5	<3	<1	<1	<0.20	<0.20	<0.20
	River Deben (Woodbridge)							
5	Robertsons Boatyard	521	202	264	550	<0.20	<0.20	<0.20
6	Tidemill Marina	95.3	35.2	44.8	15.3	5.13	<0.20	<0.20
7	Whisstocks Boatyard	18.2	96.8	59.0	26.1	4.61	<0.20	<0.20
8	Deben Yacht Club	60	37.6	<1	22.4	<0.20	<0.20	<0.20
9	Deben Yacht Club (250 m d/s)	<5	<3	<1	<1	<0.20	<0.20	<0.20
10	Waldringfield Quay	78.9	49.0	29.8	<1	<0.20	<0.20	<0.20
	WaltonBackwaters (Titchmarsh)							
11	Titchmarsh Marina (slipway)	743	386	178	204	5.18	<0.20	<0.20
12	200 m seaward of marina	929	499	256	174	<0.20	<0.20	<0.20
13	Below Marina office	1144	734	319	91.0	<0.20	<0.20	<0.20
	River Blackwater (Tollesbury)							
14	Tollesbury Marina (north entrance)	960	571	218	179	<0.20	<0.20	<0.20
15	Slipway by cruising club	1082	676	357	49.1	<0.20	<0.20	<0.20
16	Along sea wall (0.75 km)	12.5	<3	7.65	4.89	<0.20	<0.20	<0.20
17	Along sea wall (1.5 km)	<5	<3	<1	<1	<0.20	<0.20	<0.20
18	Seaward of marina (100 m)	82.2	<3	53.2	29.0	<0.20	<0.20	<0.20
19	Seaward of marina (200 m)	26.5	<3	<1	26.5	<0.20	<0.20	<0.20
	River Roach (Paglesham)							
20	Downstream of slipway (400 m)	28.7	<3	28.7	<1	2.51	<0.20	<0.20
21	Upstream of slipway (25 m)	59.5	40.3	<1	19.2	<0.20	<0.20	<0.20
22	Upstream of slipway (400 m)	34.2	<3	13.1	21.1	<0.20	<0.20	<0.20

(f): Spring 1992

Site	Sample Location	Organotin Concentration (ng g^{-1} as Sn) Total butyltin	TBT	DBT	MBT	TMT	DMT	MMT
	River Alde (Aldeburgh)							
1	Aldeburgh Yacht Club	<5	<3	<1	<1	<0.20	<0.20	<0.20
2	Slaugden Sailing club (250 m d/s)	<5	<3	<1	<1	<0.20	<0.20	<0.20
3	Slaugden (between Y.C and Quay)	<5	<3	<1	<1	<0.20	<0.20	<0.20
4	Martello Tower	<5	<3	<1	<1	<0.20	<0.20	<0.20
	River Deben (Woodbridge)							
5	Robertsons Boatyard	382	186	118	78	<0.20	<0.20	<0.20
6	Tidemill Marina	203	112	48	43	<0.20	<0.20	<0.20
7	Whisstocks Boatyard	97	45	28	24	2.68	<0.20	<0.20
8	Deben Yacht Club	<5	<3	<1	<1	<0.20	<0.20	<0.20
9	Deben Yacht Club (250 m d/s)	<5	<3	<1	<1	<0.20	<0.20	<0.20
10	Waldringfield Quay	360	24	12	<1	<0.20	<0.20	<0.20
	WaltonBackwaters (Titchmarsh)							
11	Titchmarsh Marina (slipway)	957	520	196	241	<0.20	<0.20	<0.20
12	200 m seaward of marina	251	88	102	61	<0.20	<0.20	<0.20
13	Below Marina office	887	512	216	159	3.34	<0.20	2.32
	River Blackwater (Tollesbury)							
14	Tollesbury Marina (north entrance)	1138	568	351	219	<0.20	<0.20	<0.20
15	Slipway by cruising club	768	416	212	140	<0.20	<0.20	<0.20
16	Along sea wall (0.75 km)	<5	<3	<1	<1	<0.20	<0.20	1.56
17	Along sea wall (1.5 km)	<5	<3	<1	<1	3.12	<0.20	<0.20
18	Seaward of marina (100 m)	161	68	79	14	<0.20	<0.20	<0.20
19	Seaward of marina (200 m)	53	22	14	17	<0.20	<0.20	<0.20
	River Roach (Paglesham)							
20	Downstream of slipway (400 m)	<5.0	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
21	Upstream of slipway (25 m)	63	35	16	12	<0.20	2.90	<0.20
22	Upstream of slipway (400 m)	<5.0	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20

Appendix 2: **Organotin water column data for the seasonal surveys conducted on Essex and Suffolk river estuaries (1990-1992)**

(a): Autumn 1990

Sample location	Organotin concentrations (ng l^{-1} as Sn) TBT	DBT	MBT	MMT	DMT	MMT
River Alde						
Aldeburgh Y.C	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Aldeburgh Y.C	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
River Deben						
Ramsholt Quay	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Robertsons Boatyard	18.7	10.6	3.2	<0.20	1.16	<0.20
Tidemill Marina	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Whisstocks Boatyard	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Woodbridge Y.C	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Waldringfield Quay	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Tollesbury Marina						
Tollesbury Marina Boating Slipway	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Tollesbury Marina Boat wash down area	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20

N.B: All values in bold exceed the Environmental Quality Standards set for fresh and saline waters (20 and 2 ng l^{-1} respectively).

(b): Winter 1990

Sample location	Organotin Concentrations (ng l^{-1} as Sn) TBT	DBT	MBT	MMT	DMT	TMT
River Alde						
Aldeburgh Y.C	<3.0	15.5	<1.0	<0.20	<0.20	<0.20
River Orwell						
Shotley Point	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Shotley Marina Basin	**44.0**	16.8	31.6	<0.20	1.61	<0.20
Levington Marina	**44.0**	5.90	4.20	<0.20	<0.20	<0.20
Pin Mill	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Orwell at Woolverstone	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Woolverstone Marina	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Ipswich Lock Gates	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Ipswich Wet Dock	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Bourne Creek	<3.0	14.0	<1.0	<0.20	<0.20	<0.20
Foxes Marina Basin	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
River Deben						
Tide Mill Marina	4.0	26.3	9.30	<0.20	<0.20	<0.20
Waldringfield Quay	<3.0	12.3	4.69	<0.20	<0.20	<0.20
Deben Y.C (250 m D/S)	<3.0	22.3	8.15	<0.20	<0.20	<0.20
Whisstocks Boatyard	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Robertsons Boatyard	**37.9**	<1.0	<1.0	<0.20	<0.20	<0.20
Titchmarsh Marina						
Slipway at entrance	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Below office	**50.5**	<1.0	<1.0	<0.20	<0.20	0.20
Tollesbury Marina						
Cruising club slipway	**47.4**	9.25	7.16	<0.20	<0.20	<0.20

(c): Spring 1991

Sample location	Organotin Concentrations (ng l^{-1} as Sn) TBT	DBT	MBT	MMT	DMT	TMT
River Alde						
Aldeburgh Y.C	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
River Orwell						
Shotley Point	<3.0	<1.0	8.30	<0.20	<0.20	<0.20
Shotley Marina Basin	<3.0	8.50	13.8	<0.20	<0.20	<0.20
Levington Marina	<3.0	13.0	10.4	<0.20	<0.20	<0.20
Pin Mill	<3.0	10.5	8.30	4.20	<0.20	<0.20
Orwell at Woolverstone	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Woolverstone Marina	<3.0	5.50	<1.0	<0.20	<0.20	<0.20
Ipswich Lock Gates	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Ipswich Wet Dock	<3.0	<1.0	<1.0	<0.20	<0.2	<0.20
Bourne Creek	<3.0	15.0	<1.0	<0.20	<0.20	<0.20
Foxes Marina Basin	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
River Deben						
Tide Mill Marina	<3.0	19.0	6.52	<0.20	<0.20	<0.20
Waldringfield Quay	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Deben Y.C (250 m D/S)	<3.0	20.5	<1.0	<0.20	<0.20	<0.20
Whisstocks Boatyard	**41.7**	10.3	3.95	<0.20	<0.20	<0.20
Robertsons Boatyard	**80.0**	14.8	<1.0	<0.20	<0.20	<0.20
Titchmarsh Marina						
slipway at entrance	3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Below office	**101**	11.0	<1.0	<0.20	<0.20	<0.20
Far end of marina	<3.0	31.5	8.50	<0.20	<0.20	<0.20
Cruising club slipway	**68.8**	16.4	<1.0	<0.20	<0.20	<0.20
Paglesham slipway	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20

(d): Summer 1991

Sample Location	Organotin Concentration (ng l^{-1} as Sn) TBT	DBT	MBT	TMT	DMT	MMT
River Alde						
Aldeburgh Y.C	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
River Orwell						
Shotley Point	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Shotley Marina Basin	**16.8**	<1.0	16.3	<0.20	<0.20	<0.20
Levington Marina	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Pin Mill	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Orwell at Woolverstone	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Woolverstone Marina	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Ipswich Lock Gates	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Ipswich Wet Dock	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Bourne Creek	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Foxes Marina Basin	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
River Deben						
Tide Mill Marina	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Waldringfield Quay	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Deben Y.C (250 m d/s)	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Whisstocks Boatyard	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Robertsons Boatyard	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Titchmarsh Marina						
Slipway at entrance	**13.7**	20.0	<1.0	<0.20	<0.20	<0.20
Below office	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Far end of marina	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Tollesbury Marina						
Cruising club slipway	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Paglesham slipway	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20

(e): Autumn 1991

Sample Location	Organotin Concentration (ng l^{-1} as Sn) TBT	DBT	MBT	TMT	DMT	MMT
River Aide						
Aldeburgh Y.C	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
River Orwell						
Shotley Point	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Shotley Marina Basin	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Levington Marina	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Pin Mill	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Orwell at Woolverstone	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Woolverstone Marina	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Ipswich Lock Gates	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Ipswich Wet Dock	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Bourne Creek	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Foxes Marina Basin	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
River Deben						
Tide Mill Marina	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Waldringfield Quay	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Deben Y.C (250 m d/s)	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Whisstocks Boatyard	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Robertsons Boatyard	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Titchmarsh Marina						
Slipway at entrance	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Below office	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Far end of marina	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Tollesbury Marina						
Cruising club slipway	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Paglesham slipway	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20

(f): Spring 1992

Sample location	Organotin Concentrations (ng l^{-1} as Sn) TBT	DBT	MBT	MMT	DMT	TMT
River Alde						
Aldeburgh Y.C	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
River Orwell						
Shotley Point	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Shotley Marina Basin	8.50	13.8	<0.20	<0.20	<0.20	<0.20
Levington Marina	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Pin Mill	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Orwell at Woolverstone	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Woolverstone Marina	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Ipswich Lock Gates	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Ipswich Wet Dock	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Bourne Creek	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Foxes Marina Basin	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
River Deben						
Tide Mill Marina	<3.0	19.0	6.52	<0.20	<0.20	<0.20
Waldringfield Quay	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Deben Y.C (250 m D/S)	<3.0	20.5	<1.0	<0.20	<0.20	<0.20
Wistocks Boatyard	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Robertsons Boatyard	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Titchmarsh Marina						
slipway at entrance	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Below office	11.0	<1.0	<0.20	<0.20	<0.20	<0.20
Far end of marina	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
Tollesbury Marina						
Cruising club slipway	<1.0	<1.0	<0.20	<0.20	<0.20	<0.20
Paglesham slipway	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20

Appendix 3: **Sediment core data for TBT hot spots (1990-1992)**

(a): **Variation of organotin concentrations with depth in sediment cores at Titchmarsh Marina**

Depth (cm)	Total Butyltin	Butyltin concentration (ng g^{-1} as Sn) corrected for recovery					
		TBT	DBT	MBT	TMT	DMT	MMT
0-2	5951	3697	1862	392	<0.20	1.12	1.20
2-4	4721	2928	1494	299	<0.20	<0.20	<0.20
4-6	5490	3887	1381	222	<0.20	<0.20	<0.20
6-8	4139	3407	518	214	16.6	<0.20	48.2
8-10	5681	3732	1735	214	<0.20	<0.20	<0.20
10-12	3160	1197	1629	334	<0.20	<0.20	<0.20
12-14	3401	2447	644	310	<0.20	<0.20	<0.20
14-16	3030	1796	772	462	3.52	<0.20	<0.20
16-18	2220	1151	751	318	<0.20	<0.20	<0.20
18-20	2640	1331	849	460	2.98	1.54	4.40
20-25	2004	896	640	468	2.88	5.23	7.49
25-30	1594	866	361	367	3.47	2.45	26.0
30-35	1206	579	371	256	3.47	2.45	4.41
35-40	1338	616	544	178	<0.20	<0.20	<0.20
40-45	571	229	188	154	1.07	1.06	2.58

Sediment characteristics at Titchmarsh Marina

Depth (cm)	Wet wt (g)	% Total solids	%Volatile solids
0-2	10.22	52.5	5.9
2-4	12.38	51.1	5.1
4-6	10.00	50.4	5.2
6-8	11.51	44.4	5.1
8-10	10.52	51.2	5.3
10-12	10.68	44.2	5.8
12-14	10.91	45.8	5.2
14-16	10.79	48.6	5.1
16-18	10.34	49.9	5.4
18-20	10.64	49.5	5.3
20-25	12.56	46.5	5.2
25-30	10.82	45.2	5.6
30-35	12.80	44.8	5.5
35-40	12.08	41.8	5.1
40-45	10.16	35.2	5.0

(b): Variation of organotin concentrations with depth in sediment cores at Tollesbury Marina

Depth (cm)	Total Butyltin	Butyltin concentration (ng g^{-1} as Sn) corrected for recovery					
		TBT	DBT	MBT	TMT	DMT	MMT
0-2	4906	3350	1332	224	1.16	<0.20	2.54
2-4	4525	3097	1194	234	<0.20	<0.20	<0.20
6-8	3857	2372	1197	288	0.96	1.46	4.46
8-10	3884	2449	1086	349	1.23	2.20	<0.20
10-15	4119	2469	1263	387	<0.20	2.20	4.92
15-20	3502	2193	1048	261	<0.20	<0.20	2.95
20-25	2764	1759	777	228	<0.20	<0.20	<0.20
25-30	2420	1454	783	179	<0.20	1.46	2.00
30-35	2730	1659	853	218	1.19	1.46	2.77
35-40	2662	1432	944	286	<0.20	<0.20	<0.20
40-45	2307	1238	849	220	1.25	1.05	5.54
45-50	2670	1142	958	270	<0.20	1.05	<0.20
50-55	2171	1194	760	217	<0.20	<0.20	<0.20
55-60	1216	1115	823	278	<0.20	1.06	1.65

Sediment characteristics at Tollesbury Marina

Depth (cm)	Wet wt (g)	% Total solids	%Volatile solids
0-2	10.46	47.3	4.1
2-4	13.44	54.3	4.1
4-6	11.11	54.6	4.2
6-8	12.19	55.5	3.9
8-10	12.82	52.3	4.1
10-15	10.29	51.6	4.2
15-20	11.01	53.1	4.4
20-25	11.10	54.2	4.1
25-30	11.12	58.2	5.5
30-35	10.90	53.0	5.1
35-40	10.06	53.1	4.8
40-45	10.50	54.8	4.8
45-50	10.08	54.8	4.8
50-55	10.99	52.9	5.1
55-60	11.20	49.0	5.1

(c). **Variation of organotin concentrations with depth in sediment cores at Tollesbury Marina B**

Depth (cm)	Total Butyltin	Butyltin concentration (ng g^{-1} as Sn) corrected for recovery TBT	DBT	MBT	TMT	DMT	MMT
0-4	1912	1019	547	346	5.56	3.81	<0.20
4-8	1843	1031	440	372	<0.20	2.75	1.69
8-12	2499	1394	864	241	<0.20	3.82	9.38
12-16	1906	1103	561	242	<0.20	<0.20	<0.20
16-20	1870	923	642	305	<0.20	<0.20	4.42
20-24	1847	991	638	218	<0.20	8.12	3.18
24-28	1691	860	436	395	<0.20	<0.20	4.02
28-32	1749	987	487	275	<0.20	2.88	6.25
32-36	1016	582	242	192	1.55	<0.20	<0.20
36-40	932	454	271	207	<0.20	<0.20	<0.20
40-44	534	225	195	114	<0.20	<0.20	<0.20
44-48	172	84.6	57.5	29.7	<0.20	<0.20	<0.20
48-52	87.2	<3.0	57.5	29.7	<0.20	<0.20	<0.20
52-56	<5.0	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
56-60	<5.0	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20

Sediment characteristics for Tollesbury Marina B

Depth (cm)	Wet wt (g)	% Total solids	%Volatile solids
0-4	10.38	43.9	7.6
4-8	10.45	48.6	18.9
8-12	10.42	46.2	9.4
12-16	10.32	54.6	4.7
16-20	10.72	52.2	5.4
20-24	10.65	54.3	6.3
24-28	10.09	54.8	10.0
28-32	11.35	53.1	9.7
32-36	10.40	58.2	4.8
36-40	10.60	56.2	4.1
40-44	10.65	50.2	11.0
44-48	10.76	59.1	7.1
48-52	10.68	51.6	12.6
52-56	10.25	50.4	8.8
56-60	10.72	48.4	12.0

(d): **Variation of organotin concentrations with depth in sediment cores at Paglesham**

Depth (cm)	Total Butyltin	Butyltin concentration (ng g^{-1} as Sn) corrected for recovery TBT	DBT	MBT	TMT	DMT	MMT
0-2	842	615	143	84.1	<0.20	<0.20	3.32
2-4	572	400	104	68.3	<0.20	1.28	1.69
4-6	957	743	137	76.7	1.13	2.33	<0.20
6-8	816	572	156	88.2	<0.20	1.71	5.55
8-10	900	649	160	90.9	<0.20	<0.20	<0.20
12-14	587	404	112	71.1	2.83	<0.20	<0.20
14-16	628	409	134	84.6	1.44	6.41	4.32
16-18	507	306	114	86.9	<0.20	<0.20	6.45
18-20	538	337	132	69.2	<0.20	<0.20	1.55
20-22	448	234	121	92.6	<0.20	<0.20	<0.20
22-25	334	169	86.9	78.0	<0.20	2.71	<0.20
25-30	256	109	94.4	53.0	<0.20	<0.20	<0.20
30-35	134	57.9	50.1	26.2	<0.20	0.98	<0.20
35-40	98.9	44.7	36.2	18.0	<0.20	<0.20	<0.20

Sediment characteristics at Paglesham core.

Depth (cm)	Wet wt (g)	% Total solids	%Volatile solids
0-2	10.66	57.5	8.9
2-4	10.61	61.0	5.8
4-6	11.41	66.7	6.1
6-8	10.51	65.8	6.7
8-10	10.41	68.7	6.0
10-12	10.29	68.6	5.1
12-14	11.13	67.9	7.7
14-16	10.82	68.3	4.5
16-18	10.40	70.4	5.5
18-20	10.00	70.7	6.7
20-22	10.35	68.0	4.4
22-25	10.79	67.6	5.8
25-30	10.00	70.4	5.9
30-35	10.69	71.2	7.5
35-40	10.52	68.7	8.5

(e): **Variation of organotin concentrations with depth in sediment cores at Waldringfield Quay**

Depth (cm)	Total Butyltin	Butyltin concentration (ng g^{-1} as Sn) corrected for recovery: TBT	DBT	MBT	TMT	DMT	MMT
0-2	217	136	56.4	24.7	<0.20	<0.20	<0.20
2-4	375	257	82.3	35.5	1.41	<0.20	3.69
4-6	-	-	-	-	-	-	-
6-8	600	434	116	50.1	2.93	1.23	1.40
8-10	420	335	54.5	30.7	1.56	3.57	4.91
10-12	390	275	89.5	25.7	<0.20	<0.20	1.63
12-14	372	278	69.2	24.9	<0.20	<0.20	<0.20
14-16	-	-	-	-	-	-	-
16-18	385	268	94.4	22.8	2.89	1.41	<0.20
18-20	267	171	63.9	31.6	<0.20	<0.20	1.63
20-22	249	144	66.8	37.8	<0.20	2.63	6.55
22-24	177	96.8	45.6	34.6	1.48	<0.20	<0.20
24-26	90.1	41.5	30.3	18.3	<0.20	2.33	<0.20
26-28	82.9	48.0	20.3	14.6	<0.20	2.63	2.37

Note: The sediment at 4-6 cm and 14-16 cm was not suitable for analysis due to the presence of large stones and shell cases.

Sediment Characteristics at Waldringfield Quay.

Depth (cm)	Wet wt (g)	% Total solids	%Volatile solids
0-2	10.63	52.9	10.8
2-4	10.25	41.3	12.7
4-6	10.72	53.9	8.7
6-8	11.01	28.6	7.6
8-10	10.52	41.6	11.9
10-12	10.32	46.1	10.4
12-14	10.79	52.1	9.6
14-16	10.52	47.1	11.6
16-18	10.23	44.0	15.8
18-20	10.19	45.4	10.7
20-22	10.39	38.2	7.4
22-24	10.68	42.6	8.6
24-26	10.92	45.5	14.1
26-28	10.70	52.9	4.78

(f): **Variation of organotin concentrations with depth in sediment cores at Robertsons Boatyard**

Depth (cm)	Total Butyltin	Butyltin concentration (ng g^{-1} as Sn) corrected for recovery					
		TBT	DBT	MBT	TMT	DMT	MMT
0-3	283	179	65.5	38.9	<0.20	<0.20	<0.20
3-6	459	360	66.8	32.2	<0.20	<0.20	1.72
6-9	304	241	47.5	15.7	<0.20	2.61	2.94
9-12	461	337	82.1	42.1	2.80	<0.20	3.12
12-15	641	512	82.2	46.4	<0.20	<0.20	<0.20
15-20	402	276	82.7	43.6	<0.20	1.91	<0.20
20-25	250	193	34.4	22.2	2.05	2.51	<0.20
25-30	208	191	<1.0	16.8	<0.20	4.16	4.48
30-35	86.2	51.9	25.1	9.16	<0.20	1.52	<0.20
35-40	94.8	60.3	24.0	10.8	<0.20	<0.20	<0.20
40-45	19.5	<3.0	19.5	<1.0	<0.20	<0.20	3.34
45-50	<5	<3.0	<1.0	<1.0	<0.20	<0.20	1.63
55-60	<5	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20
60-64	<5	<3.0	<1.0	<1.0	<0.20	<0.20	<0.20

Sediment characteristics at Robertsons Boatyard.

Depth (cm)	Wet wt (g)	% Total solids	%Volatile solids
0-3	10.62	43.32	7.97
3-6	10.91	46.43	5.70
6-9	10.22	52.24	8.70
9-12	10.36	42.16	14.7
12-15	10.17	37.91	13.6
15-20	10.52	42.42	12.7
20-25	10.69	50.83	21.3
25-30	10.49	43.30	17.7
30-35	10.80	49.85	10.5
35-40	10.19	48.38	8.9
40-45	11.20	44.03	8.07
45-50	10.70	41.88	8.99
50-55	10.16	45.19	12.0
55-60	10.42	47.89	10.20
60-64	10.32	47.12	8.2

(g): **Variation of organotin concentrations with depth at Oulton Broad**

Depth (m)	Total Butyltin	Butyltin concentration (ng g^{-1} as Sn) corrected for recovery TBT	DBT	MBT	TMT	DMT	MMT
0-2	268	165	69.2	32.8	<0.20	4.52	4.00
2-4	260	176	47.4	37.1	2.61	1.23	1.34
4-6	511	319	141	50.9	2.78	2.24	6.52
6-8	553	328	148	77.4	2.96	1.29	<0.20
8-10	345	235	68.7	41.7	1.21	2.46	1.40
10-12	279	190	60.6	28.5	<0.20	<0.20	<0.20
12-14	269	178	55.1	35.8	2.21	<0.20	1.78
14-18	179	144	34.6	<1.0	<0.20	2.51	<0.20
18-22	174	131	28.1	15.1	<0.20	<0.20	1.50

Sediment characteristics at Oulton Broad

Depth (cm)	Wet wt (g)	% Total solids	% Volatile solids
0-2	10.61	52.33	9.11
2-4	11.06	37.73	14.1
4-6	10.73	32.24	16.3
6-8	10.48	28.28	15.9
8-10	10.59	42.90	8.72
10-12	11.26	44.96	12.2
12-14	11.10	41.64	11.1
14-16	10.20	38.05	17.5
16-18	10.91	50.20	9.72
18-22	10.55	50.91	13.5

(h): Variation of organotin concentrations with depth at Ipswich Docks

Depth (cm)	Total Butyltin	Butyltin concentration (ng g^{-1} as Sn) corrected for recovery TBT	DBT	MBT	TMT	DMT	MMT
0-2	167	80.6	59.1	27.1	<0.20	<0.20	<0.20
2-4	211	129	54.5	27.1	<0.20	<0.20	<0.20
4-6	178	115	31.4	31.4	<0.20	2.63	6.40
6-8	304	162	82.7	59.6	<0.20	2.33	<0.20
8-10	130	66.5	45.3	17.9	<0.20	1.34	3.32
10-12	406	200	126	79.7	<0.20	<0.20	<0.20
12-14	196	107	62.3	26.8	2.88	2.00	<0.20
14-16	174	71.7	69.6	32.1	<0.20	<0.20	2.92

Sediment characteristics at Ipswich Wet Docks.

Depth (cm)	Wet wt (g)	% Total solids	%Volatile solids
0-2	10.61	65.4	7.70
2-4	10.42	56.6	8.30
4-6	10.91	53.0	12.2
6-8	11.01	59.3	9.70
8-10	11.12	55.7	9.91
10-12	10.29	32.1	20.2
12-14	10.11	38.8	6.50
14-16	10.77	38.8	9.54

Appendix 4: Butyltin concentrations for laboratory based tank degradation experiments

(a): Initial analysis of sediemnts (Time 0)

		Organotin conc. (ng g^{-1} as Sn)			
Tank	Replicate	Total	TBT	DBT	MBT
R.1	A	808	411	185	212
	B	820	386	217	217
	C	755	379	173	183
	mean		*392*	*192*	*204*
	S.D		*±17*	*±23*	*±18*
	%S.D		*±4*	*±12*	*±9*
R.2	A	1215	830	194	191
	B	1090	743	161	186
	C	1090	798	144	148
	mean		*790*	*166*	*175*
	S.D		*±44*	*±25*	*±24*
	%S.D		*±6*	*±15*	*±13*
T.1	A	1269	699	329	241
	B	1275	774	246	255
	C	1114	628	262	224
	mean		*700*	*279*	*240*
	S.D		*±73*	*±44*	*±16*
	%S.D		*±10*	*±16*	*±7*
T.2	A	1632	1061	290	281
	B	1670	1111	316	243
	C	1687	1192	272	223
	mean		*1121*	*293*	*249*
	S.D		*±66*	*±22*	*±29*
	%S.D		*±6*	*±8*	*±12*

(b): October 1991

Tank	Depth (cm)	Organotin concentration (ng g^{-1} as Sn) Total butyltin	TBT	DBT	MBT	% VS	Redox	pH
R.1	0-5	841	449	209	183	11.9	-	-
	5-15	656	361	171	124	17.1	-	-
	15-25	611	362	129	120	12.3	-	-
	25-35	740	384	170	186	11.8	-	-
	35-45	715	425	180	110	12.5	-	-
R.2	0-5	1283	926	191	166	13.4	-	-
	5-15	985	721	162	102	5.6	-	-
	15-25	1036	770	156	110	10.4	-	-
	25-35	1019	706	174	139	11.1	-	-
	35-45	1098	760	211	127	12.3	-	-
T.1	0-5	1354	711	304	339	14.3	-	-
	5-15	1155	650	253	252	10.2	-	-
	15-25	1270	699	255	316	11.8	-	-
	25-35	1211	716	235	260	9.5	-	-
	35-45	1236	723	254	259	11.9	-	-
T.2	0-5	1850	1290	309	251	14.9	-	-
	5-15	1470	1020	233	217	14.5	-	-
	15-25	1809	1242	322	245	6.6	-	-
	25-35	1520	1096	226	198	7.4	-	-
	35-45	1527	1019	285	223	10.3	-	-

(c): **November 1991**

Tank	Depth (cm)	Organotin concentration (ng g^{-1} as Sn) Total butyltin	TBT	DBT	MBT	% VS	Redox	pH
R.1	0-5	793	405	182	206	15.7	61	7.08
	5-15	809	414	197	198	18.5	-190	7.05
	15-25	659	370	140	149	10.2	-220	7.02
	25-35	624	354	139	131	11.4	-245	7.00
	35-45	735	406	168	161	11.8	-251	7.03
	water	67	32	17	18	-	-	-
R.2	0-5	1229	886	197	146	18.3	75	7.06
	5-15	1123	789	179	155	11.5	-165	7.07
	15-25	1133	796	173	164	12.3	-221	7.04
	25-35	1053	710	186	155	9.0	-241	7.04
	35-45	1109	756	190	163	9.8	-248	7.02
	water	57	19	23	15	-	-	-
Controls	R.1.A	728	400	175	153	-	-	-
	R.1.B	719	381	181	157	-	-	-
	R.1.C	751	394	189	168	-	-	-
T.1	0-5	1276	711	279	286	19.6	92	7.13
	5-15	1308	741	282	285	3.4	-90	7.16
	15-25	1151	638	268	245	10.8	-165	7.15
	25-35	1218	750	234	234	8.3	-205	7.13
	35-45	1182	706	248	228	8.0	-241	7.12
	water	39	19	23	15	-	-	-
T.2	0-5	1724	1165	287	272	20.1	101	7.20
	5-15	1583	1059	286	238	13.6	-62	7.16
	15-25	1574	1092	262	220	17.2	-148	7.16
	25-35	1706	1171	273	262	9.4	-187	7.14
	35-45	1585	1006	257	322	7.8	-230	7.11
	water	73	26	28	19	-	-	-
Controls	T.1.A	1179	676	240	263	-	-	-
	T.1.B	1212	712	254	246	-	-	-
	T.1.C	1193	696	257	240	-	-	-

(d): December 1991

Tank	Depth (cm)	Organotin concentration (ng g^{-1} as Sn) Total butyltin	TBT	DBT	MBT	% VS	Redox	pH
R.1	0-5	772	397	190	185	4.8	106	7.24
	5-15	724	389	184	151	4.9	-151	7.15
	15-25	724	402	166	156	4.0	-206	7.10
	25-35	673	379	140	154	3.89	-230	7.12
	35-45	728	388	186	154	4.3	-254	7.10
	water	55	14	19	22	-	-	-
R.2	0-5	1172	850	176	146	24.1	89	7.09
	5-15	1231	896	188	147	10.8	-157	7.12
	15-25	1075	760	168	147	5.3	-206	7.06
	25-35	1050	727	159	164	5.6	-222	7.06
	35-45	1148	825	168	155	9.8	-239	7.05
	water	62	19	29	14	-	-	-
Controls	R.1.A	753	391	194	168	-	-	-
	R.1.B	766	418	201	147	-	-	-
	R.1.C	727	402	186	139	-	-	-
T.1	0-5	1254	759	266	229	25.4	96	7.22
	5-15	1223	696	294	233	10.9	-75	7.19
	15-25	1247	720	259	268	8.0	-155	7.21
	25-35	1207	716	267	224	7.3	-216	7.12
	35-45	1175	708	223	244	5.8	-248	7.16
	water	61	23	19	19	-	-	-
T.2	0-5	1685	1151	285	249	15.2	110	7.33
	5-15	1594	1112	257	225	4.8	-75	7.19
	15-25	1589	1090	274	260	6.8	-157	7.18
	25-35	1737	1150	317	270	8.1	-196	7.16
	35-45	1586	1066	279	241	11.4	-239	7.21
	water	46	24	14	8	-	-	-
Controls	T.1.A	1221	716	259	246	-	-	-
	T.1.B	1179	698	249	232	-	-	-
	T.1.C	1222	725	260	237	-	-	-

(e): **January 1992**

Tank	Depth (cm)	Organotin concentration (ng g^{-1} as Sn) Total butyltin	TBT	DBT	MBT	% VS	Redox	pH
R.1	0-5	747	359	186	202	11.5	111	7.11
	5-15	747	396	170	181	9.8	-121	7.13
	15-25	698	381	149	168	14.9	-189	7.12
	25-35	731	391	168	172	10.5	-202	7.13
	35-45	754	411	171	172	9.4	-229	7.11
	water	30	0	14	16	-	-	-
R.2	0-5	1201	842	188	171	19.8	111	7.12
	5-15	1102	742	192	168	12.1	-138	7.15
	15-25	1141	790	171	180	9.1	-195	7.11
	25-35	1039	691	179	149	7.0	-217	7.09
	35-45	1129	780	174	175	11.0	-229	7.09
	water	40	13	11	16	-	-	-
Controls	A	755	402	201	152	-	-	-
	B	739	391	186	162	-	-	-
	C	746	397	190	158	-	-	-
T.1	0-5	1244	692	281	271	16.3	117	7.18
	5-15	1191	642	268	281	8.9	-65	7.18
	15-25	1236	691	272	273	17.4	-129	7.22
	25-35	1282	731	280	271	14.5	-189	7.19
	35-45	1218	698	259	261	10.0	-222	7.18
	water	27	0	17	10	-	-	-
T.2	0-5	1600	1129	302	270	29.1	147	7.21
	5-15	1619	1086	258	265	13.2	-53	7.22
	15-25	1642	1110	281	251	8.1	-138	7.19
	25-35	1638	1119	278	241	6.1	-172	7.20
	35-45	1659	1106	292	261	8.9	-221	7.2
	water	35	15	12	8	-	-	-
Controls	A	1167	682	256	229	-	-	-
	B	1203	700	264	239	-	-	-
	C	1206	710	250	246	-	-	

(f): February 1992

Tank	Depth (cm)	Organotin concentration (ng g^{-1} as Sn) Total butyltin	TBT	DBT	MBT	% VS	Redox	pH
R.1	0-5	752	368	174	210	15.7	99	7.08
	5-15	775	415	188	172	18.5	-129	7.05
	15-25	770	384	143	152	10.2	-187	7.02
	25-35	704	384	159	161	11.3	-221	7.00
	35-45	725	398	182	145	11.8	-229	7.03
	water	92	35	36	21	-	-	-
R.2	0-5	1096	806	171	186	18.3	86	7.06
	5-15	1093	769	176	148	11.6	-97	7.07
	15-25	1072	741	169	162	12.3	-192	7.04
	25-35	1049	715	162	172	9.0	-221	7.04
	35-45	1062	742	162	158	9.8	-240	7.02
	water	68	18	31	19	-	-	-
Controls	A	750	413	182	155	-	-	-
	B	745	387	191	167	-	-	-
	C	723	391	183	148	-	-	-
T.1	0-5	1168	623	290	289	19.6	135	7.13
	5-15	1228	669	286	270	3.4	-96	7.16
	15-25	1205	686	260	259	10.8	-164	7.15
	25-35	1272	721	271	280	8.3	-196	7.13
	35-45	1260	728	266	266	8.1	-209	7.12
	water	74	25	30	19	-	-	-
T.2	0-5	1597	1172	290	298	20.1	109	7.21
	5-15	1609	1115	246	248	13.7	-85	7.16
	15-25	1657	1129	269	259	17.2	-148	7.16
	25-35	1673	1131	291	251	9.4	-201	7.14
	35-45	1573	1072	269	232	7.8	-230	7.11
	water	83	26	33	24	-	-	-
Controls	A	1188	696	261	231	-	-	-
	B	1208	709	254	245	-	-	-
	C	1202	713	248	241	-	-	-

(g): March 1992

Tank	Depth (cm)	Organotin concentration (ng g^{-1} as Sn) Total butyltin	TBT	DBT	MBT	% VS	Redox	pH
R.1	0-5	714	321	187	206	11.9	89	7.20
	5-15	722	392	161	169	35.3	-29	7.10
	15-25	713	386	156	171	9.6	-189	7.18
	25-35	730	401	162	167	14.3	-222	7.15
	35-45	705	392	157	156	10.8	-238	7.16
	water	70	22	33	15	-	-	-
R.2	0-5	1097	745	179	173	15.4	111	7.19
	5-15	1065	758	161	146	15.2	-68	7.15
	15-25	1069	754	158	157	8.7	-191	7.14
	25-35	1089	769	171	149	8.6	-211	7.15
	35-45	1059	738	160	161	12.7	-221	7.16
	water	86	28	36	22	-	-	-
Controls	A	729	406	169	154	-	-	-
	B	713	386	179	148	-	-	-
	C	734	395	177	162	-	-	-
T.1	0-5	1195	603	298	294	6.1	65	7.10
	5-15	1206	682	265	259	3.0	-121	7.11
	15-25	1173	674	251	248	18.7	-198	7.09
	25-35	1194	662	268	264	3.5	-211	7.12
	35-45	1204	687	257	260	3.0	-209	7.11
	water	86	28	36	22	-	-	-
T.2	0-5	1692	1120	311	261	19.6	77	7.13
	5-15	1612	1110	268	234	8.3	-45	7.13
	15-25	1654	1138	275	241	10.8	-154	7.15
	25-35	1646	1131	285	230	3.4	-188	7.16
	35-45	1582	1098	271	213	8.1	-205	7.14
	water	85	35	28	22	-	-	-
Controls	A	1186	686	259	241	-	-	-
	B	1193	679	268	246	-	-	-
	C	1200	705	257	238	-	-	-

(h): April 1992

Tank	Depth (cm)	Organotin concentration (ng g^{-1} as Sn) Total butyltin	TBT	DBT	MBT	% VS	Redox	pH
R.1	0-5	712	309	182	221	9.0	141	7.08
	5-15	730	391	158	181	15.2	-125	7.10
	15-25	738	396	163	179	10.3	-188	7.09
	25-35	702	372	167	163	14.2	-205	7.10
	35-45	715	385	159	171	5.2	-221	7.10
	water	80	28	33	19	-	-	-
R.2	0-5	1157	783	186	188	5.4	123	7.20
	5-15	1050	736	166	148	14.4	-80	7.16
	15-25	1088	761	171	156	12.2	-201	7.16
	25-35	1067	752	164	151	6.3	-230	7.18
	35-45	1092	753	175	164	4.2	-224	7.16
	water	97	26	52	19	-	-	-
Controls	A	750	399	189	162	-	-	-
	B	738	411	176	151	-	-	-
	C	752	402	182	168	-	-	-
T.1	0-5	1171	592	298	281	7.4	146	7.30
	5-15	1198	671	267	260	8.4	-86	7.30
	15-25	1192	663	274	255	11.3	-178	7.30
	25-35	1238	711	259	268	3.7	-230	7.28
	35-45	1194	682	263	249	8.4	-246	7.28
	water	51	17	21	13	-	-	-
T.2	0-5	1702	1098	308	296	13.3	161	7.18
	5-15	1630	1120	259	251	11.2	-80	7.15
	15-25	1645	1126	271	248	15.4	-211	7.18
	25-35	1630	1131	267	232	8.7	-230	7.18
	35-45	1650	1138	271	241	8.2	-230	7.16
	water	71	29	20	22	-	-	-
Controls	A	1210	705	254	251	-	-	-
	B	1213	711	261	241	-	-	-
	C	1202	689	266	247	-	-	-

(i): May 1992

Tank	Depth (cm)	Organotin concentration (ng g^{-1} as Sn) Total butyltin	TBT	DBT	MBT	%VS	Redox	pH
R.1	0-5	719	296	191	232	11.5	89	7.11
	5-15	726	378	162	186	12.6	-123	7.12
	15-25	691	361	147	183	5.6	-189	7.10
	25-35	714	351	172	191	14.2	-216	7.09
	35-45	755	410	181	164	8.9	-226	7.08
	water	138	46	61	31	-	-	-
R.2	0-5	1123	736	196	191	4.8	161	7.20
	5-15	1092	746	184	162	8.9	-64	7.11
	15-25	1065	731	163	171	8.6	-191	7.16
	25-35	1075	758	149	168	4.8	-218	7.09
	35-45	1088	748	169	171	15.6	-232	7.12
	water	109	32	61	16	-	-	-
Controls	A	735	375	178	182	-	-	-
	B	710	349	165	196	-	-	-
	C	733	377	181	175	-	-	-
T.1	0-5	1103	511	295	297	11.6	121	7.20
	5-15	1174	658	271	245	8.4	-101	7.18
	15-25	1170	673	261	236	5.6	-191	7.16
	25-35	1222	696	264	262	8.9	-232	7.16
	35-45	1199	686	242	271	14.3	-241	7.17
	water	97	35	41	21	-	-	-
T.2	0-5	1654	1029	321	304	13.2	65	7.18
	5-15	1624	1096	261	267	11.3	-69	7.18
	15-25	1682	1134	267	281	5.9	-185	7.20
	25-35	1637	1092	281	264	9.5	-209	7.16
	35-45	1663	1109	284	270	6.5	-221	7.18
	water	65	19	33	13	-	-	-
Controls	A	1167	620	261	286	-	-	-
	B	1212	672	249	291	-	-	-
	C	1175	635	279	261	-	-	-

(j): June 1992

Tank	Depth (cm)	Organotin concentration (ng g^{-1} as Sn) Total butyltin	TBT	DBT	MBT	%VS	Redox	pH
R.1	0-5	679	248	202	229	9.3	141	7.14
	5-15	731	382	174	175	12.5	-68	7.16
	15-25	745	402	186	157	7.3	-152	7.13
	25-35	692	391	142	159	8.6	-199	7.14
	35-45	721	386	163	172	16.5	-210	7.16
	water	86	19	45	22			
R.2	0-5	1094	689	212	193	3.9	121	7.10
	5-15	1093	769	152	172	7.9	-159	7.09
	15-25	1093	763	181	149	15.6	-168	7.09
	25-35	1104	768	168	168	8.4	-191	7.09
	35-45	1091	751	178	162	6.6	-219	7.08
	water	119	61	35	23	-	-	-
Controls	A	808	386	161	261	-	-	-
	B	799	364	159	276	-	-	-
	C	783	355	173	255	-	-	-
T.1	0-5	1123	516	302	305	8.9	98	7.12
	5-15	1210	676	269	265	18.3	-128	7.09
	15-25	1222	686	264	272	5.5	-187	7.10
	25-35	1238	702	291	245	8.6	-201	7.09
	35-45	1228	697	285	246	7.9	-198	7.08
	water	44	0	12	32	-	-	-
T.2	0-5	1630	975	330	325	8.6	69	7.18
	5-15	1667	1105	276	286	9.1	-111	7.16
	15-25	1730	1190	281	259	7.3	-201	7.15
	25-35	1691	1141	294	256	9.6	-198	7.14
	35-45	1673	1181	252	240	8.7	-210	7.14
	water	115	70	32	13	-	-	-
Controls	A	1207	661	282	264	-	-	-
	B	1120	619	257	244	-	-	-
	C	1157	625	263	269	-	-	-

(k): July 1992

Tank	Depth (cm)	Organotin concentration (ng g^{-1} as Sn) Total butyltin	TBT	DBT	MBT	%VS	Redox	pH
R.1	0-5	727	271	211	245	16.0	63	7.21
	5-15	687	366	159	162	18.5	-63	7.18
	15-25	726	376	171	179	8.6	-191	7.18
	25-35	728	381	175	172	11.4	-222	7.16
	35-45	705	375	167	163	12.3	-224	7.15
	water	91	29	21	41	-	-	-
R.2	0-5	1097	691	203	203	11.9	89	7.21
	5-15	1065	729	172	164	5.9	154	7.22
	15-25	1088	754	167	167	15.6	-220	7.16
	25-35	1059	748	154	157	11.5	-205	7.14
	35-45	1083	749	153	181	13.2	-213	7.13
	water	99	23	42	34	-	-	-
Controls	A	669	332	172	165	-	-	-
	B	718	368	178	172	-	-	-
	C	653	354	158	141	-	-	-
T.1	0-5	1089	480	293	316	7.6	141	7.16
	5-15	1179	641	281	257	15.3	-101	7.26
	15-25	1222	651	291	280	3.6	-197	7.23
	25-35	1191	673	241	277	6.9	-185	7.21
	35-45	1195	675	261	259	7.9	-226	7.21
	water	118	35	62	21	-	-	-
T.2	0-5	1568	942	325	301	8.6	59	7.20
	5-15	1628	1120	247	261	17.6	-168	7.15
	15-25	1622	1106	243	273	12.6	-201	7.16
	25-35	1618	1080	258	280	3.9	-206	7.13
	35-45	1645	1122	268	255	10.5	-225	7.13
	water	101	22	47	32	-	-	-
Controls	A	1207	629	287	291	-	-	-
	B	1200	664	268	268	-	-	-
	C	1150	635	258	257	-	-	-

(I): **August 1992**

Tank	Depth (cm)	Organotin concentration (ng g^{-1} as Sn) Total butyltin	TBT	DBT	MBT	% VS	Redox	pH
R.1	0-5	707	255	201	251	11.6	189	7.21
	5-15	747	382	178	187	15.2	-65	7.18
	15-25	727	389	151	187	7.6	-158	7.17
	25-35	680	346	152	182	19.6	-213	7.20
	35-45	703	396	149	158	5.9	-219	7.21
	water	64	35	18	11	-	-	-
R.2	0-5	1085	651	219	215	6.9	89	7.12
	5-15	1069	748	164	157	10.2	-129	7.13
	15-25	1077	762	158	157	14.3	-213	7.21
	25-35	1127	772	172	183	11.6	-223	7.18
	35-45	1038	709	164	165	5.8	-240	7.17
	water	73	18	32	23	-	-	-
Controls	A	736	401	172	163	-	-	-
	B	708	380	181	147	-	-	-
	C	702	369	154	179	-	-	-
T.1	0-5	1091	442	324	325	17.3	142	7.12
	5-15	1221	653	291	277	9.6	-98	7.14
	15-25	1208	661	276	271	7.4	-185	7.16
	25-35	1238	694	286	258	6.3	-189	7.11
	35-45	1228	682	265	281	7.6	-209	7.11
	water	69	25	12	32	-	-	-
T.2	0-5	1561	876	346	339	8.4	171	7.15
	5-15	1764	1180	294	290	11.6	-54	7.15
	15-25	1653	1122	267	264	12.2	-196	7.12
	25-35	1702	1164	267	271	8.2	-222	7.11
	35-45	1583	1094	248	241	9.6	-230	7.08
	water	75	37	23	15	-	-	-
Controls	A	1207	657	282	268	-	-	-
	B	1167	676	242	249	-	-	-
	C	1209	645	289	275	-	-	-

(m): September 1992

Tank	Depth (cm)	Organotin concentration (ng g^{-1} as Sn) Total butyltin	TBT	DBT	MBT	% VS	Redox	pH
R.1	0-5	707	240	206	261	17.6	124	7.30
	5-15	748	392	164	192	11.6	-101	7.222
	15-25	672	343	168	161	5.9	-196	7.21
	25-35	717	379	171	167	7.8	-201	7.22
	35-45	737	390	175	172	6.9	-235	7.22
	water	71	14	35	22	-	-	-
R.2	0-5	1038	615	222	201	11.3	89	7.19
	5-15	1047	725	159	163	14.3	-178	7.16
	15-25	1094	749	164	181	12.3	-221	7.16
	25-35	1075	744	177	154	5.9	-208	7.16
	35-45	1094	753	178	163	9.6	-228	7.14
	water	96	41	29	26	-	-	-
Controls	A	761	401	178	182	-	-	-
	B	699	375	165	159	-	-	-
	C	691	365	159	167	-	-	-
T.1	0-5	1050	414	317	319	5.5	136	7.19
	5-15	1204	661	279	264	18.5	-57	7.16
	15-25	1194	648	285	261	9.6	-186	7.16
	25-35	1203	699	262	242	7.5	-221	7.14
	35-45	1198	678	274	246	16.5	-208	7.15
	water	54	30	15	9	-	-	-
T.2	0-5	1546	832	366	348	12.2	89	7.19
	5-15	1617	1090	276	251	6.6	-124	7.22
	15-25	1614	1098	249	267	7.8	-196	7.17
	25-35	1672	1141	275	256	16.2	-222	7.18
	35-45	1711	1153	286	272	15.2	-224	7.17
	water	75	37	23	15	-	-	-
Controls	A	1157	632	286	239	-	-	-
	B	1181	642	274	265	-	-	-
	C	1157	662	249	246	-	-	-