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Tributyltin (TBT) and the decline of the Norfolk Broads: Hickling Broad and Barton Broad

Second report on boat-derived toxic contamination

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Executive Summary

This study furthers the work of Sayer et al (2001), in which a model was presented regarding the collapse of the plant-dominated state in the aquatic ecosystem of the Norfolk Broads, E. England. The boat antifouling biocide tributyltin (TBT) was implicated as a toxic switching mechanism from evidence gathered in a palaeolimnological study of Wroxham Broad.

Replication and verification of this previous work has been conducted through analysis of sediment cores collected from two navigable lakes, Hickling Broad and Barton Broad. Organotin contamination, radiometric dating and remains of biological proxies were quantified through each core sequence. This palaeolimnological approach has allowed the history of the lake ecosystems to be established, with dates and TBT contamination concentrations linked to the observed biological changes. The data from Hickling Broad suggests, as at Wroxham Broad, that major changes in the biology of the lake were coincident with the first use of TBT. The Barton Broad core had high TBT concentrations which when compared to other dated cores from the site, demonstrated that plant loss had occurred in the lake, again close to the time that TBT was initially used in antifouling.

Our data suggest that the use of TBT as an antifoulant in freshwaters may have caused catastrophic ecological damage similar to that experienced in contaminated marine systems.

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Table of Contents

1 Introduction

Following the work of Sayer et al. (2001) and Jackson et al. (in prep.), on the ecological impacts of the antifoulant biocide tributyltin (TBT) in the Norfolk Broads, E. England, further quantification of the contamination history in this region has been conducted. In these previous studies focusing on the palaeolimnological record of Wroxham Broad, loss of submerged plants in the early 1960's was found to occur coincident with the beginning of a strong TBT signal. A model was proposed whereby TBT contamination eliminated important invertebrate and zooplankton grazers leading to the breakdown of the internal ecological buffers of the plant dominated state and a consequent rapid shift to phytoplankton dominance. This study aims to replicate and verify this previous work. DEFRA funding has enabled the concentration of TBT and it's degradation products dibutyltin (DBT) and monobutyltin (MBT) to be determined in cores taken from Hickling Broad and Barton Broad.

1.1 Core Sites and Sampling

Hickling Broad is an internationally important wetland site designated as an NNR, Ramsar site and cSAC. It lies in the upper catchment of the River Thurne, in close proximity to the North Sea (see Fig 1). Intensive drainage of the surrounding low-lying grazing marsh, and saline clay deposits in the underlying aquifer, produce brackish water in the broad. It is shallow (<1.5 m) and holds populations of several species of macroalgal stoneworts (Characeae), including the Red Data Book species *Chara intermedia*. Barton Broad is a NNR and SSSI, fed by the River Ant, which drains a relatively large, predominantly arable catchment. This broad is also shallow (<1.8 m), but with sparse submerged plant coverage. It has been the focus of an extensive restoration programme initiated by the Broads Authority, which has included lake-wide sediment removal and biomanipulation of isolated bays. Both sites are popular boating areas and have at least one marina/boatyard along their edge.

Sediment cores were collected from the Heigham Corner area of Hickling Broad, core code HICK1, (National Grid Reference TG 421209), on 27/4/02 and from the Neatishead Arm of Barton Broad, core code BART9 (TG 355214), on 10/9/01 with a 7.4 cm I.D. Livingstone coring system.

Figure 1. Location of Hickling and Barton Broads

2 Methods

2.1 Core Extrusion

Both HICK1 and BART9 extended back to basal medieval peat indicating that a complete sediment sequence was collected in each case. HICK1 was extruded at 0.5 cm and BART9 at 1 cm intervals respectively. Sub-samples for organotin analysis were removed from the centre of slices to avoid contamination during extrusion. In practice approximately 20 cm^3 of wet sediment was placed in a 30 ml glass vial with a foil-lined lid. Samples were stored in the dark in a Cool-Box and frozen to –20^oC as quickly as possible. The sampling interval for organotin analyses through the HICK1 core was shorter than for BART9 as the overall sediment depth was smaller. This is reflected in the number of samples analysed for organotin, which was 13 for HICK1 and 18 from BART9. All other sediment samples for geochemical and macrofossil analyses were stored in plastic bags in the dark at 4^oC.

2.2 Radiometric dating

Sediment samples from HICK1 and BART9 were analysed for ^{210}Pb, ^{226}Ra and ^{137}Cs by direct gamma assay using Ortec HPGe GWL series well-type coaxial, low background intrinsic germanium detectors (Appleby et al. 1986). ^{210}Pb was determined via its gamma emissions at 46.5keV, and ^{226}Ra by the 295keV and 352keV γ-rays emitted by its daughter isotope ^{214}Pb following 3 weeks storage in sealed containers to allow radioactive equilibration. ^{137}Cs and ^{241}Am were measured by their emissions at 662keV and 59.5keV respectively. The absolute efficiencies of the detectors were determined using calibrated sources and sediment samples of known activity. Corrections were made for the effect of self-absorption of low energy γ-rays within the sample (Appleby et al. 1992).

2.3 Organotin analysis

Organotin compounds were extracted from the sediment matrix by sodium hydroxide and methanol, converted to hydrides and partitioned into hexane. Derivatives were then analysed by gas chromatography with flame photometric detection (GC-FPD) (Waldock et al. 1989). The detection limit for the method was approximately 2 ng g^{-1} for all organotin species identified. Operationally this detection limit was slightly

higher, in response to the percentage recovery of an internal standard added to each sample prior to extraction.

2.4 Lithostratigraphy

Percentage water content of each sediment sample was determined by drying a weighed sub-sample in a crucible to constant mass at 105^{o}C and by calculating weight loss. Subsequently percentage organic matter and carbonate were determined using standard loss-on-ignition (LOI) procedures (Dean 1974).

2.5 Biostratigraphy

Sub-fossil diatoms and macrofossils were extracted and analysed using standard procedures (Battarbee et al. 2001; Birks 2001). Principal Component Analysis (PCA) was used to explore the main patterns of variation in the diatom data and to determine degree of assemblage change throughout the core (expressed as PCA axis 1 scores) using CANOCO version 4 (ter Braak & Smilauer 1998). Macrofossil data from HICK1 was expressed as number of remains per g (dry weight) cm^{-3}, to correct for the increase in sediment density found down the core.

3 Results

3.1 HICK1 radiometric dating

The results of radiometric analyses for core HICK1 are given in Table 1 and shown graphically in Figure 2.

Lead-210 Activity

Total ^{210}Pb activity reaches equilibrium with the supporting ^{226}Ra at a depth of around 23 cm (Figure 2a). Unsupported ^{210}Pb activities, calculated by subtracting ^{226}Ra activity from total ^{210}Pb activity, declines relatively slowly with depth in the top 10 cm of the core. At this point there is a relative abrupt change in the gradient of the profile (Figure 2b), with a much steeper rate of decline in the deeper sediments. Within this deeper zone the profile more or less follows an exponential relationship, apart from a possible non-monotonic feature near the base of the ^{210}Pb record.

Artificial Fallout Radionuclides

^{137}Cs activity versus depth profile (Figure 2c) has a relatively well-resolved peak between 13-16 cm that almost certainly records the 1963 fallout maximum from the atmospheric testing of nuclear weapons. This interpretation is supported by the detection of traces of ^{241}Am in the 14.5-15.5 cm sample.

Core Chronology

Figure 3 shows ^{210}Pb dates calculated using the CRS and CIC dating models (Appleby & Oldfield 1978), together with the 1963 depth determined from the ^{137}Cs stratigraphy. The CRS model places 1963 at a depth of 11.75 cm, significantly above the depth suggested by the ^{137}Cs record. The CIC model gives a better agreement, placing 1963 at a depth of 14 cm, though dates calculated by this model are generally more irregular. Better results, also shown in Figure 3 and given in detail in Table 1, are obtained by the CRS model using the 1963 ^{137}Cs date as a reference point (Appleby 2002). These calculations suggest that since 1950 sedimentation rates have fluctuated between 0.031-0.055 g cm^{-2} y^{-1}, with a mean value of 0.041 ± 0.009 g cm^{-2} y^{-1} (0.31 cm y^{-1}). They also suggest that sedimentation rates were significantly lower during the period 1920-50, but because of the low ^{210}Pb concentrations below 15 cm, dating values from this period have a larger uncertainty attached.

Table 1. **^{210}Pb chronology of Hickling Broad core HICK1 (dated using the corrected CRC model)**

Depth		Chronology			Sedimentation Rate		
		Date	Age				
cm	g cm^{-2}	AD	y	±	g cm^{-2} y^{-1}	cm y^{-1}	± (%)
0.0	0.00	2002	0				
1.0	0.07	2001	1	1	0.055	0.67	11.9
2.0	0.18	1999	3	2	0.054	0.57	12.7
3.0	0.29	1997	5	2	0.053	0.50	13.4
4.0	0.40	1995	7	2	0.053	0.44	14.2
5.0	0.50	1993	9	2	0.052	0.44	14.9
6.0	0.62	1990	12	2	0.050	0.40	16.2
7.0	0.74	1988	14	2	0.047	0.36	17.4
8.0	0.86	1985	17	2	0.043	0.36	18.1
9.0	0.99	1982	20	2	0.039	0.31	18.3
10.0	1.11	1979	23	3	0.035	0.29	18.9
11.0	1.25	1975	27	3	0.037	0.29	20.5
12.0	1.38	1971	31	4	0.038	0.27	22.1
13.0	1.52	1968	34	4	0.043	0.26	23.6
14.0	1.69	1964	38	5	0.046	0.27	26.8
15.0	1.87	1960	42	9	0.037	0.21	30.8
16.0	2.06	1956	46	10	0.031	0.16	46.8
17.0	2.24	1949	54	11	0.042	0.14	62.7
18.0	2.45	1940	63	13	0.035	0.12	60.9
19.0	2.66	1931	72	15	0.025	0.11	53.3
20.0	2.88	1922	81	16	0.014	0.11	45.6

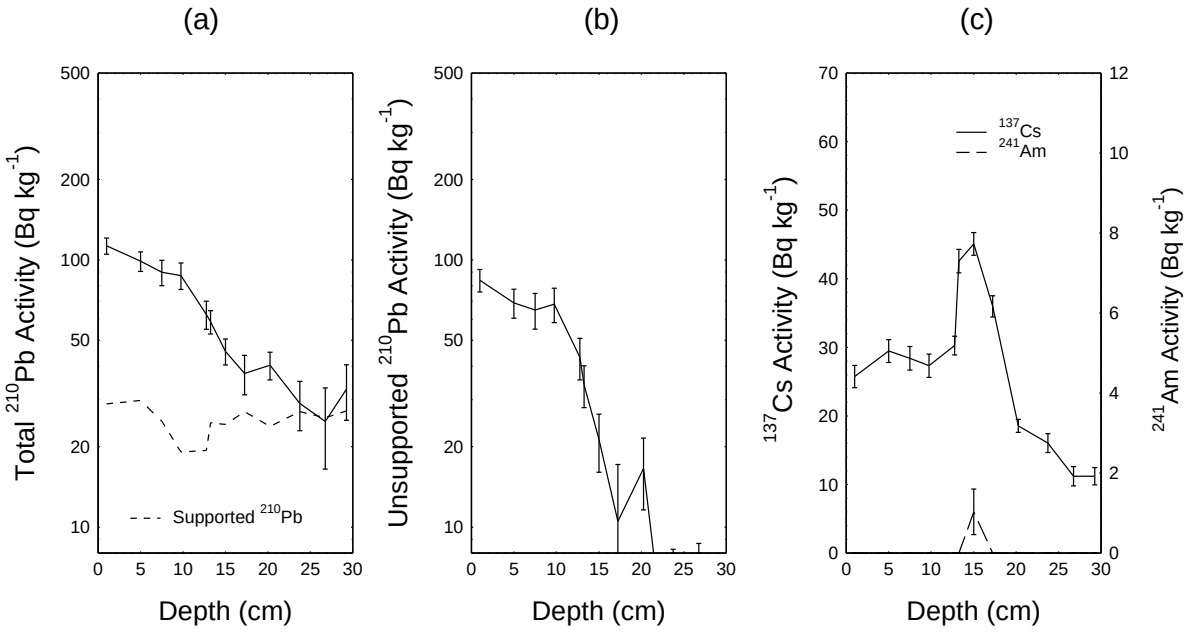

Figure 2. Fallout radionuclides in the Hickling Broad core HICK1 showing (a) total and supported ^{210}Pb, (b) unsupported ^{210}Pb, (c) ^{137}Cs and ^{241}Am concentrations versus depth.

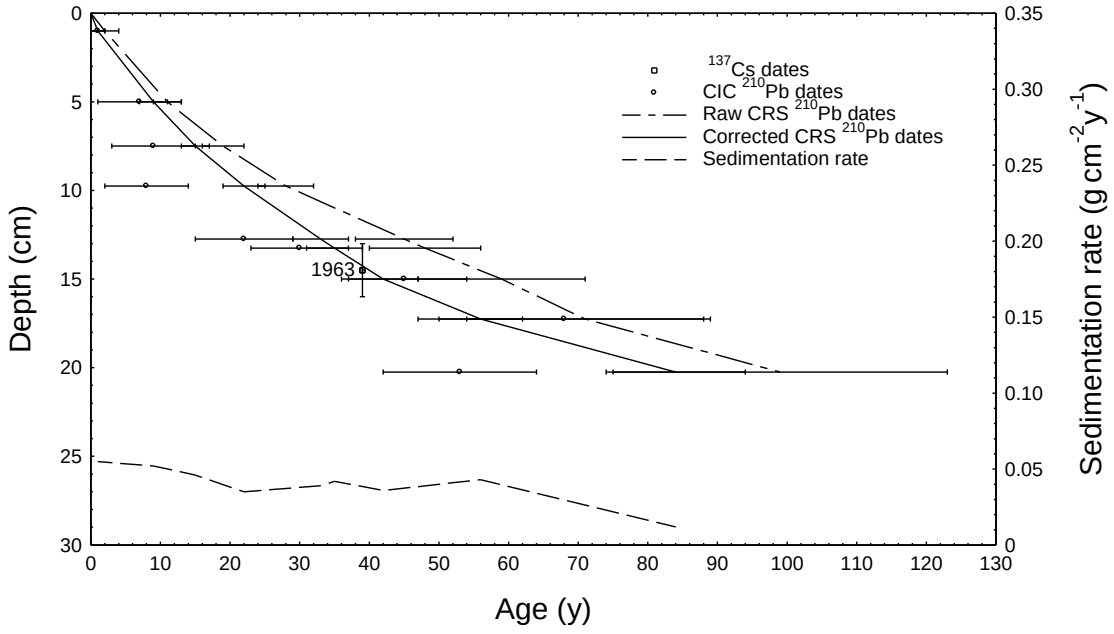

Figure 3. Radiometric chronology of Hickling Broad core HICK1 showing the CRS and CIC model ^{210}Pb dates and the 1963 depth determined from the ^{137}Cs stratigraphy. Also shown are the corrected ^{210}Pb dates and sedimentation rates calculated using the ^{137}Cs date as a reference level.

3.2 BART9 radiometric dating

The results of the radiometric analyses for core BART9 are given in Table 2 and shown graphically in Figure 4.

Lead-210 Activity

^{210}Pb concentrations in excess of the supporting ^{226}Ra were above limits of detection down to a depth of between 25-35 cm. Unsupported ^{210}Pb concentrations (Figure 4b) were however very low. The mean value was just 16 ± Bq kg^{-1}, implying a ^{210}Pb dating horizon of not more than c.30 years. The unsupported ^{210}Pb inventory in the core was 950 Bq m^{-2}. This corresponds to a mean ^{210}Pb supply rate of 30 Bq m^{-2} y^{-1}, around 50% of the estimated atmospheric flux.

Artificial Fallout Radionuclides

The ^{137}Cs activity has a relatively well-resolved peak at a depth of 30.5 ± 4.5 cm (Figure 4c) recording the 1963 fallout maximum from the atmospheric testing of nuclear weapons.

Core Chronology

Figure 5 compares ^{210}Pb dates calculated using the CRS model (Appleby et al. 1978) with the 1963 date determined from the ^{137}Cs record. Use of the CIC model was precluded by the non-monotonic variation in unsupported ^{210}Pb activity. The initial ^{210}Pb results place 1963 at a depth of 20.5 cm, significantly above the depth of the ^{137}Cs peak. The discrepancy is almost certainly due to errors in the ^{210}Pb inventory arising from the very low concentrations. Revised ^{210}Pb dates were calculated using the ^{137}Cs date as a reference point (Appleby 2002). The corrected results, also shown in Figure 5 and given in detail in Table 2a, suggest significant fluctuations in the net rate of accumulation of sediment during the past 50 years, ranging from ~0.5 cm y^{-1} in the late 1950s and late 1970s to 1.3 cm y^{-1} in the late 1960s and late 1990s. Since the validity of the CRS model in this environment is questionable, Table 2b presents an alternative chronology using the mean sedimentation rate of 0.15 ± 0.02 g cm^{-2} y^{-1} determined from the ^{210}Pb and ^{137}Cs records. Differences between the two chronologies are however for the most part fairly small.

Table 2. Radiometric chronology of Barton Broad core BART9

(**a**) Corrected CRS model

Depth		Chronology			Sedimentation Rate		
		Date	Age				
cm	g cm^{-2}	AD	y	±	g cm^{-2} y^{-1}	cm y^{-1}	± (%)
0.0	0.0	2001	0	0			
0.5	0.0	2001	0	1	0.16	1.38	46.3
5.5	0.8	1997	4	2	0.21	1.25	62.8
10.5	1.6	1993	8	3	0.21	0.83	61.5
15.5	2.6	1985	16	4	0.09	0.50	30.7
20.5	3.6	1973	28	6	0.09	0.66	48.0
25.5	4.7	1970	31	6	0.57	1.48	28.3
30.5	5.9	1966	35	5	0.12	0.62	16.8
35.5	7.1	1954	47	11	0.07	0.40	16.8

(b) Assuming a uniform sedimentation rate

Depth		Chronology			Sedimentation Rate		
		Date	Age				
cm	g cm^{-2}	AD	y	±	g cm^{-2} y^{-1}	cm y^{-1}	± (%)
0.0	0.0	2001	0				
0.5	0.0	2001	0	0	0.15	1.04	17.5
5.5	0.8	1996	5	1	0.15	0.93	17.5
10.5	1.6	1990	11	2	0.15	0.80	17.5
15.5	2.6	1983	18	3	0.15	0.74	17.5
20.5	3.6	1976	25	4	0.15	0.72	17.5
25.5	4.7	1969	32	6	0.15	0.65	17.5
30.5	5.9	1961	40	7	0.15	0.62	17.5
35.5	7.1	1953	48	8	0.15	0.63	17.5

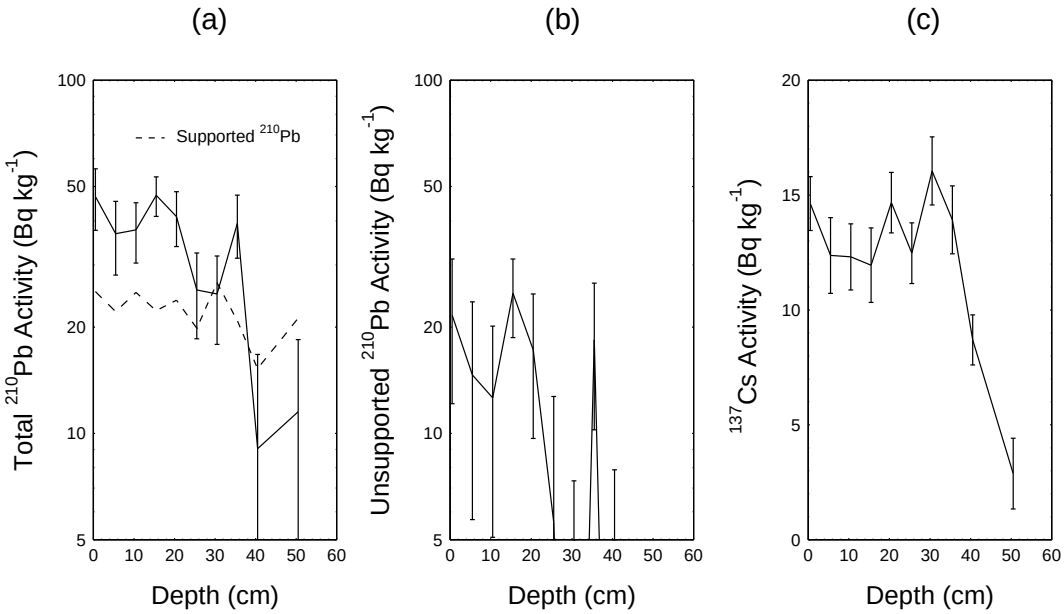

Figure 4. Fallout radionuclides in Barton Broad core BART9 showing (a) total and supported ^{210}Pb, (b) unsupported ^{210}Pb, (c) ^{137}Cs concentrations versus depth.

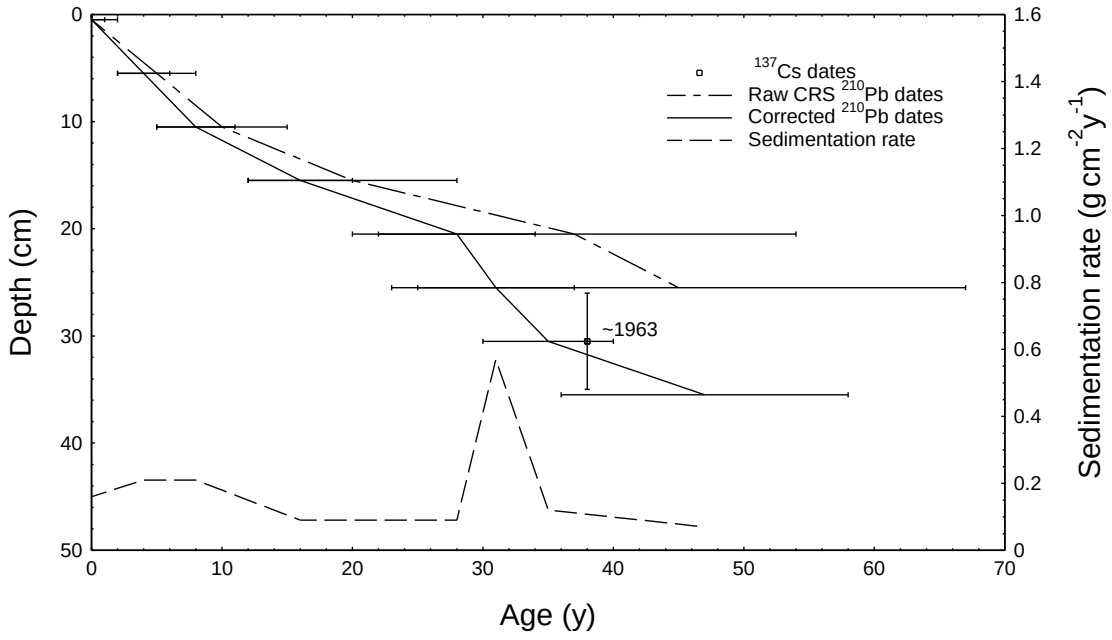

Figure 5. Radiometric chronology of Barton Broad core BART9 showing the CRS model ^{210}Pb dates and the 1963 depth determined from the ^{137}Cs stratigraphy. Also shown are corrected CRS model dates calculated using the ^{137}Cs date as a reference point, and the sedimentation rate versus time.

3.3 Organotin profiles

Organotin profiles for core HICK1 and BART9 are given in Figures 6 and 7 respectively (see Appendix 1 for concentration results). The main breakdown processes of TBT in the environment are UV radiation and biological degradation, with stepwise dealkylation to DBT, monobutyltin (MBT) and ultimately elemental tin.

HICK1 has a TBT concentration range of 55-102 ng g^{-1} between 12-1 cm (dated 1971 ± 4 yrs – 2001 ± 1 yr), declining steadily towards the sediment surface. Below 12 cm no TBT was detected in HICK1. The small amount (13 ng g^{-1} TBT) detected at 27 cm is well below the oldest dated depth at 20 cm (1922 ± 16 yrs). Contamination with younger sediment at the time of sample collection, or a mis-identified peak occurring at the same retention time as TBT during the GC-FPD analysis, are probable causes of this erroneous result. No detectable concentrations of monobutyltin were found in HICK1 at any depth.

BART9 has a high TBT concentration between 36-9 cm (dated 1954 ± 11 yrs – 1993 ± 3 yrs), with levels in the region of 250 ng g^{-1}. There is then a decline towards the surface and lower down there is a tailing off to 51 cm, the lowest depth analysed. This lowest measured depth is beyond the range of the ^{210}Pb dating for this core. The lowest dated depth is 36 cm, aged at 1953-54 using both models presented in Tables 2a and 2b. All depths analysed for TBT in BART9 gave a positive result. The very large data point at 24 cm (4051 ng g^{-1} TBT, 271 ng g^{-1} DBT) is almost certainly the result of a TBT containing paint flake being present in the sediment sample analysed (B. Jones, pers. comm.). The date of this sample, using the corrected CRS model (Table 2a) is given as 1970 ± 6 yrs, a period of intense TBT-based antifouling paint use in the Norfolk Broads.

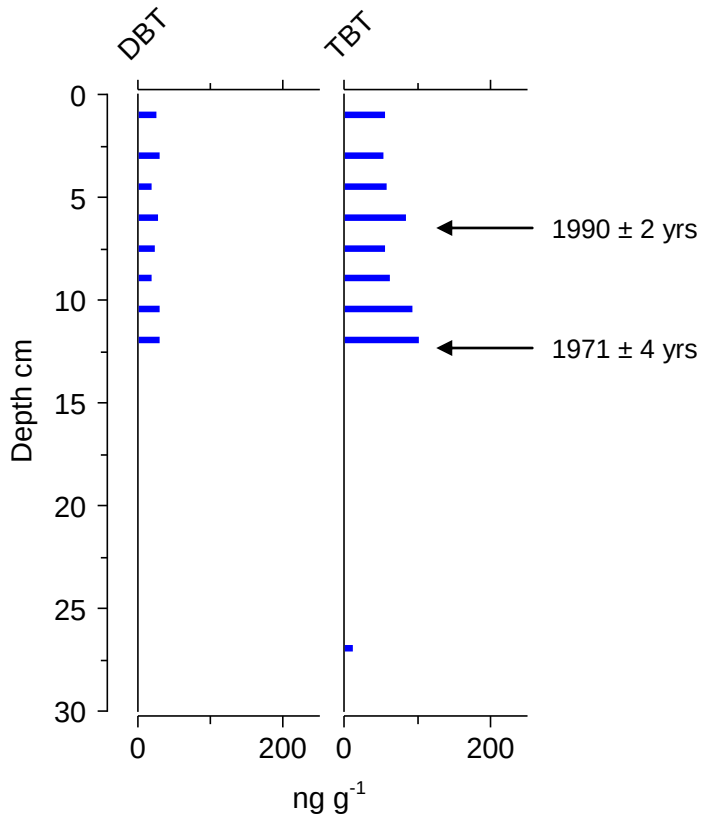

Figure 6. Organotin profile for HICK1 (dates from Table 1)

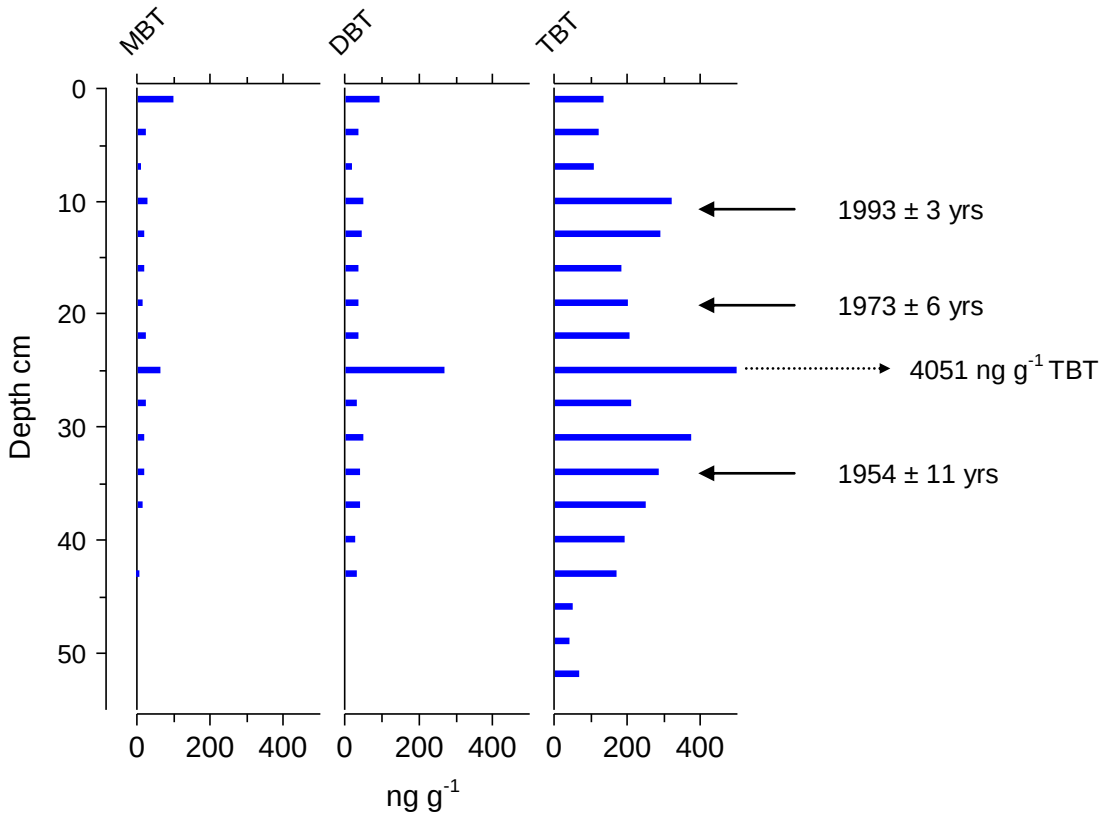

Figure 7. Organotin profile for BART9 (dates from CRC model, Table 2a)

The presence of organotins in sediments dated before TBT containing antifoul paint usage and to some extent after the retail ban in 1987, can be explained through processes continually occurring in lake surface sediments. This includes the equilibrium partitioning of hydrophobic compounds between the water and sediment phases and *in-situ* sediment mixing. TBT has a strong affinity to bind to solid particles in suspension or in the bottom sediments (Hoch & Schwesig 2004). This process is however reversible, with equilibrium between the solid and water phases establishing under ideal conditions. Desorption of organotins to the water phase is assisted by resuspension of surface sediments, as the equilibrium state is disturbed (Watanabe et al. 1995). Factors causing sediment resuspension in lakes include wave action, especially in shallower marginal areas (Søndergaard et al. 1992); disturbance from boat propellers (Garrad & Hey 1987); and the action of bottom feeding organisms, such as fish (Havens 1991) e.g. bream *Abramis brama*, which are abundant in the Norfolk Broads. The burrowing action of non-biting midge larvae (Chironomidae) and bivalve molluscs also cause bioturbation and physical mixing of material within the surface layer of lake sediments (Phillips et al. 1994; McCall et al. 1995).

MBT and DBT concentrations are consistently lower than TBT at all core depths, as expected from the degradation kinetics of the butyltin species (Maguire & Tkacz 1985). At the surface (0-1 cm) of BART9, DBT and MBT appear to have elevated concentrations (DBT 98 ng g^{-1}, MBT 101 ng g^{-1}) in relation to the rest of the core and compared to the other cores analysed. Release of these more soluble compounds during the sediment removal operation at Barton Broad between 1995 and 2001 is the probable cause of these elevated surface concentrations. The greater solubility of the degradation products compared to TBT (Maguire et al. 1983), and therefore greater likelihood of desorption from resuspended solid particles, explains why TBT itself is not significantly elevated at the sediment surface. The exposure of buried material, laden with sediment-bound butyltins and TBT-containing paint flakes, provides a direct route for such secondary contamination to the water column and redistribution across the lake.

3.4 Biostratigraphy

HICK1 (see Appendix 2 for diagram)

Plant macrofossil remains were abundant in HICK1, with dominance by stonewort oospores of the characean genera, *Chara* and *Nitella*. There is a variable but

persistent record of oospore numbers between 21.5 to 13.5 cm, with very few *Chara* spp. and no *Nitella* spp. found throughout the TBT contaminated period. Seeds of the Holly-leaved naiad (*Najas marina*) were also found in the core but in low numbers and in no particular pattern. Macroinvertebrate remains were numerically dominated by the brackish water mollusc *Potamopyrgus antipodarum*, with *Gyraulus crista* also common. Mollusc abundance follows a similar pattern to the charophyte oospores, with variable numbers up to 13.5 cm and very low numbers above 12 cm. Three other mollusc species, *Lymnaea peregra, Valvata cristata* and *Valvata piscinalis* were also found in the core in small numbers, with virtually all records occurring below 12 cm.

The diatom results suggest a change in community composition at the same time as TBT first appears in the core profile. In particular there is a reduction in the relative contribution of the epiphyte *Cocconeis placentula* and an increase in small benthic *Fragilaria* spp. Reflecting this change, PCA axis 1 scores change markedly at this point in the profile. Furthermore there is a distinct increase in the proportion of organic matter in the sediment above 13 cm (dated 1968 ± 4 yrs) and a corresponding drop in the carbonate content of the sediments. A shift to a higher trophic state in the lake can result in greater organic matter accumulation and in this case an increase in phytoplankton production seems a likely cause. The carbonate source in Hickling includes mollusc shells and that precipitated on growing charopytes. This decrease may reflect reduced abundances in both groups as observed in the macrofossil remains.

Historic botanical records for Hickling Broad have been compiled from Norwich Castle Museum, English Nature archives and Broads Authority survey data. These indicate that plant loss in the broad and an increase in phytoplankton abundance occurred in the late 1960's/early 1970's. Reduction of the area covered by macrophytes, loss of plant species, and an increasing turbidity of the once "gin clear" water (Jackson 1978), were the main responses observed at the time. Figure 8 shows how the number of species of charophytes found in Hickling Broad crashed at the same time as the peak TBT usage period, and recovered after the 1987 ban.

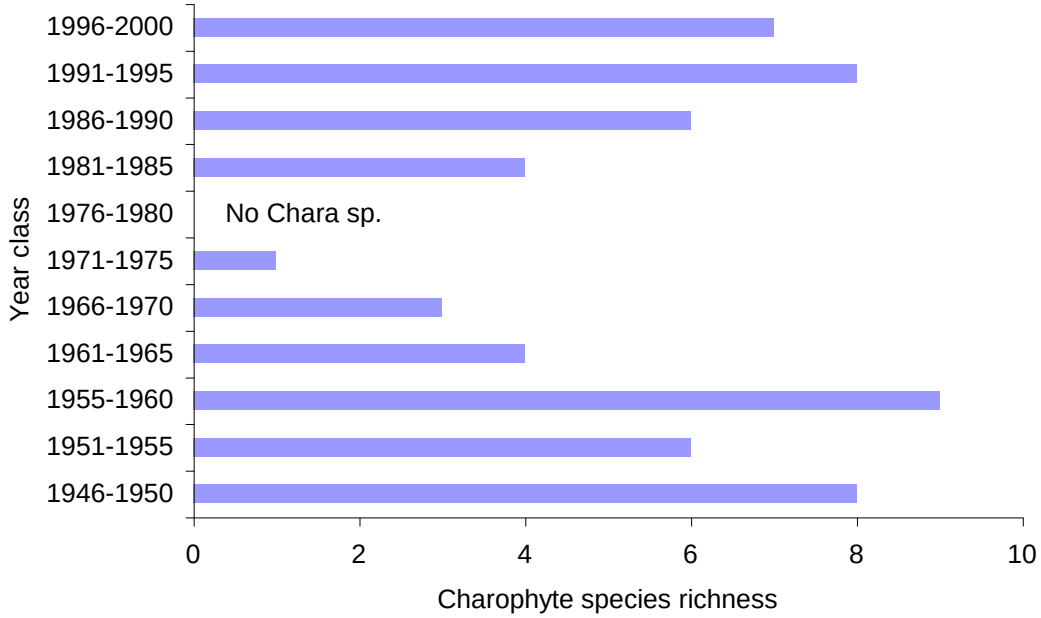

Figure 8. **Historical charophyte data for Hickling Broad**

BART9 (see Appendix 3 for diagram)

No macrofossil or diatom analyses have been performed on the BART9 core, so previously dated cores collected from Barton Broad (BART1 and BART5) have been used to make biostratigraphic comparisons. Depths dated 1960 from each core (around the time of macrophyte loss) are marked with a solid line to allow core comparison.

The macrofossils from BART5 suggest *Chara* sp. dominance early in the history of the lake, at a depth corresponding to the very organic rich (peat) period in the LOI profile of BART9 (below 62 cm). The other plant remains of water soldier (*Stratiotes aloides*) and water lily (Nymphaeaceae spp) are variable, but high, up to 30 cm (dated 1960), with reduced abundance to the surface. Botanical records of water soldier from Barton Broad indicate that the species has not been present since around 1969 (Jackson 1978). Presence of the spines in sediment samples dated after this time suggest that a certain amount of sediment mixing has occurred, which makes interpretation of the data less straight-forward.

The diatom community in BART1 shows a decrease of small *Fragilaria* spp. after about 1960, with increasing abundance of planktonic species. A similar pattern of decreased *Fragilaria* spp. and increased planktonic taxa abundance was also observed in Wroxham Broad (WROX1 core) in synchrony with the onset of TBT

usage (Sayer et al. 2001). Together with the macrofossil results the data suggests a switch in lake state coincident with the beginning of TBT usage in the early 1960's.

4 Discussion

Contamination of organotin compounds derived from boats coated with TBT-containing antifoul paints has been shown to be widespread within the Norfolk Broads (Waite 1989; Dowson et al. 1994; Sayer et al. 2001). Variation in relative concentration levels measured in the sediment cores presented here may be due to different volumes of boat traffic during TBT usage (exposure) and differences in TBT degradation post-burial. Data collected by the Broads Authority on the number of boat movements per day, shows the Upper Thurne and Hickling Broad to be one of the less boated areas of the Norfolk Broads (Broads Authority Boat Census 1998). Boat registration data also reveals a much greater number of boats moored at Barton Broad and upstream along the River Ant, compared to the limited amount of moorings at Hickling Broad (Broads Authority Boat Registry 2003). It is assumed that this pattern has remained relatively similar over time, and in turn this suggests that differences in exposure are predominantly responsible for the higher TBT contamination levels detected in Barton Broad. Boat numbers registered on the river Bure upstream of Wroxham Broad (Sayer et al. 2001) are similar to Barton Broad, both of which have correspondingly higher concentration TBT profiles than at Hickling.

The persistence of TBT over time has been highlighted with this study, as well as the continued contamination source from TBT and other biocides (Thomas et al. 2003) bound in paint flakes from boats. The environmental persistence of TBT contained in anaerobic sediments is very high. Work by Dowson et al. (1996) found that the half-life of TBT was not discernible over the duration of their experiment, but appeared to be in the order of tens of decades, which this study confirms. Contamination from TBT is shown to be a relevant contemporary issue with regard to dredging and sediment removal operations at affected sites. The propensity of DBT and MBT to desorb from disturbed sediments makes what was once considered a past pollution problem of potential current relevance. Toxicological data on the impact of the degradation products upon aquatic organisms is somewhat limited, but generally indicates a lower risk than TBT itself. The result obtained from 27 cm depth in Barton Broad indicates that much higher average sediment TBT concentrations may occur where there is paint flake presence. Further sampling to obtain information on the spatial variability of organotin sediment concentration, within a sampling site, would reveal the extent and significance of this problem.

The overall picture from the quantified remains is one of reduced macrophyte abundance and associated diatoms and molluscs post TBT use. Changes in the diatom community assemblage occur through both of the cores analysed, with a shift in HICK1 being coincident with the initial detection of TBT in the sediment samples. The diatom community shift in BART9 also occurs at the time of TBT introduction as an antifoulant. Macrophyte remains are greatly reduced or absent during the TBT contaminated phase, with a similar pattern observed for mollusca in the Hickling core. The proposed model of TBT's toxic effects in these shallow lakes as proposed by Sayer et al. (2001) and Jackson et al. (in prep.) is therefore fully supported by the data gathered herein.

5 Conclusions

This study shows that the contamination from organotin containing antifoul paint is widespread in the Norfolk Broads. Further, changes in the biostratigraphical data, particularly macrofossils, suggest large-scale alteration to the Broads aquatic ecosystem coincident with TBT usage, with evidence consistently pointing to substantial loss of aquatic plants and associated invertebrate fauna. Moreover, there has been little demonstration of any sustained plant recovery since this time.

We suggest that TBT contamination induced considerable degradation of the aquatic ecosystem in the Norfolk Broads, and potentially presents a contemporary toxicological hazard despite the 1987 retail ban. TBT has been found to have caused havoc in marine systems and may have had equally as damaging effects when used in freshwaters.

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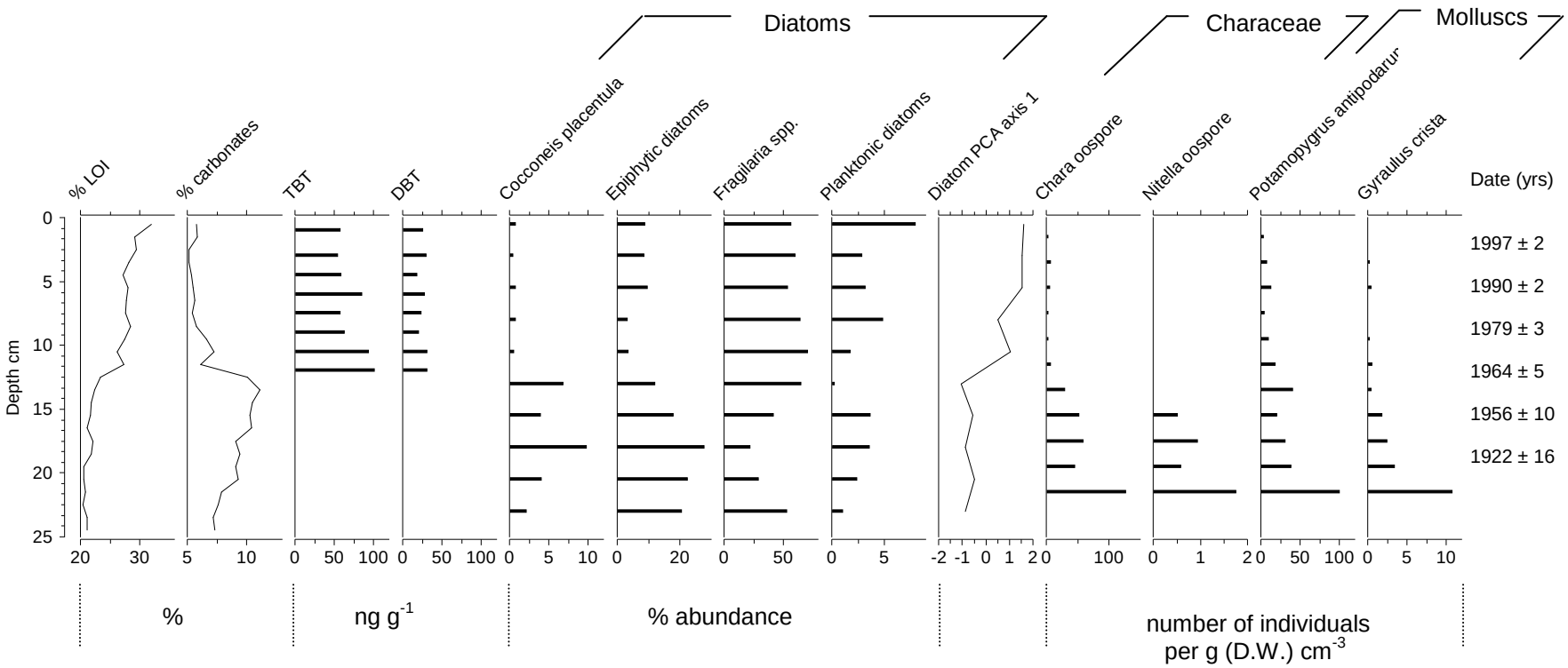
Appendix 1 Table of organotin concentration with depth

Core	Depth	TBT	DBT	MBT
	cm		ng g^{-1}	
HICK1	1.0 - 1.5	58	27	<8
	3.0 - 3.5	55	31	<8
	4.5 - 5.0	59	19	<5
	6.0 - 6.5	86	29	<8
	7.5 - 8.0	58	24	<7
	9.0 - 9.5	64	21	<4
	10.5 - 11.0	95	32	<5
	12.0 - 12.5	102	32	<9
	15.0 - 15.5	<6	<5	<5
	18.0 - 18.5	<5	<4	<4
	21.0 - 21.5	<5	<4	<4
	24.0 - 24.5	<7	<5	<5
	27.0 - 27.5	13	<3	<3
BART9	0 - 1	139	98	101
	3 - 4	123	41	25
	6 - 7	112	24	14
	9 - 10	322	53	33
	12 - 13	292	50	22
	15 - 16	184	39	24
	18 - 19	205	40	17
	21 - 22	206	38	27
	24 - 25	4051	271	68
	27 - 28	214	36	25
	30 - 31	378	52	21
	33 - 34	289	42	23
	36 - 37	252	44	19
	39 - 40	194	30	<4
	42 - 43	174	34	20
	45 - 46	51	<10	nd
	48 - 49	46	<10	nd
	51 - 52	69	<10	nd

< values mean the compound's response was below the operational LOD
nd – no data

Appendix 2. Biostratigraphy of HICK1



Appendix 3. Biostratigraphy of composite dated Barton Broad cores (1960 dateline added for comparison between cores)