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Tributyltin (TBT) and the decline of the Norfolk Broads

Final Report to the Department for Environment, Food & Rural Affairs

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December 2001

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Final Report to the Department for Environment, Food & Rural Affairs (DEFRA)

Tributyltin (TBT) and the decline of the Norfolk Broads

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December 2001

Executive Summary

1. This is the final report to the Department for Environment, Food & Rural Affairs (DEFRA) on the contract "Tributyltin (TBT) and the decline of the Norfolk Broads".

2. Palaeolimnological investigations have been on-going to determine potential links between TBT and the decline of the Norfolk Broads aquatic ecosystem.

3. The project had the following objectives:

    - To determine the history of contamination of Wroxham Broad by organotin compounds and heavy metals.

    - To determine the relationship between toxic contamination and biological change, particularly the loss of submerged macrophyte beds.

4. The report describes/gives the results of a series of palaeolimnological procedures applied to a sediment core from the southern basin of Wroxham Broad (core WROX2), including organotin and heavy metal analysis, radiometric dating and sub-fossil diatom, Cladocera, ostracod and macrofossil analysis.

5. The main findings were as follows:

    - TBT concentrations were extremely high between 28-10 cm (dated 1962 ± 6 yrs - 1987 ± 3 yrs), above which there is a steady decline to the sediment surface (in line with the 1987 ban on TBT use).

    - Exactly synchronous with the start of the TBT signature, diatom and cladoceran assemblages suggest rapid changes in community structure and a decline in macrophyte-associated species. Such changes are indicative of the loss of submerged macrophytes and a rapid shift to a turbid, phytoplankton-dominated lake state.

    - There is a sharp rise in Cu concentrations within the uppermost 6 cm of the core which mirrors the TBT decline. This may reflect the more recent (post-TBT) use of antifoulants that contain one of a number of 'booster biocides' (including Irgarol 2051 and Diuron) in addition to an elevated Cu content.

6. The data provide strong evidence to suggest that TBT may have been a significant factor in the widespread loss of submerged macrophytes from the Broads ecosystem in the early 1960s. High TBT concentrations in the waters of the Broads could have significantly reduced numbers of grazing snails and large filter-feeding cladoceran zooplankton (as evidenced from the surveys of Jackson (1999)). In turn this could have resulted in increases in periphyton and phytoplankton leading to a decline in the light available for macrophyte photosynthesis.

7. The results highlight an urgent need for further research into the de-stabilising role that toxic micro-pollutants may have played in the Norfolf Broads, including:

    - Analysis of additional sediment cores for toxic contaminants (including organotin, metals, herbicides and pesticides) from additional broads (including 'boated' and 'non-boated' control sites).

    - Analysis of surface sediments (upper 1 cm) across the Broads (rivers and lakes) system to determine contemporary toxic contamination and likely sources.

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Such concentrations are beyond the established lethal toxicity thresholds of many freshwater macroinvertebrates (Jackson, 1999). Hence the possibility that boats (albeit indirectly), may have been partly responsible for the degradation of the Broads ecosystem has been resurrected (Jackson & Sayer, in prep.).

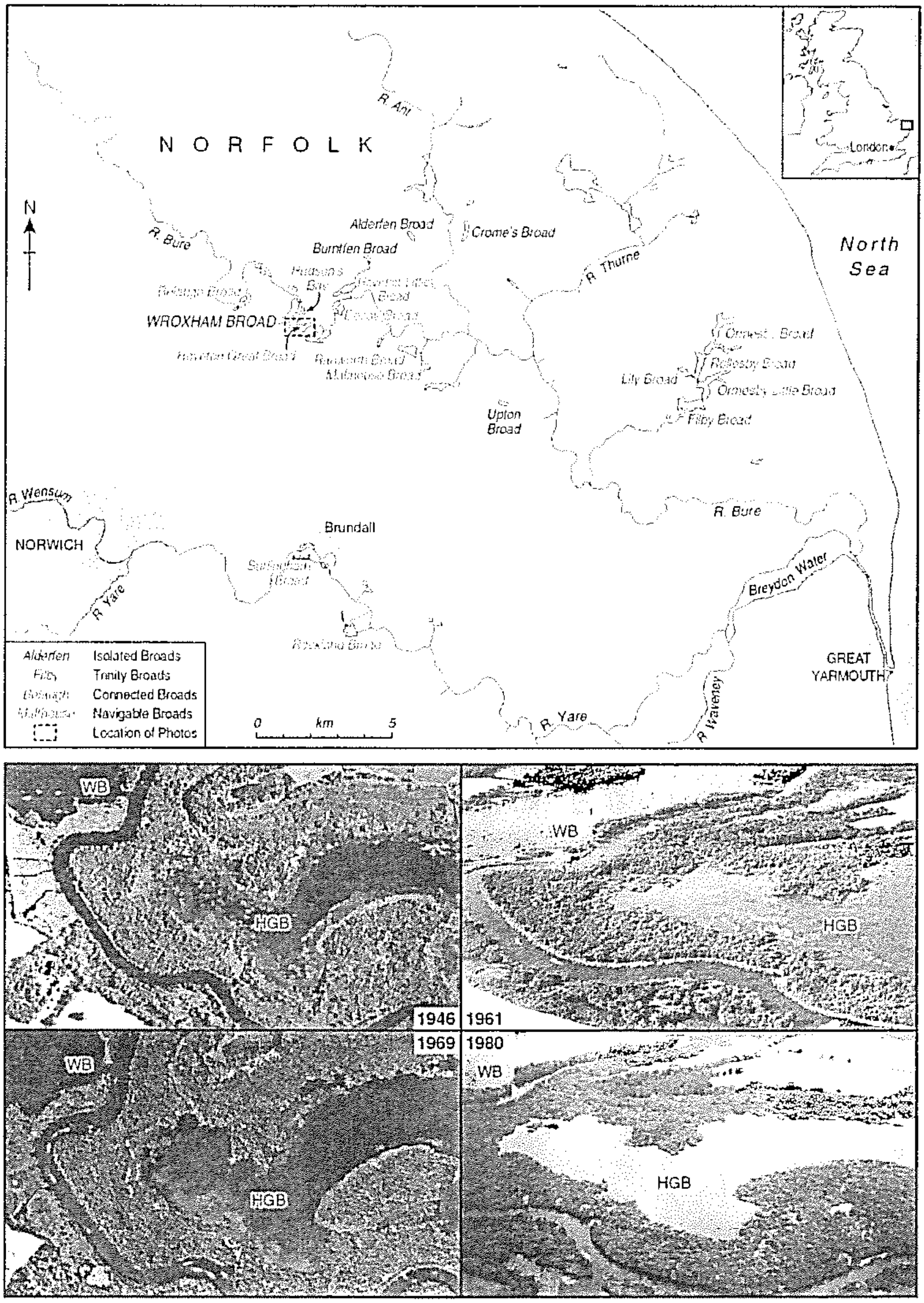

Figure 1. Map of the Norfolk Broads with aerial photograph series. Photographs (boxed area of map) compare Hoveton Great Broad (HGB) and Wroxham Broad (WB) during the summers of 1946, 1961, 1969 and 1980. These illustrate the almost total loss of aquatic vegetation from HGB between 1961 and 1980.

1.4 Palaeolimnological investigations

Palaeolimnological investigations to determine potential links between TBT and the decline of the Broads aquatic ecosystem have been on-going at Wroxham Broad (Jackson & Sayer, in prep.). A short (96 cm) sediment core (core code WROX2) was collected from Wroxham Broad in July 2000 and analysed for TBT, DBT (analyses undertaken under the supervision of Dr. Mike Waldock (CEFAS)) and heavy metals (analyses undertaken by Dr. John Boyle, University of Liverpool). The present study funded by DEFRA, has involved; (i) radiometric dating of the WROX2 core, and; (ii) analysis of selected sediment levels for diatom, macrofossil, cladoceran and ostracod sub-fossils.

2 Objectives

- To determine the history of contamination of Wroxham Broad by organotin compounds and heavy metals.
- To determine the relationship between toxic contamination and biological change, particularly the loss of submerged macrophyte beds.

3 Methods

3.1 Sediment coring and sample storage

The sediment core WROX2 was collected from the southern basin of Wroxham Broad using a modified Livingstone corer (internal diameter 7.4 cm) from a water depth of 158 cm. The core was sliced at 1 cm intervals and sub-samples for organotin analysis were immediately frozen and stored in sterile glass containers. All other samples were stored at 4°C.

3.2 Organotin analysis

Organotin compounds were extracted from the sediments by sodium hydroxide and methanol, converted to hydrides and partitioned into hexane. The derivatives were then analysed by gas chromatography with flame photometric detection (GC-FPD). The detection limit for the method was 0.002 $\mu g\ g^{-1}$ for TBT and DBT.

3.3 Heavy metal analysis

Heavy metal concentrations were determined using a Unicam 939 atomic absorption spectrophotometer. Dried samples were reacted with concentrated nitric acid for 1 hour at 90°C, and diluted with double distilled water. Cu, Pb and Zn concentrations were determined using an air-acetylene flame under standard operating conditions. A STATS tube was used to enhance sensitivity for Pb. Hg was determined using a standard cold vapour procedure, with tin (II) chloride as a reducing agent. Three international reference materials; Buffalo River Sediment (NIST SRM2704), Pond Sediment (NIES CRM2) and Stream Sediment (MC GWB7309); were used to verify analytical accuracy.

3.4 Radiometric Dating

Sediment samples from core WROX2 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 three weeks storage in sealed containers to allow radioactive equilibration. ^{137}Cs was measured by its emissions at 662keV. 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).

3.5 Biostratigraphy

Sub-fossil diatoms, Cladocera, ostracods and macrofossils were extracted and analysed using standard procedures (Berglund, 1986). Principal Components Analysis (PCA) was used to explore the main patterns of variation in the diatom and cladoceran 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).

4 Results

4.1 Radiometric Dating

The results of the radiometric analyses are given in Table 1 and shown graphically in Figure 2. ^{210}Pb activity significantly in excess of the supporting ^{226}Ra was detected only in the surficial sample (Figure 2a). In consequence it was not possible to date this core by ^{210}Pb using conventional methods.

The ^{137}Cs activity versus depth profiles (Figure 2b) has a sub-surface peak between 20-30 cm that almost certainly records the 1963 fallout maximum from the atmospheric testing of nuclear weapons. From the distribution of ^{137}Cs in the peak the best estimate of the 1963 depth is 27 ± 4 cm. Hence the mean post-1963 sedimentation rate is calculated to be 0.26 ± 0.04 g cm^{-2} y^{-1} (0.73 cm y^{-1}), significantly lower than the value of 0.37 ± 0.05 g cm^{-2} y^{-1} (1.3 cm y^{-1}) determined for an earlier (1995) core from Wroxham Broad (Bennion et al. 2001).

Although conventional ^{210}Pb dating was not possible at this site, using the relation:

$$C = P/r,$$

where P is the atmospheric ^{210}Pb flux, the surficial ^{210}Pb concentration C can be used to estimate the contemporary sedimentation rate r. From the mean annual rainfall (c.620 mm y^{-1}) it is estimated that the atmospheric ^{210}Pb flux is c.50 Bq m^{-2} y^{-1}. Since $C = 16.6 \pm 3.8$ Bq kg^{-1} (Table 1) the sedimentation rate r is calculated to be 0.30 ± 0.07 g cm^{-2} y^{-1}, in good agreement with the value determined from the ^{137}Cs record. It is thus reasonable to suppose that sedimentation rates at the core site have remained relatively constant throughout the past 40 years or so. Table 2 gives a chronology for this period based on this assumption.

Depth		^{210}Pb Total		^{210}Pb Unsupported		^{210}Pb Supported		^{137}Cs	
cm	g cm^{-2}	Bq kg^{-1}	±	Bq kg^{-1}	±	Bq kg^{-1}	±	Bq kg^{-1}	±
0.5	0.1	39.9	3.6	16.6	3.8	23.3	1.0	10.7	0.7
10.5	3.5	28.2	3.2	3.1	3.3	25.1	0.9	9.7	0.6
20.5	7.3	16.9	5.5	-2.8	5.6	19.7	1.3	14.1	1.1
30.5	10.9	27.9	4.8	-2.6	5.0	30.6	1.4	16.0	1.3
40.5	14.0	25.6	3.3	-0.1	3.4	25.7	1.0	3.5	0.5
50.5	17.2	21.8	6.0	2.7	6.1	19.1	1.3	4.0	1.1

Table 1. Fallout radionuclide concentrations in core WROX2

Depth		Chronology			Sedimentation Rate		
cm	g cm^{-2}	Date AD	Age y	±	g cm^{-2} y^{-1}	cm y^{-1}	± (%)
0.0	0.0	2000	0	0			
10.0	3.3	1987	13	3	0.26	0.8	15.4
15.0	5.2	1980	20	4	0.26	0.7	15.4
20.0	7.1	1973	27	5	0.26	0.7	15.4
25.0	9.0	1965	35	6	0.26	0.7	15.4
30.0	10.7	1959	41	7	0.26	0.8	15.4
35.0	12.2	1953	47	8	0.26	0.8	15.4
40.0	13.8	1947	53	9	0.26	0.8	15.4

Table 2. ^{210}Pb chronology for core WROX2

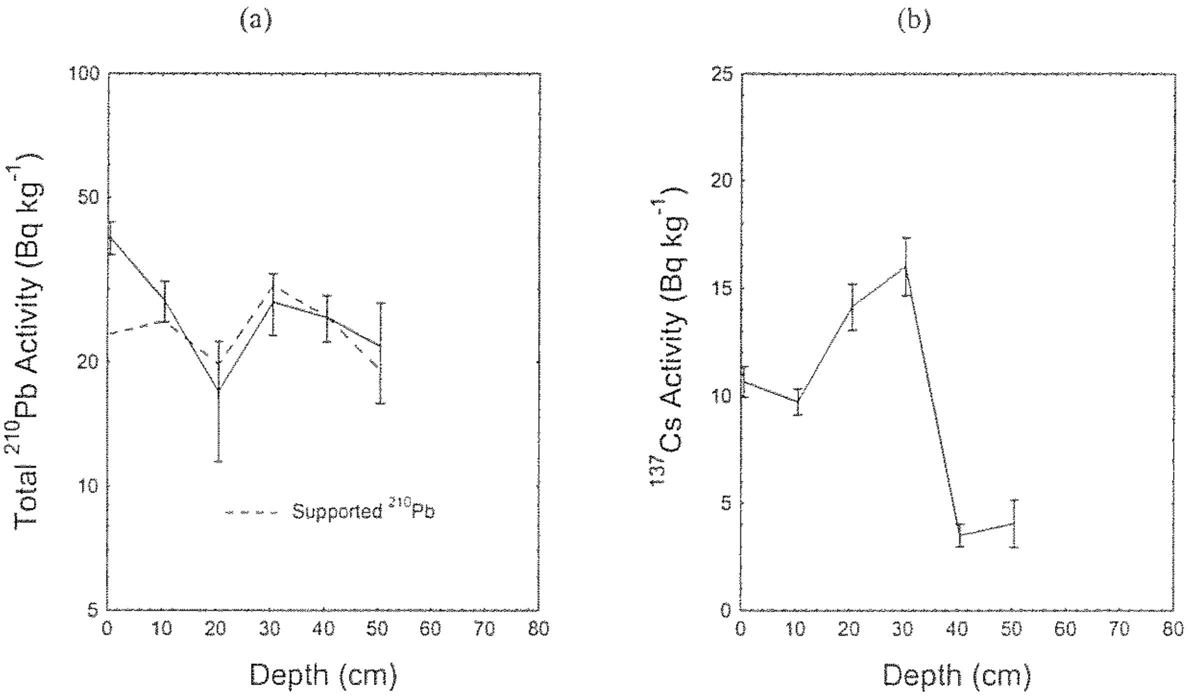

Figure 2. Fallout radionuclides in core WROX2 showing; (a) total and supported ^{210}Pb, and; (b) ^{137}Cs concentrations versus depth.

4.2 Organotin and heavy metal profiles

Organotin and heavy metal profiles for core WROX2 are given in Figure 3. TBT concentrations are high between 28-10 cm (dated 1962 ± 6 yrs - 1987 ± 3 yrs.), with levels constant at around 0.75 mg kg^{-1}, followed by a decline to the surface interface. The high TBT/DBT ratio indicates negligible post-burial degradation. Pb and Zn show very similar concentration profiles with a decline above 25-30 cm. Hg behaves differently with an earlier step-like decline matching the start of the TBT record. There is a sharp increase in Cu within the top 6 cm, which corresponds with the decline in TBT.

4.3 Biostratigraphy

Macrofossil remains of aquatic plants were sparse in the core as might be expected of an open water core site. All other sub-fossil remains were abundant and well preserved however. Figure 3 provides a summary of the diatom, cladoceran and fish scale data. The ostracod data (Appendix 1) are not commented on in this report as they are preliminary and require further analysis.

Substantial changes occur in the diatom, cladoceran and fish scale macrofossil groups in synchrony with the onset of the TBT signature. PCA axis scores show that diatom and cladoceran assemblages change markedly at this point (Fig. 3). In the diatom assemblages there is a decline in littoral *Fragilaria* taxa and of the planktonic species *Aulacoseira ambigua*, accompanied by an increase in several small centric planktonic species with differing seasonal preferences. In the cladoceran assemblages there is a marked reduction in littoral chydorid taxa (driven largely by the species *Alona guttata* and *A. rectangula*). At the same point, sedimentary fish scale data also suggest a shift towards the increased prevalence of cyprinid relative to percid fish.

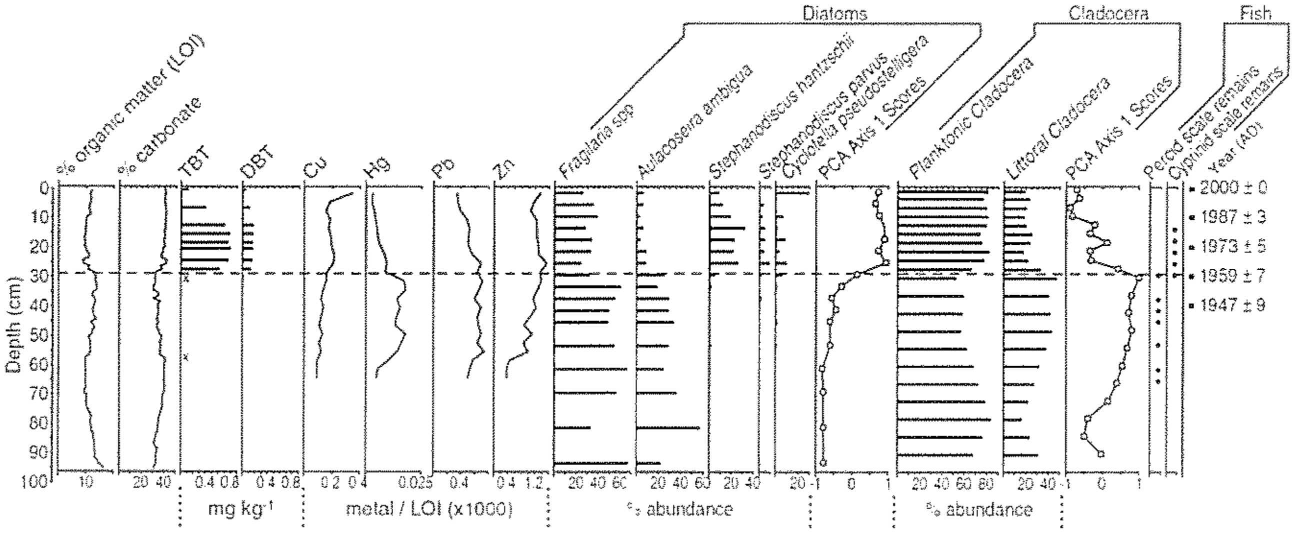

Figure 3. Summary butyltin (mg kg $^{-1}$), heavy metal (µg g^{-1}/LOI) and biostratigraphy for core WROX2 from Wroxham Broad. Heavy metals are expressed as loss-on-ignition (LOI) ratios and fish scale remains are expressed as presence/absence. The section of the core with measured levels of TBT is shaded.

5 Discussion and Conclusions

The measured TBT concentrations in the core are high compared to lake sediment measurements taken elsewhere in the world during the 1980s (Fent et al. 1991; Maguire et al. 1982), tailing off as expected after the 1987 ban. Exactly synchronous with the start of the TBT signature (c. 1962) diatom and cladoceran assemblages suggest a decline in plant-associated species and rapid changes in community structure. Such changes are indicative of the loss of submerged macrophytes and a shift to year-round phytoplankton dominance and are consistent with aerial photographic evidence for the dramatic loss of littoral vegetation from the surrounding area at this time (Fig. 1).

High TBT concentrations in the waters of the Norfolk Broads could have resulted in significantly reduced numbers of grazing snails (as evidenced from the surveys of Jackson (1999)) and large filter-feeding cladocerans (e.g. *Daphnia magna*). In turn this could have resulted in increases in periphyton and phytoplankton leading to a decline in light availability for macrophyte photosynthesis. The consequences of the loss of grazing macroinvertebrates are of particular importance given the critical role that these animals play in structuring freshwater communities (Jones et al. in press). Indirectly, therefore, TBT could have significantly depleted macrophyte beds.

Undoubtedly several factors may have acted to de-stabilise the Norfolk Broads during the 1960s, not least of which is progressive nutrient-enrichment. Similarly, in addition to TBT, a suite of toxic micro-pollutants (e.g. dioxins, organochloride pesticides and PCBs) may have exerted negative effects during this period (Moss, 2001). In shallow lakes, it is likely that the collapse of aquatic vegetation results from the 'stacking up' of different stresses and the critical stressor that leads to failure of the ecosystem need not always be the same one. It is significant, however, that, in the case of the Broads, nothing has been as directly linked to the disappearance of macrophytes as TBT.

Today, TBT may be a declining environmental issue. However, the replacement antifoulants currently in use within the Norfolk Broads contain high levels of Cu and a suite of 'booster biocides' (such as Irgarol 2051, Diuron, Zinc Pyrithone and Zineb) known to be extremely detrimental to aquatic organisms. The sharp rise in Cu within the top 6 cms of core WROX2 (Fig. 3) mirrors the TBT decline and may reflect the more recent introduction of this new generation of paints. There is clear need, therefore, to investigate the ecological effects of these new antifoulant additives which may also be exerting considerable pressure upon the Broadland ecosystem.

6 Future Research Needs

The results of this study highlight an urgent need for further research into the de-stabilising role that toxic micro-pollutants have played in the Norfolk Broads, including:

- Palaeolimnological analysis of additional sediment cores from different parts of the Broads system (including 'boated' and 'non-boated' control sites) to evaluate and replicate the Wroxham Broad results. These analyses should also include a broader range of toxic contaminants (organotin, pesticides, herbicides, PCBs, dioxins etc.).
- Analysis of surface sediments (upper 1 cm) across the Broads (rivers and lakes) system to determine contemporary toxic contamination and likely sources.

7 Acknowledgements

Thanks to James Quinn for drawing Figures 1 and 3. Thanks also to the Broads Authority for additional financial support and for site access. Photograph acknowledgements for Figure 1 are as follows: 9/7/1946 (© Crown copyright 1946); 27/7/1961 (© Copyright Aerofilms.com); 13/6/1969 (© Crown Copyright NC/01/25423); 16/8/1980 (Norfolk Museums & Archaeology Service; Photograph: Derek A. Edwards).

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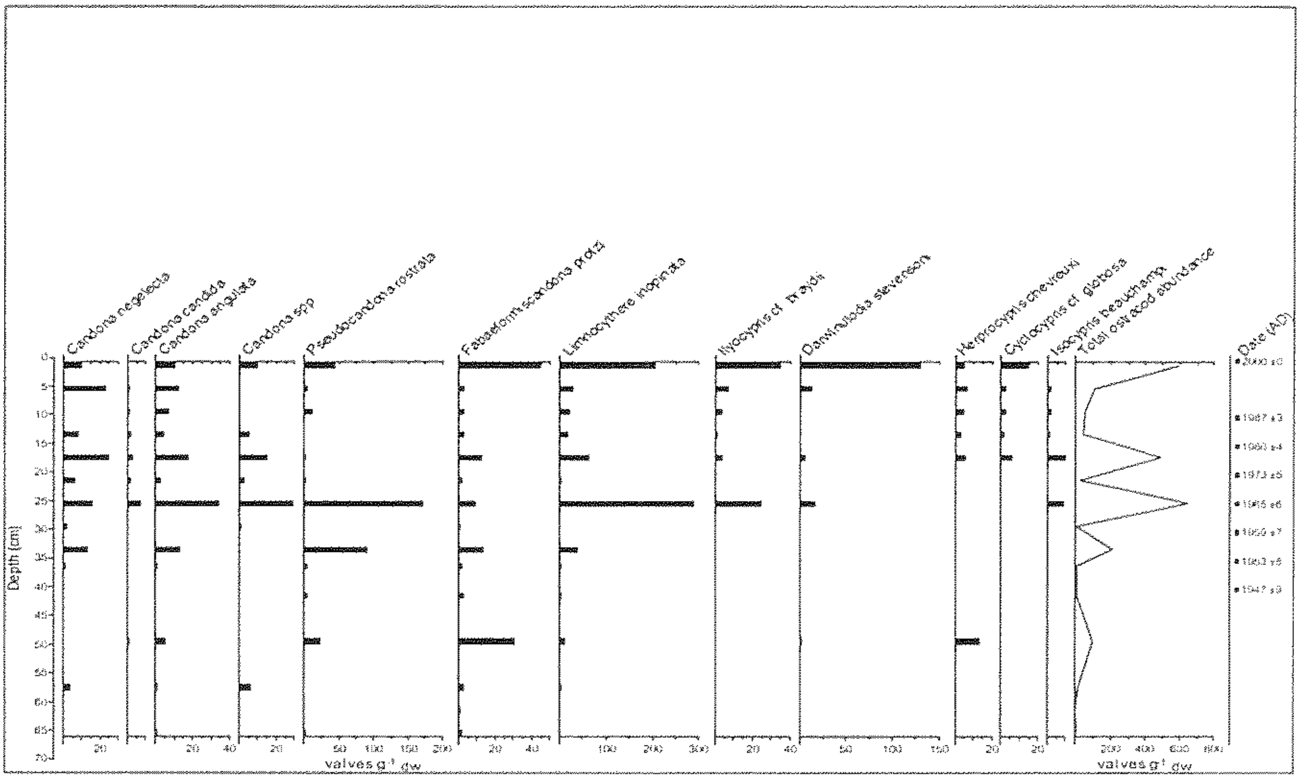
9 Appendices



Appendix 1. Summary ostracod sub-fossil stratigraphy for core WROX2