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Recent heavy metal contamination of the Thurne Broads

Report to the Broads Authority

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Cover photograph: Meadow dyke (photo: Carl Sayer 16th February, 2013)

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Background and Aims

The banning of tributyltin (TBT) from boat antifouling paints in the late 1980s led to its replacement by alternative biocide additives (Voulvoulis *et al.,* 2000; Marcheselli *et al.,* 2010), including Cu (Dahl & Blanck, 1996) and Zn as active ingredients. It has been reported that Cu and Zn compounds associated with these biocides have caused substantial contamination of harbour and marina sediments (Eklund *et al.,* 2010; Parks *et al.,* 2010), with negative toxic consequences for aquatic organisms (Ytreberg *et al.,* 2010). Indeed, it is evident that Cu and Zn compounds present in paint fragments are readily leached into the water column allowing entry into aquatic food webs (Jessop & Turner, 2011). Nevertheless, relatively little is known regarding antifoulant-derived metals contamination in freshwater lakes.

The Norfolk and Suffolk Broads (Eastern England, UK) have been contaminated by antifoulant-derived heavy metals, particularly Cu and Zn which have increased since the banning of TBT (post-1987) in parts of the boated system (Boyle *et al.,* in prep.). Further, recent studies suggest that current levels of sediment contamination by Cu may have negative ecological effects for aquatic ecosystems including inhibition of aquatic macrophyte germination and performance (Boyle *et al.,* submitted; S. Lambert, unpublished data).

In Hickling Broad (Thurne Broads system), post-TBT increases in Cu and Zn are also evident, with an interesting peak in Cu for the late 1990s in core HICK1 (Figure 1). This coincides with the large-scale loss of aquatic macrophytes (especially Characeae) from the lake in 1999 (Barker *et al.,* 2008). HICK1 was collected in 2003. In the proposed study we sought to gain a fuller understanding of recent metal contamination in Hickling Broad up to the present day, whilst looking to verify and better contextualise the late 1990s Cu peak. Further, we aimed to determine whether the peak in Cu for Hickling Broad was also recorded at Horsey Mere which is used as a control site in this study i.e. is it just a Hickling phenomenon? Or is it a Thurne Broads system-wide effect?

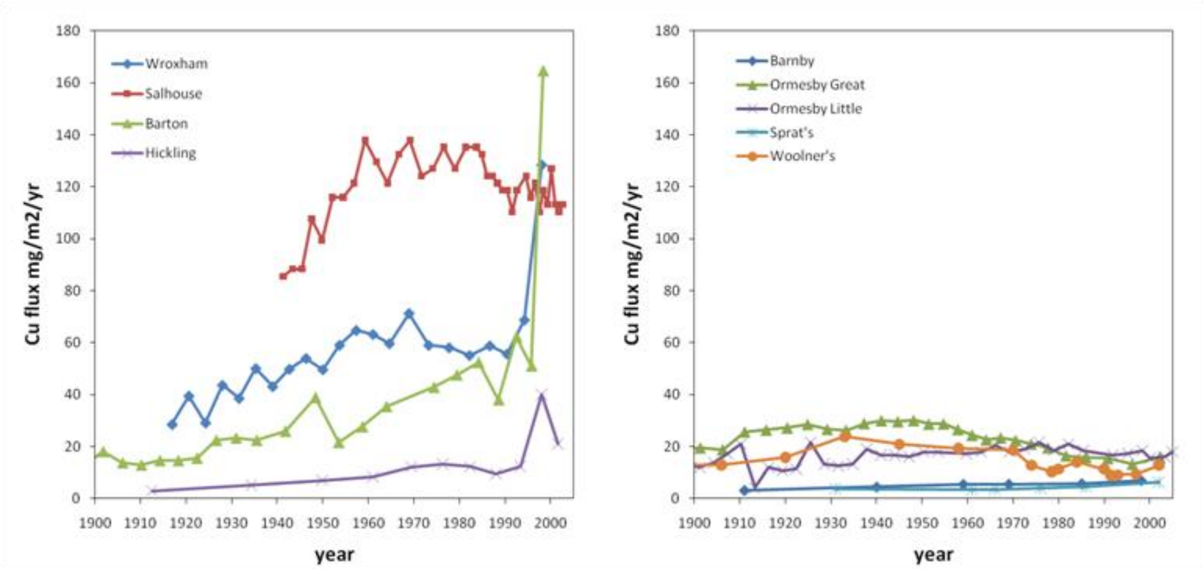

Figure 1. Cu fluxes in cores from the Norfolk Broads (sites to left are boated Broads and sites to right are non-boated Broads). This figure is derived from Boyle et al. (in prep).

Sites and Methods

On 16/2/2013 we collected five short (30-40 cm) “Glew” cores (Glew, 1991) from each of Hickling Broad and Horsey Mere respectively. The position of each core site was recorded using a GPS. One core from each broad was selected as a “master core” for sediment dating and for the analysis of TBT and PAH concentrations: core HICK3 collected from Heigham Corner in Hickling Broad (the same location as HICK1) and HORSEY3 collected from the centre of Horsey Mere. Colour changes with depth in the cores were determined in the field. All the cores were sliced at 0.5 cm intervals on 17/2/2013. Sub-samples for TBT and PAH analysis (work undertaken at Imperial College London under the supervision of Nick Vouvoulis) were taken at 1 cm intervals from both the master cores and immediately deep frozen. This report presents the data for master cores HICK3 and HORSEY3 and all other cores have been archived for potential future analysis in the UCL Department of Geography cold store.

Core details

Details on the collected cores including core codes, locations, lengths and water depths and are given in Table 1. The cores ranged from 20-45 cm in length and several of the cores from Hickling Broad extended to peat, including cores HICK3, HICK6 and HICK6.

Core	Location	Water depth	Core length (on collection)
HICK3 (Heigham Corner)*	**TG 41823 20941**	**107**	**32**
HICK4	**TG 41286 21405**	**135**	**30**
HICK5	**TG 41082 22053**	**116**	**30**
HICK6 (pleasure Boat Inn)	**TG 41252 22376**	**118**	**27**
HICK7	**TG 41807 21877**	**139**	**21**
HORSEY1	**TG 45069 22235**	**160**	**29**
HORSEY2	**TG 44792 22410**	**141**	**45**
HORSEY3 (centre)*	**TG 44794 22167**	**162**	**34**
HORSEY4	**TG 44673 22199**	**142**	**30**
HORSEY5	**TG 44901 22039**	**158**	**20**

Table 1. Locations for the sediment cores collected from Hickling Broad and Horsey Mere. Water depths and core lengths are also given. Master cores represented by *

LOI and metals analysis

Loss-on-ignition (LOI) analysis was performed on master cores HICK3 and HORSEY3 according to Dean (1974). Radiometric dating of cores HICK3 and HORSEY3 based on ^{210}Pb and ^{137}Cs analysis was undertaken following standard protocols (Appleby *et al.,* 1986) in the Bloomsbury Environmental Isotope (BEIF) laboratory at UCL. Sub-samples for metals analysis were freeze dried prior to analysis using Isotope source X-ray fluorescence analysis (XRF). XRF analysis was undertaken using a Bruker S2 Ranger energy dispersive XRF analyser at the University of Liverpool and calibration and quality control was based on a suite of 20 suitable certified reference materials. The data were normalised by dividing the concentration results by LOI (organic matter).

Sediment dating methods

Radiometric dating of master cores HICK3 and HORSEY3 based on ^{210}Pb and ^{137}Cs analysis was undertaken following standard protocols (Appleby *et al.,* 1986) in the Environmental Radiometric Facility at UCL.

Lead-210 (half-life is 22.3 year) is a naturally-produced radionuclide, derived from atmospheric fallout (termed unsupported ^{210}Pb). Cesium-137 (half-life is 30 years) and ^{241}Am are artificially produced radionuclides, introduced to the study area by atmospheric fallout from nuclear weapons testing and nuclear reactor accidents. They have been extensively used in the dating of recent sediments. Dried sediment samples from HORSEY3 and HICK3 cores were analysed for ^{210}Pb, ^{226}Ra, ^{137}Cs and ^{241}Am by direct gamma assay using ORTEC HPGe GWL series well-type coaxial low background intrinsic germanium detector. Lead-210 was determined via its gamma emissions at 46.5keV, and ^{226}Ra by the 295keV and 352keV gamma rays emitted by its daughter isotope ^{214}Pb following 3 weeks storage in sealed containers to allow radioactive equilibration. Cesium-137 and ^{241}Am were measured by their emissions at 662keV and 59.5keV (Appleby et al, 1986). The absolute efficiencies of the detector were determined using calibrated sources and sediment samples of known activity. Corrections were made for the effect of self absorption of low energy gamma rays within the sample (Appleby et al, 1992).

Results and Discussion

LOI data

Data for percentage dry mass and LOI for master cores HICK3 and HORSEY3 are given in Figure 2. In both cores LOI (organic matter) increases towards the sediment surface. The pattern of LOI change in HICK3 very closely matches that in HICK1 (see Sayer *et al.,* 2006; Holmes *et al.,* 2010) which was also collected from the Heigham Corner area of Hickling Broad. A common feature in the LOI profile for these cores is a rapid mid-core organic matter increase which occurs at 12.5 cm in HICK1 (corresponding to 1970 +/- 4 yrs) and at 15.5 cm in HICK3. This sediment feature will be useful for future analysis of cores from Hickling Broad, especially when it comes to sediment dating.

Sediment dating for core HORSEY3

Equilibrium of total ^{210}Pb activity with the supported ^{210}Pb occurs at around 10 cm in the core (Fig. 3a). Unsupported ^{210}Pb activity, calculated by subtracting ^{226}Ra activity (as supported ^{210}Pb) from total ^{210}Pb activity, declines irregularly with depth (Fig. 3b). In particular there is a rapid decline below 9 cm potentially suggesting a major change in the source of sediment to the core site.

^{137}Cs activity versus depth shows a poorly resolved peak at 8.25 cm (Fig. 3c). Since ^{137}Cs activities are low and similar over 6.5-8.5 cm, it is not possible to confidently assign a depth for the 1963 fallout maximum from the atmospheric testing of nuclear weapons.

Use of the CIC (constant initial concentration) model was precluded by the non-monotonic variation in unsupported ^{210}Pb activities. ^{210}Pb chronologies were calculated using the CRS (constant rate of ^{210}Pb supply) dating model (Appleby and Oldfield, 1978). The CRS dating model places the 1963 depth in 6.8 cm, in the section with relatively high ^{137}Cs activities, suggesting the radiometric chronologies are reasonable. Sedimentation rates exhibit a gradual increase from the 1880s to the 1970s, following by further increased sedimentation rates in recent years, which are about ten times of those in 100 years before.

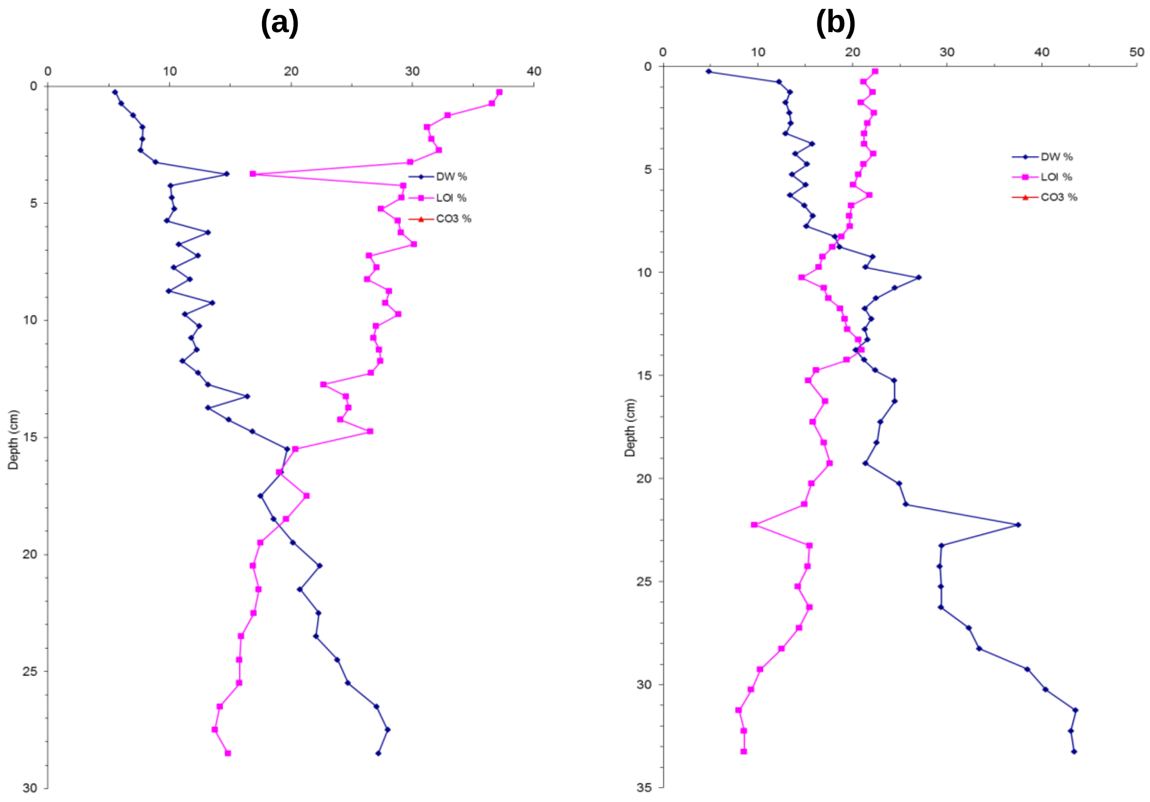

Figure 2. Loss-on-ignition data for core HICK3 from Hickling Broad (a) and core HORSEY3 from Horsey Mere (b).

Sediment dating for core HICK3

Total ^{210}Pb activity reaches equilibrium with the supported ^{210}Pb activity at a depth of c. 26 cm in the core (Fig. 5a). There is little net decline of unsupported ^{210}Pb activitiy in the top 12.5 cm, and maximum unsupported ^{210}Pb activity is below the surface sediment (Fig. 5b), suggesting an increase in the sedimentation rates in recent years. Over 12-17 cm unsupported ^{210}Pb activity decline more or less exponentially with depth, indicating relatively uniform sedimentation rates within this section.

Artificial Fallout Radionuclides

The ^{137}Cs activity versus depth shows some small poorly resolved peaks between 8 and 19 cm (Fig. 5c). The ^{137}Cs profile of the core is poor for dating, however, the 1963 depth of fallout maximum from the atmospheric testing of nuclear weapons likely occurs over 8-19 cm.

Because of non-monotonic variation in unsupported ^{210}Pb activity, the chronology for HICK3 was also calculated using the CRS model. The CRS dating model places 1963 at a depth of 12.5 cm - the section suggested by the ^{137}Cs record. Sedimentation rates show that apart from the 1930s, rates are relatively uniform with a mean at 0.03 g cm^{-2} yr^{-1} before the 1980s, although sedimentation has increased (more than 2-fold) in the last ten years or so.

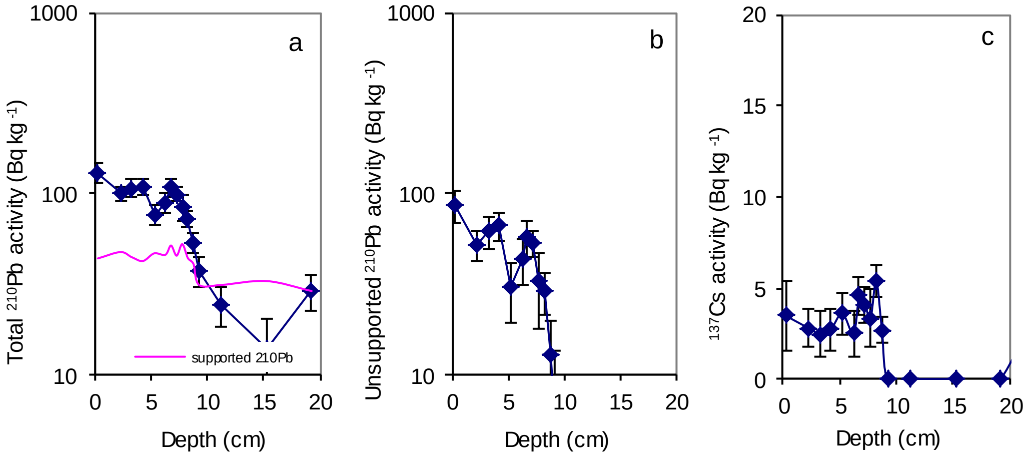

Figure 3. Fallout radionuclide concentrations for core HORSEY3 collected from Horsey Mere, England, showing (a) total ^{210}Pb, (b) unsupported ^{210}Pb and (c) ^{137}Cs concentrations versus depth.

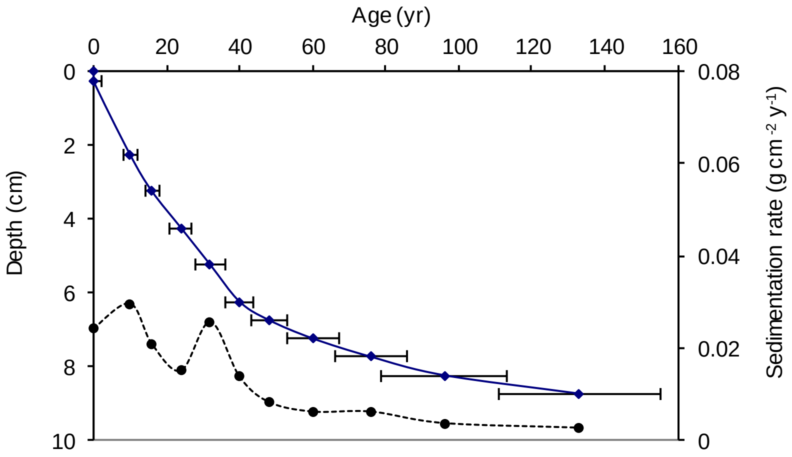

Figure 4. Radiometric chronology of core HORSEY3 collected from Horsey Mere, England, showing the CRS model ^{210}Pb dates and sedimentation rates. The solid line shows age while the dashed line indicates sedimentation rate.

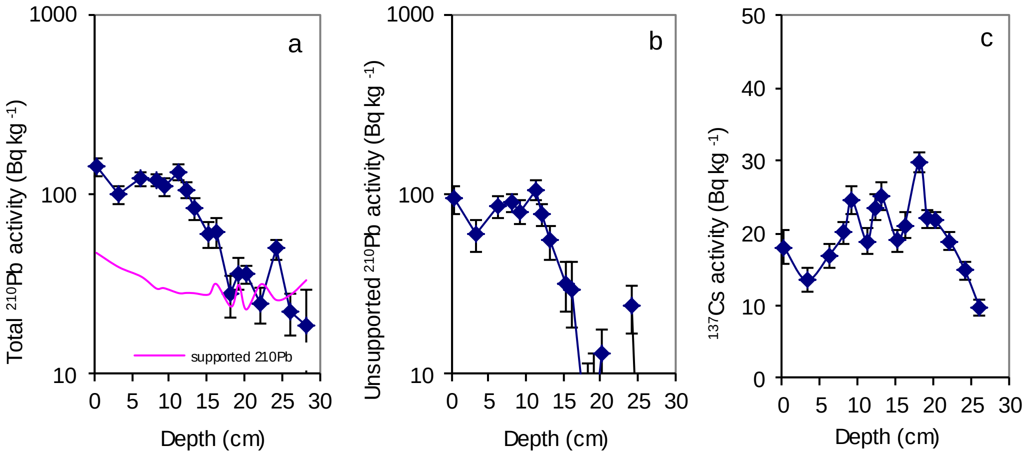

Figure 5. Fallout radionuclide concentrations in core HICK3 collected from Hickling Broad, England, showing (a) total ^{210}Pb, (b) unsupported ^{210}Pb and (c) ^{137}Cs concentrations versus depth.

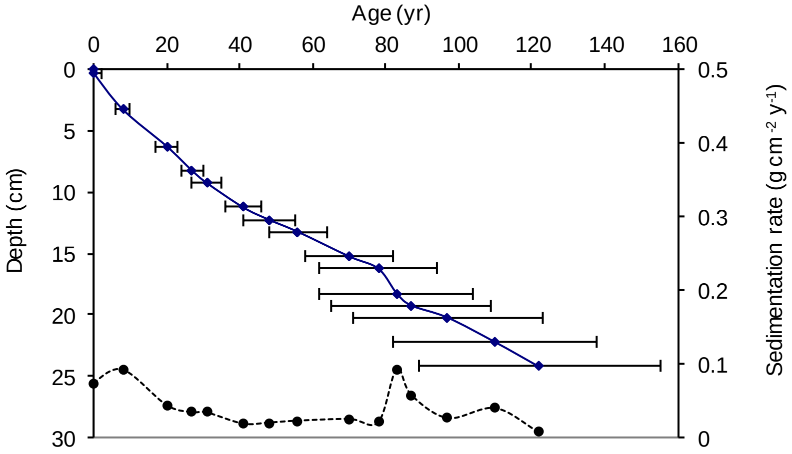

Figure 6. Radiometric chronology of core HICK3 collected from Hickling Broad, England, showing the CRS model ^{210}Pb dates and sedimentation rates. The solid line shows age while the dashed line indicates sedimentation rate.

Metals data

Data exists for several metal species for cores HICK3 and HORSEY3, but only Cu and Zn (major anti-foul constituents) are plotted here.

HICK3 (Fig. 5) shows growing Cu enrichment since about 1940, with a step increase that occurs between the late 1960s and early 1980s. However, in contrast to HICK1, there is no mid 1990s Cu enrichment. HORSEY3 shows no clear 20th century Cu contamination signal. It does, however, show a small surficial Cu enrichment (Fig. 3) in the uppermost sample. This is probably associated with Cu cycling in the lake rather than evidence for a change in external supply. Zn (Fig. 6) shows a similar pattern to Cu, except that there is no surface enrichment in HORSEY3.

The absence of a 1990s metal enrichment from HICK3, when such an enrichment was prominent in HICK1, is consistent with several different explanations. First, it is conceivable that widespread recent Cu and Zn enrichment is present in Hickling Broad but absent from HICK3. Local sediment erosion is not uncommon in shallow lakes. However, this must be regarded as unlikely, as the ^{210}Pb profiles of HICK1 and HICK3 are very similar; this would not be expected if 20-25 years of recent sediment was missing from the latter. Second, it may be that the Cu and Zn enrichment seen in the post 1990 sediment of HICK1 did not in fact represent permanently buried sediment, but rather temporary enrichment of the surface sediment that was subsequently lost to the water column. Such enrichments are observed most commonly in deep lakes, where exchange between the water column and the sediment can represent a considerable amount of metal. This is clearly not the case at Hickling Broad, but there is instead scope for lateral migration of Cu and Zn, both of which are abundantly present. We may ask why temporary enrichment was seen in HICK1 but not HICK3? It is possible that this represents a change in the system, but it is also possible that neither core is representative of the water body for the corresponding time periods, temporary enrichment being variable in both space and time. In other words, temporary Cu and Zn enrichment may be no less likely now than 20 years ago, despite the sediment record evidence. And, such an enrichment can occur with or without pollution enhanced Cu or Zn fluxes; so the surface Cu enrichment is HORSEY3 need not be seen as evidence for pollution.

Regardless of the circumstances around the temporary Cu and Zn peaks, the absence of an enrichment signal in the upper sediment of HICK3 rules out an abrupt increase in Cu and Zn loading during the last few decades. This argues against elevated use of Cu and Zn-based antifouling paints following the TBT ban. However, it is also clear that both Cu and Zn increased in concentration during the period c. 1940 to ca 1960 at Hickling Broad, evidence present in both HICK1 and HICK3, rising in parallel with growing boat usage. From c. 1990 we have evidence for reduced TBT contamination of the sediment; here we see no sign of reduced Cu and Zn contamination. Continued contamination of Hickling Broad by Cu and Zn from antifouling paints is therefore likely.

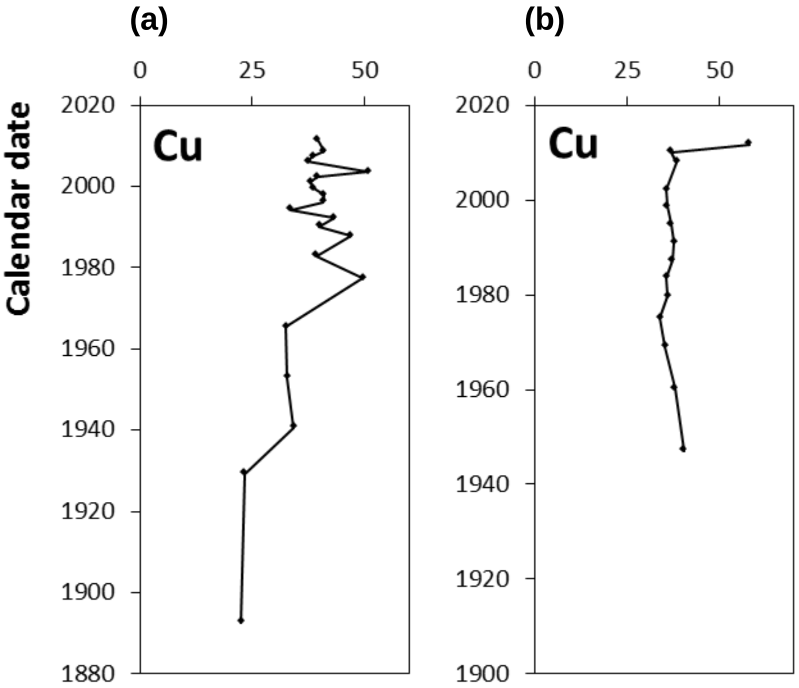

Figure 7. Cu concentrations plotted against sediment age (Calendar years) in cores HICK3 (a) and HORSEY3 (b).

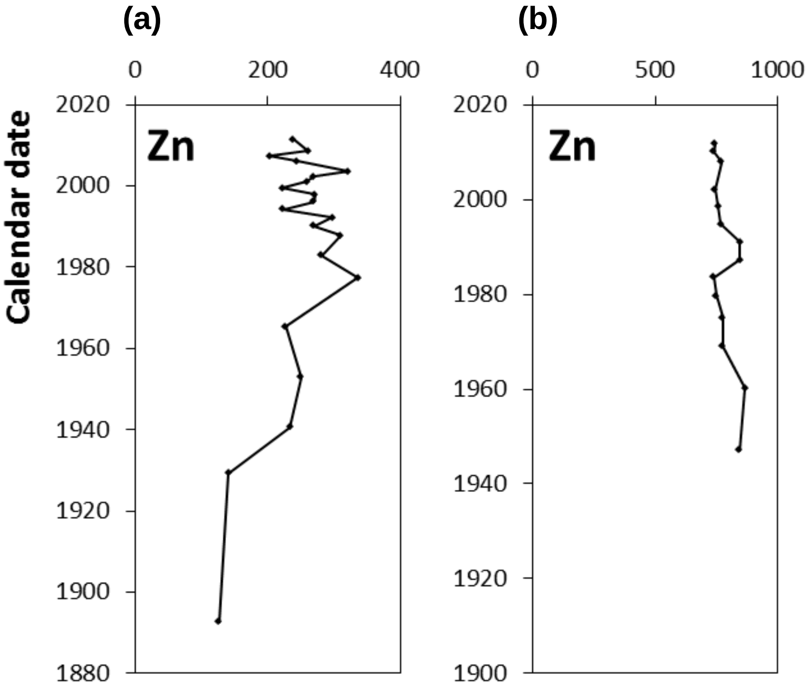

Figure 8. Zn concentrations plotted against sediment depth (cm) in cores HICK3 (a) and HORSEY3 (b).

Conclusions and recommendations

We examined lake sediment records from Hickling Broad and Horsey Mere for contamination by Cu and Zn, to assess their occurrence and potential for causing environmental harm in these important freshwater ecosystems. Our data from Horsey Mere fail to show a clear 20th century Cu/zn contamination signal. By contrast, the results, from Hickling Broad (cores HICK1 and HICK3), consistent with data from other lakes in the Broads system (Boyle *et al.,* submitted), reveal increases in Cu and Zn contamination in tandem with increases in boating activity since the mid-twentieth century and undoubtedly driven by use of antifouling paints. Further, and importantly, no evidence is available for a decline in Cu and Zn pollution since TBT-based antifouling paints were banned in 1987 – contamination has clearly continued unabated. We consider it likely that present day exposure of the Broads ecosystem to antifouling paint derived metals (especially Cu) may be sufficient to cause ecological harm. If so, then current regulations banning only TBT-based antifouling paints do not provide adequate protection to the Broads ecosystem.

We recommend further research be undertaken which examines the potential ecological effects of Cu-contamination in the boated Broads. We also recommend that more cores are analysed for metals (the 8 unanalysed cores collected during this study have been archived in the UCL coldstore) so that spatial patchiness in metals signals can be characterised and our results better interpreted. This may be particularly useful in Horsey Mere, to check whether HORSEY3 is representative of the lake in general.

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