

Sediment Heavy Metals Record and Historical Boating in the Broads
Report by Senior Ecologist

Summary: This paper summarises the recent research commissioned and supported by the Broads Authority over the past 15 years. Working with Severn Trent Laboratory and universities (University of East Anglia (UEA), Cambridge University, Imperial College London (ICL) and University College London, (UCL)) the Broads Authority has investigated the impact of heavy metals such as tributyltin (TBT), Copper (Cu) and Zinc (Zn) used as biocides in antifouling paint on the Broads aquatic ecosystem. This research, which has resulted in peer reviewed papers, has been influential in informing the Authority's policy and strategic conservation direction with regards to ecoboating and informing antifoulant use in the Broads. This evidence-based approach is central to the 'Improving our knowledge to enable a stronger evidence based approach to habitats and species management' objective of the Broads Biodiversity and Water Strategy (2013). By having this high quality of evidence of the impact of now banned pollutants, such as TBT, has facilitated the Broads Authority's important work on education work with boating business and the some 13,000 registered boat owners on the Broads.

1 Context

- 1.1 The banning of TBT in 1987 from boat antifouling paints led to its replacement by alternative biocide including Cu and Zn. Cu and Zn compounds 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.
- 1.2 The research commissioned by the Broads Authority shows that the Broads have been contaminated by antifoulant-derived heavy metals, particularly Cu and Zn which have increased since the banning of TBT in parts of the boated system. In addition, recent unpublished studies suggest that current levels of sediment contamination by Cu may have negative ecological effects for aquatic ecosystems including inhibition of aquatic macrophyte germination and performance (Boyle *et al.*, in prep; S. Lambert, unpublished data).

- 1.3 The theory of 'alternative stable states' sets out the well documented principle of lake ecosystems being able to tolerate the pressure of increasing nutrient input (eutrophication) until a switch, such as increasing pollution from heavy metals or extreme weather event causes a shift to an algal dominated state. A reversal to clear water and plant dominated state can also occur via alternation of the fish community for example (Kelly, 2008).

Year	Research	University / Contractor
2006	Spatial distribution of contaminants across the Broads rivers and lakes	Severn Trent Laboratory (STL)
2012	Spatial distribution of contaminants across the Broads rivers and lakes	Imperial College London (ICL)
Various	Various sediment cores dated and analysed for heavy metals	University College London (UCL)
2007	PhD investigation into the concentration of TBT in the sediments in isolated and connected broads and the link between TBT and ecological change in the Broads.	University College London (UCL)
2007	PhD investigation into the ecology of stoneworts (water plants sensitive to pollution)	University of East Anglia (UEA)
2012	Investigation of the concentrations of dissolved metals in sediments of the Thurne Broads	University of East Anglia (UEA)
2014 (in draft)	Recent heavy metal contamination of the Thurne Broads	University College London (UCL)
2009	Bivalves as Biomonitors of Freshwater Pollution	University of Cambridge
2012	An investigation of polycyclic aromatic hydrocarbon (PAH)* contamination in sediments of the Broads <i>Note: Related study not part of this paper on heavy metals</i> * PAH's are products of the incomplete combustion of organic material (e.g. fuel)	Imperial College London (ICL)

Table 1. List of Broads Authority Commissioned and Supported Heavy Metal Research

2 Results

- 2.1 *Spatial distribution of contaminants across the Broads rivers and lakes* Data from Severn Trent Laboratory (STL), used to inform the Broads Sediment Management Strategy, and Imperial College London (ICL) studies provided a systematic assessment of the TBT and Cu in the Broads sediment. TBT levels were compared to published sediment quality guidelines shows levels exceeded the lower limit at which further assessment is recommended and may still poses a threat to the aquatic ecology (Raven, 2012). These guidelines however do not take into account the reduced bioavailability of TBT due to adsorption onto organic matter and variation with sediment depth, and may be quite conservative.
- 2.2 Release of TBT from the sediment can result from resuspension and is may be increased by dredging activity in the short term, although the desorption rate from suspended matter is unknown.
- 2.3 Cu was significantly correlated with boat density and boatyard proximity suggesting that boat antifoul paint is an important source. Cu in sediment thought not to pose a severe hazard to most aquatic biota across the Broads (although some species may be more sensitive such as stonewort's) although around boatyards some samples exceeded the threshold where adverse effects are possible.
- 2.4 *Heavy metals in boated and non-boated broads*
Results showed a strong association between the history of TBT use and the sediment TBT record, including sharp reduction following the ban. This has been well documented (Sayer *et al*, 2006)

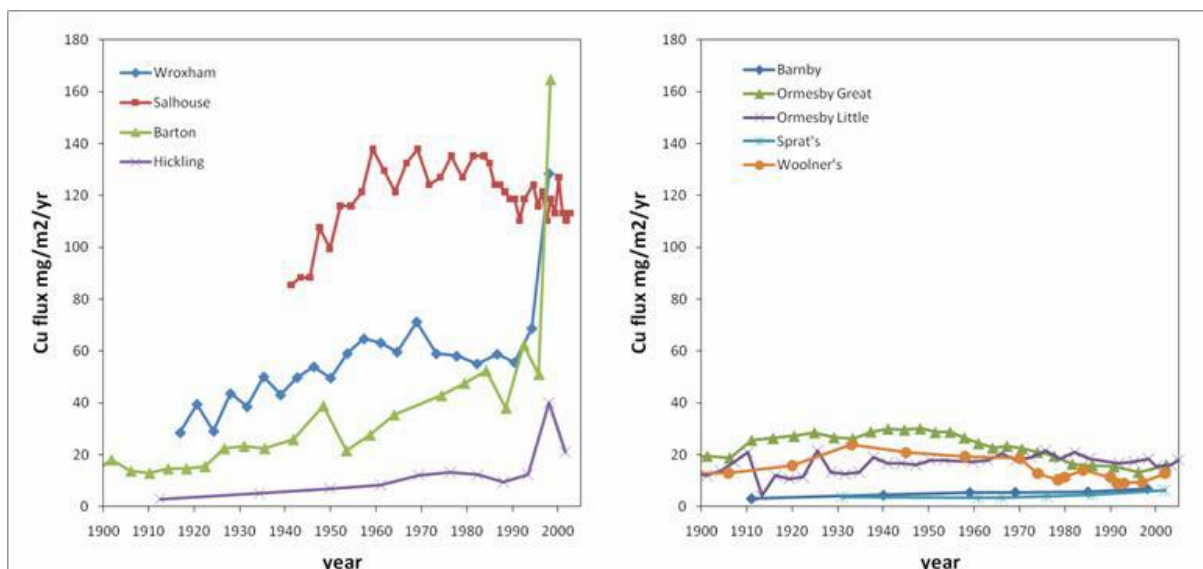


Figure 1. Copper (Cu) fluxes in cores from the Broads (sites to left are boated Broads and sites to right are non-boated Broads). Diagram from Boyle *et al.* (in prep).

- 2.5 Results shows that Cu concentrations have increased over time at the boated sites. At the lightly/non-boated sites, for example Ormesby Great and Little on the Trinity Broads (Figure 1), it rises early, but then levels out or fall. The data on Cu shows that overall there is not much difference due to boating, though Cu is higher post 1950. The peaks at the surface are not showing an increase in supply but they represent cycling processes in the sediment.
- 2.6 In Hickling Broad, post-TBT increases in Cu and Zn are also evident, with an interesting peak in Cu for the late 1990s (Figure 1). This coincides with the large-scale loss of aquatic macrophytes in Hickling Broad (especially stoneworts) from the lake in 1999 (Barker *et al.*, 2008).
- 2.7 Zn shows a similar profile to Cu, though with less marked reduction in Zn at the lightly/non-boated sites.
- 2.8 Lead (Pb) is different from Cu and Zn. Lead is more of an indicator of general pollution that is unrelated to boating. Lead is somewhat higher at the boated sites (which are, after all close to settlements), but with similar pattern through time at all sites. General peaks early to mid 20th Century, and then falls.

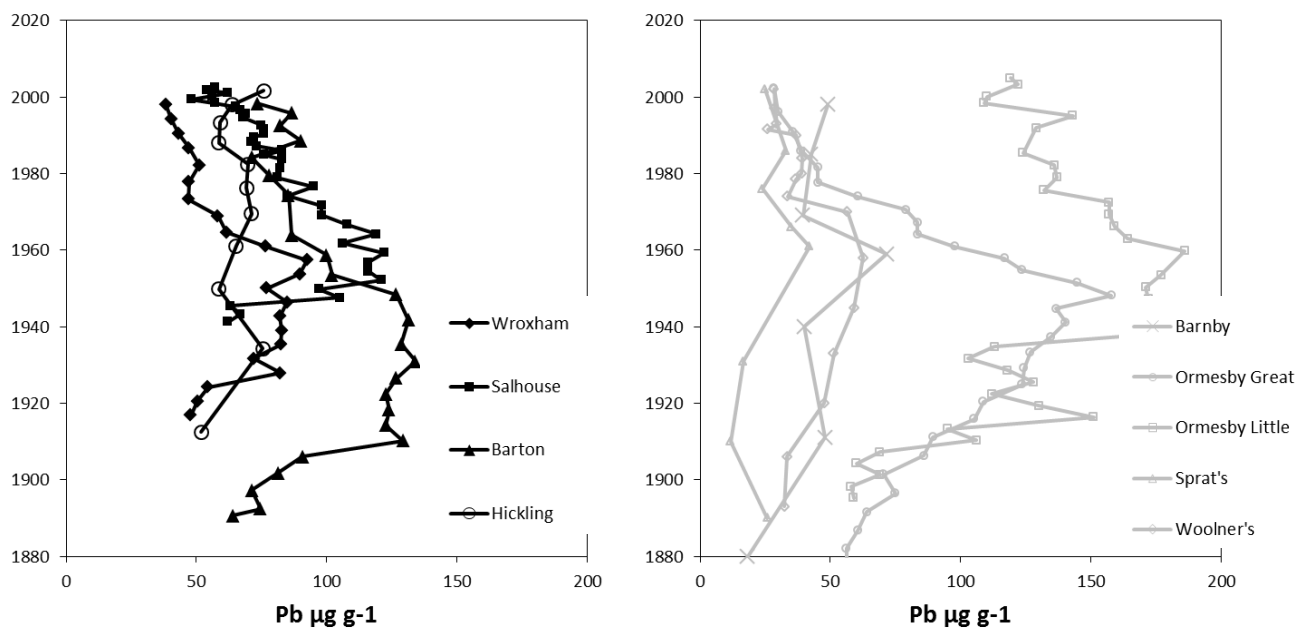


Figure 2. Lead (Pb) fluxes in cores from the Broads (sites to left are boated Broads and sites to right are non-boated Broads). Diagram from Boyle *et al.* (in prep).

- 2.9 These previous points are emphasised in these scatter plots (Figure 3). At the lightly boated sites, Cu correlates with lead both before and after 1950. This indicates that the Cu inputs are likely to be unrelated to boating. At Barton, and the other boated sites, the relationship between Cu and lead is the same before 1950 but very different after. Cu continues to rise, while lead falls. It is this excess of Cu that is linked to boating.

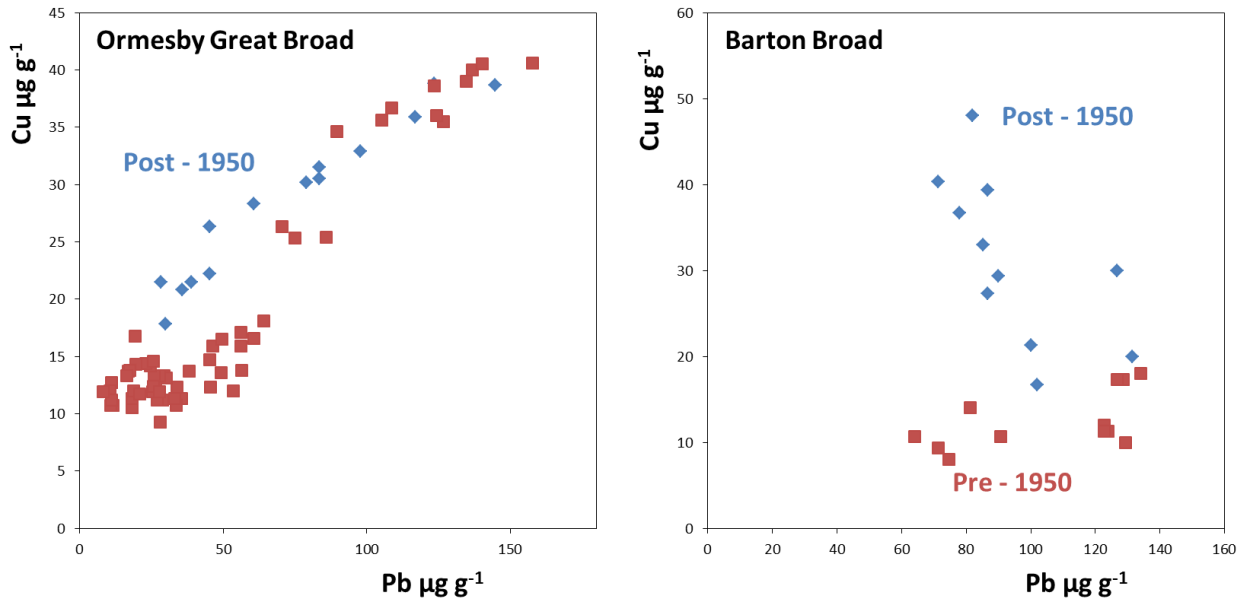


Figure 3. Relationship between Copper (Cu) and Lead (Pb) fluxes in cores from the Ormesby and Barton Broads (Ormesby is non-boated and Barton is boated). Diagram from Boyle et al. (in prep).

2.10 The Hickling core shown here was collected in 2003, so further work has been commissioned by the Broads Authority to gain a fuller understanding of recent metal contamination in Hickling Broad. Although the 2003 data alone verifies and better contextualise the late 1990s Cu peak. In addition, the Broads Authority commissioned sediment from Horsey Mere to be assessed to provide a greater context for the Thurne Broads. The report is yet to be finalised, however the Cu and Zn data from Hickling and Horsey show similar levels to that found in 2003.

2.11 *Impact of heavy metals*

The impacts of TBT on the marine system and the freshwater ecosystem of the Broads have been negative and well documented.

2.12 Cu and Zn are also heavy metals which if in sufficient concentration are toxic. Recent, but unpublished 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., in prep; S. Lambert, unpublished data).

2.13 *Bivalves as Biomonitors of Freshwater Pollution*

Deformations in shells of the Asian Clam have been found in the current day Broads and the fossil record. A study from Cambridge university has shown that contaminants in the soft tissue suggest that TBT and other heavy metals do not play a role in shell deformations.

3 Conclusions from this research

- The spatial distribution of contaminants across the Broads rivers and lakes show that the heavy metals Copper, Zinc and tributyltin are greater at concentration closer to boat yards.

- The heavy metals records show excess Copper and Zinc at boated compared with lightly/non-boated sites
- Copper and Zinc rise with tributyltin close to 1960
- In the 1990s tributyltin fall, but excess Copper and Zinc remain high.

4 Awareness raising and Best Practice

4.1 Cu and Zn remain as an active ingredient for commonly used antifouling paint. As a consequence of the research the Broads Authority has commissioned, as well as media coverage (among other articles - The Times "*Boat paint to blame for Norfolk Broads' desolation*" 1 page, The Telegraph "*Barnacle paint destroyed Norfolk Broads*" 1 page, The Guardian "*Boat paint clue to lakes havoc*" 1/2 pages) the Broads Authority initiated a campaign to promote environmentally-friendly antifoulant use in the Broads system; such as its leaflet Greener and Cleaner, along with promoting the The Green Blue's information see: <http://www.thegreenblue.org.uk/> which is endorsed by the Royal Yachting Association and British Marine Federation.

4.2 Some additional examples of best practice are outlined below:

4.2.1 Broads Authority

The Broads Authority have provided extensive advice to boaters on best practice and have worked with The Green Blue to produce guidance to all boaters in the form of regular reminders to boaters in its publications.

4.2.2 The Broads Authority has undertaken investigation of the fouling environments present in all the Broads rivers. Informed with this information, and following trials with various products all Broads Authority vessels are treated with environmentally friendly products. This means that no herbicides, fungicides or heavy metals (copper, zinc, tin) are applied. The products used include: Epifanes Foul-Away, a peroxide-base paint; Sea Jet, a silicon-based coating, which has lasted four seasons without recoating. The large vessels use a general hard wearing marine paint. Further information on these products and their use can be given by Dan Hoare, Environment & Design Supervisor at the Broads Authority.

4.2.3 The Broads Authority have also used some of the evidence of Cu and Zn in the boated and non-boated broads to communicate to yards and customers of the levels of these chemicals. A simple display of the information on heavy metals, along with what people can do to avoid polluting the Broads has also been presented at the 2013 Green Boat Show event in the Broads.

4.2.4 Boatyards

A few boatyards have invested in innovative systems to remove any impact of antifouling entering the waterways following routine pressure washing. Gallyon Mooring and Storage at Beccles, , has invested in a closed loop washdown system that filters the washdown water as well as investing in dry storage to minimise the need for antifouling. This washdown facility was supported by the Broads SDF. Coxes Boatyard has invested in a similar closed loop washdown system and other boatyards are likely to follow, such

as Brundall Gardens Marina. Simple collection of particles and avoiding them going into the waterways may be being practiced by other boatyards that the Broads Authority may not be aware of.

5 Recommendations for Future Work

- Continue to monitor the concentrations of heavy metals as required and support research to confirm their impact on sensitive aquatic species
- Work with boat yards, boat hire companies and boat owners to increase the use of environmentally friendly products
- Work with boat yards to reduce the inputs of wash down water that may contain herbicide, fungicide or metal-based antifoulants
- Work with boat yards on the sustainable management of sediments to reduce the risk from high concentrations of pollutants near boat yards
- Continue partnership work with the Royal Yachting Association, British Marine Federation, Broads Hire Boat Federation to share knowledge in the Broads and promote best practice

- References:** Barker T, Hatton K, O'Connor M, Connor L, Bagnell L. & Moss, B (2008) Control of ecosystem state in a shallow, brackish lake: implications for the conservation of stonewort communities. *Aquatic conservation: marine and freshwater ecosystems* **18**: 221-240.
- Boyle JF, Sayer CD, Hoare D, Heppel K & Lambert S (in prep.) Cu and Zn contamination of shallow lakes by boat antifouling paint inferred from palaeolimnology. *Environmental Science & Technology*.
- Jessop A. & Turner A (2011) Leaching of Cu and Zn from discarded boat paint particles into tap water and rain water. *Chemosphere* **83**: 1575-1580.
- Eklund B, Elfström M, Gallego I, Bengtsson, B-E. & Breitholtz M (2010) Biological and chemical characterization of harbour sediments from the Stockholm area. *Journal of Soils & Sediments* **10**:127-141.
- Kelly A, (2008) Lake Restoration Strategy. Broads Authority report.
- Parks R, Donnier-Marechal M, Frickers PE, Turner A. & Readman JW (2010) Antifouling biocides in discarded marine paint particles. *Marine Pollution Bulletin* **60**:1226-1230.
- Raven J, (2012) Tributyltin and copper in the norfolk broads: an assessment of antifouling biocide contamination in shallow lake sediments. Msc thesis, Centre For Environmental Policy, Imperial College London
- Sayer, C et al (2006) TBT Causes Regime Shift in Shallow Lakes. *Environ. Sci. Technol.*, 40, 5269-5275
- Ytreberg E, Karlsson J. & Eklund B (2010) Comparison of toxicity and release rates of Cu and Zn from anti-fouling paints leached in natural and artificial brackish seawater. *Science of the Total Environment* **408**: 2459-2466.

Author: Andrea Kelly
 Date of report: 10 July 2014

Broads Plan Objectives: BD2, BD3.2

Appendices: None