Sediment and Stream Water Quality in a Changing Environment: Trends and Explanation
(Proceedings of the Vienna Symposium, August 1991) IAHS Publ. no. 203, 1991.

LAKE SEDIMENTS: A SURROGATE MEASURE OF SEDIMENT ASSOCIATED HEAVY METAL TRANSPORT IN FLUVIAL SYSTEMS?

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ABSTRACT Records of atmospheric and catchment derived heavy metal pollution are contained in sediments accumulating in lakes and reservoirs. Two problems exist in utilizing the lake sediment record as proxy hydrological data. The first concerns accurate quantification of heavy metal flux through time; the second relates to the methods which might be used to distinguish the atmospheric and fluvial derived metal influx to the lake sediment. This paper considers these problems in relation to Zn enriched lake sediments in three regions of the UK.

INTRODUCTION

Heavy metals are released into the environment as a result of natural and anthropogenic processes (Forstner & Wittmann, 1983). Anthropogenically derived metals enter the fluvial system from both point and diffuse sources. Point sources include industrial discharges and sewage treatment works whereas diffuse sources include atmospherically transported material delivered to the catchment by dry and wet deposition. In the UK, as in many other parts of the world, long term records of sediment-associated and dissolved heavy metals in river waters are not available. In consequence, attempts have been made to derive information on heavy metal contamination through time by reference to the changing concentration and/or metal accumulation rates in lakes and reservoirs. In some situations, the heavy metal record is associated with particular forms of catchment disturbance, such as mining or industrial pollution (Baudo *et al.*, 1989; Dearing, in press) whilst in others the metal record is dominated by atmospheric pollution (Foster & Dearing, 1987; Battarbee, 1988; Verta *et al.*, 1989). Other studies have found that the metal record reflects a combination of atmospheric and catchment sources which may be difficult to quantify independently (Johnson & Nicholls, 1988; Foster *et al.*, in press).

In order that lake sediments may be used to provide a historical record of pollutant loading, Alderton (1985) argued for the necessity of three preconditions: (1) the pollutant must have an affinity for the sediment; (2) once deposited, pollutants should not degrade or remobilize; and (3) the sedimentary record must not be disturbed after deposition. All of these requirements have, to a greater or lesser extent, been falsified by empirical studies yet, in the absence of suitable alternatives, the lake sediment record probably provides the most complete long term record of the history of pollutant loadings from drainage basin processes available to date. It is not the purpose of this paper to repeat the arguments relating to these three issues, but to examine the hydrological benefits, assumptions and requirements in utilizing the lake sediment record as a source of hydrological proxy data on sediment associated metal transport with reference to 3 regions in the UK.

FIELD STUDIES

Field sampling has been undertaken in rural lakes and reservoirs remote from local and regional sources of atmospheric pollution and with no direct catchment sources of metal contamination (Isles of Scilly, SW England); in rural locations in close proximity to, and downwind of, Midland England industrial conurbations, again with no direct catchment sources of metal contamination (North Warwickshire); and in urban lakes which have both atmospheric and catchment sources of metal contamination (Coventry). These sites have been specifically selected in order to illustrate some of the problems in providing a hydrological interpretation of the lake sediment heavy metal record. Regional locations are given in Fig. 1A and site details in Table 1. Two of the lakes sampled have no channelled inflow, Big Pool, Isles of Scilly and Swanswell Pool, Coventry. The other 4 lakes possess channelled inflows, but sedimentation rates in Merevale lake are known to have remained fairly constant over the last 130 years (Foster *et al.*, 1985). For each of the three areas, therefore, the sampling scheme has been designed to independently assess catchment and atmospheric metal contamination using paired lake-catchments. Absolute radiometric chronologies based on ^{210}Pb and ^{137}Cs are, as yet, only available for the two North Warwickshire Lakes.

TOWARDS A HYDROLOGICAL INTERPRETATION

In most paleolimnological studies, lake sediment cores have been sampled at regular intervals and sliced into 1 or 0.5 cm thick samples. The sediments have been subjected to either a total metal analysis or a fractionation procedure designed to determine different forms of metal species in the sediment. The results are frequently expressed in units of mg or μg g^{-1} of dry sediment. If rates of sedimentation are known for a single core, then metal accumulation rates in g m^{-2} $year^{-1}$ may be calculated. In situations where total sediment influx to the basin is known, total loadings to the lake from all sources may be calculated and results expressed in units of kg ha^{-1} $year^{-1}$. The following sections consider the value of concentration and mass units for hydrological purposes and illustrates a method by which fluvially transported metals might be distinguished from direct atmospheric inputs to the lake.

Concentration data

Although Zn, Pb, Cu, Ni and Cd measurements are available, space does not permit consideration of all heavy metals and the present discussion will focus on the behavior of Zn since it is clearly represented in the lake sediment records at all sites. Total Zn concentrations for six lake cores are given in Fig. 1B, with a fractionation of Zn in Wyken Slough, based on the method of Tessier. *et al.* (1979), in Fig. 1C. Results in Fig. 1B are expressed as the excess Zn concentration over background by subtracting the minimum Zn concentrations in the basal sediments. Several features are immediately apparent. First, concentrations are much higher, by an order of magnitude, in the urban lakes than on Scilly, with Midland rural lakes occupying an intermediate position. Secondly, rates of sedimentation vary between all sites since the heavy metal record in excess of background starts at between 25cm depth and 1.15m depth. This assumes time synchronous initial metal inputs to the lakes, an assumption supported by the work of Batterbee (1988) over large regions of N Wales, N England and Scotland. Thirdly, the trends in Seeswood Pool and Porth Hellick

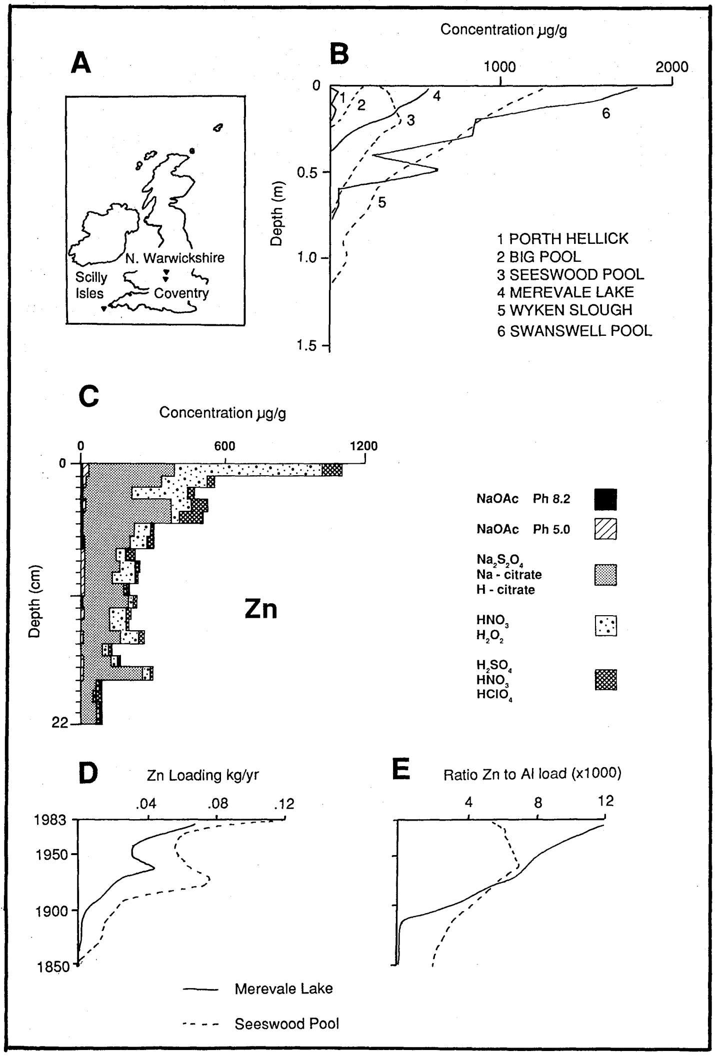

FIG. 1 Site Locations (A). Zn Concentrations in Scilly Isles, N. Warwickshire and Urban Lake sediments (B). Zn fractionation in Wyken Slough sediments (C). Excess Zn loading over background, N. Warwickshire Lakes (D). Ratio of Zn to Al loading, N. Warwickshire Lakes (E).

Pool contrast significantly with the other four lakes. In Seeswood Pool, Zn concentrations decrease above 25cm depth whereas in Porth Hellick, concentrations have a double maximum and decrease significantly at the surface.

Concentrations in the other four lakes increase towards the mud-water interface. Evidence exists in the watersheds of Porth Hellick and Seeswood Pool for recent accelerated erosion, the former based on significant decreases in organic matter content in surficial sediments and the latter based upon calculations of total sediment influx (Foster *et al.*, 1986). Merevale lake exhibits a general increase in Zn concentration towards the mud-water inter-

TABLE 1 Site locations and characteristics.

	Scilly Isles		North Warwickshire		Urban Lakes Coventry	
Lake	Big Pool	Porth Hellick	Merevale Lake	Seeswood Pool	Swanswell Pool	Wyken Slough
Grid Ref	SW878086	SW924109	SP300970	SP327905	SP335795	SP363833
1	0.50	1.25	6.5	6.7	0.73	2.25
2	15.0	158.25	201.0	238.0	220.0*	4500.0
3	30.0	126.6	30.0	33.0	10.0*	2000.0
4	8.0	46.0	175.0	160.0	105.0	112.0
5	2.1	3.0	118.0	125.0	70.0	85.0
6	5.9	43.0	57.0	35.0	35.0	27.0
7	0.75	1.70	8.0	3.5	1.3	0.8
8	0.4	0.95	4.0	1.5	0.9	0.6
9	2010	11 875	154 219	103 241	6389	13 050
10	?	?	1838	1765	c1265	c1850
Land Use (% Catchment Area)						
11	0	1	78	4	0	0
12	0	3	8	0	0	0
13	0	5	14	55	0	60
14	0	0	0	11	0	0
15	15	90	0	30	0	0
16	0	0	0	0	100	40
17	85	1	0	0	0	0

* Basin area 1850 reduced to c1.4 ha. (River Culverting)

1= Lake area (ha), 2= Basin Area (ha), 3= Ratio 1:2, 4= Max. Alt. (m), 5= Lake Level (m AOD), 6= Rel. Relief (m), 7= Max Lake Depth (m), 8= Mean Lake Depth (m), 9= Lake Volume (m^3), 10= Yr. Impounded, 11= Decid. Wood., 12= Conif. Wood., 13= Perm. Pasture, 14= Grass Ley, 15= Arable, 16= Urban, and 17= Rough Grazing.

face at a site where sediment yields over the last 130 years have varied little under continuous forest cover. (Ranging from 61.8 to 147 kg ha^{-1} $year^{-1}$ with a time weighted mean of 77.1 kg ha^{-1} $year^{-1}$). This site, like the closed basins of Big Pool and Swanswell Pool, probably contains a record dominated by atmospheric loading directly to the lake surface. The pattern at Wyken Slough, however, is further complicated by a recent (post 1960) influx of metal enriched fluvial sediments from industrial point source inputs and, since c 1930, the presence of landfill sites within the basin where Zn and other heavy metal-rich wastes have been deposited and are currently leaching into surface waters. Trends in point source loading are therefore superimposed upon the background atmospheric influx although, by examining trends in Zn concentration alone, there is a similarity in pattern between Big Pool, Wyken Slough, Merevale Lake and Swanswell Pool. Further information on the stability and bioavailability of heavy metals was achieved by fractionation of the sediment by sequential extraction methods (see Fig. 1C). Although these data are a useful supplement to total concentration, especially in estimating likely metal mobility in the future, it does not readily assist in distinguishing sediment sources.

Accumulation and sedimentation rates

Heavy metal accumulation rates may be determined in a variety of ways. Renberg (1986), for example, in a study of varved sediments in several lakes in northern Sweden, has argued that the use of metal concentration data alone was inadequate to quantitatively define the trends in atmospheric pollutant loading, since concentration was a function of sediment influx as determined by varve thickness. Johnson & Nicholls (1988) used multiple coring and radiometric chronologies in Lake Simcoe, Ontario, to determine metal influx to the lake basin. Norton (1986) also used radiometric chronologies, but on single cores taken from a range of lakes in the Adirondack Mountains in order to examine the variability in atmospheric influx. Analysis of accumulation rates based on single cores is not without difficulty, however, since sediments may be reworked and redeposited and any individual coring location may not be representative of mean accumulation rates for the lake basin as a whole or be linearly related to average sedimentation rate over the whole basin through time (Dearing, 1983; 1986).

In an earlier paper, Foster & Dearing (1987) argued that the units chosen to report contaminant loading to lakes should take account of predominant sources and suggested that for phosphorus loading, for example, units of mass influx per unit of time was most appropriate for hydrological interpretations. For metal contamination in areas receiving atmospheric pollution, however, units of mass loading per unit area of lake surface were argued to be most appropriate. These arguments were based on the perceived dominant source of pollutants which would determine whether catchment yield, or hydrological units, were more relevant rather than units expressed in terms of atmospheric fallout. However, a re-evaluation of these conclusions is necessary at sites with variable sediment influx histories and where there is potential for erosion and transport of pollutants originally arriving at the catchment from the atmosphere.

Based on multiple coring and sediment yield reconstruction at Seeswood Pool and Merevale Lake, results indicate that, despite the decrease in concentration (Fig. 1B), Zn loading to the recent (1961-1983) sediments of Seeswood Pool was only slightly higher (110%) than the influx to Merevale lake over the same time period (Fig. 1D). The difference between the two sites over this period is well within the standard deviation of Zn loadings calculated for several cores in each lake. Calculation of background corrected Zn loading to the two lakes for the period 1861-1983, however, gives 89.85 kg Zn ha^{-1} of lake surface at Merevale and 164.00 kg Zn ha^{-1} of lake surface area at Seeswood Pool, i.e. 83% more than would be expected from atmospheric fallout alone assuming that the lakes receive roughly the same atmospheric influx. The difference, 74.15 kg Zn ha^{-1} of lake surface area, may reflect eroded sediment-associated Zn in the Seeswood catchment over 122 years.

In order to establish whether the atmospheric loading of Zn to the Seeswood Pool catchment could account for metal enrichment in catchment soils, it was assumed that Merevale Lake provided a quantitative estimate of atmospheric metal influx and that the loading to both catchments in North Warwickshire has been the same. The increase in soil Zn concentrations over the last 122 years is predicted to be 25.38 μg g^{-1}. This assumes a ploughing depth of 30 cm, a bulk density of 1.18 g cm^{-3} and no loss of Zn over 122 years. Preliminary analysis of Zn concentrations in the <2 mm fraction of two arable and one pastoral soil profiles in the Seeswood Pool catchment gives excess concentrations over subsoil background of 8.0, 62.38 and 23.8 μg g^{-1} respectively. Although only three soil cores have been analyzed to date, the reasonable correlation between predicted and actual concentrations in the stable permanent pasture suggests that the predicted value of 25.0 μg g^{-1} is close to reality. The variability in the arable soils will reflect varying soil redistribution and sediment loss from the hillslopes. Although the excess Zn concentrations in soils are low, and much lower than lake sediment concentrations, it is well known that heavy metals concentrate in the finer particle size fractions and eroded silts and clays from the catchment will be significantly enriched relative to source area. This is illustrated by the fourfold increase in background Zn concentrations between the subsoils of the catchment and the basal lake sediments. Further analyses of soil cores are currently being undertaken to verify these predictions.

The preliminary results given above suggest that paired lake catchment studies may provide a particularly useful technique for separating the fluvially transported and direct atmospheric influx of heavy metals to lakes. These results also have implications for studies which have normalized atmospheric loadings to lake sediments by using ratios of metal concentration to concentrations of stable soil-derived elements such as Ti (Norton, 1986). The normalization procedure assumes a constant ratio of Ti to heavy metal in catchment-derived sediments. However the ratio of metal influx from the catchment relative to direct atmospheric input, at least in the Seeswood Pool catchment, appears to have changed significantly over time as sediment source areas have changed and would appear to invalidate this assumption in these lowland sites (Fig. 1E).

The results given above would suggest that there is some potential in using paired lake catchments in order to compare sites dominated by atmospheric inputs but where soil erosion rates and sediment sources vary through time at one of the sites. However, these results are only applicable to non-point pollution and further research is currently being undertaken in the urban catchments in an attempt to discriminate point and non-point sources.

Discriminating point and non-point metal pollution

The Wyken Slough and Swanswell Pool catchments are currently being used in an attempt to compare the relative contribution of point and non-point metal contamination in urban lake catchments. The closed Swanswell Pool basin, located in the city centre, provides a record of atmospheric influx alone. In total, 20 cores have been retrieved and total sediment influx estimated for the period 1850 to 1989. Heavy metal analyses have only been determined on 2 cores to date and radiometric chronologies are not available. However, the atmospheric influx of Zn above background, estimated on the basis of these limited data, gives a loading of 1045 kg ha^{-1} of lake surface area, some 12 times higher than the loading to Merevale lake over a similar time period. Similar calculations using four cores for which heavy metal data are available at Wyken Slough, a lake with both point and non-point inputs, gives a total loading over the same time period of 1312 kg ha^{-1} of lake surface area, some 26% higher.

It would be tempting to suggest that the difference between the two estimates reflects fluvially transported metal-enriched sediments to the Wyken Slough over the last 149 years. However, there are a number of factors which suggest that the combined point source and re-eroded atmospheric influx may be much higher than 26%. First, the gradient of atmospheric fallout between city centre (Swanswell Pool) and city marginal (Wyken Slough) sites is known to be high and attempts are currently being made to compare fallout rates between the two sites in order to calibrate the atmospheric record. Sampling is also being undertaken in order to compare measured with predicted soil metal enrichment. Calculations based on the Swanswell Pool atmospheric loadings predict a metal enrichment in the upper 30 cm of arable soils as 295 $\mu g\ g^{-1}$ for non eroding areas of the Wyken Slough basin. Secondly, with two channelled inflows to the Wyken Slough, opportunities exist for metal storage within the fluvial system. To date, 42 bed-sediment samples have been collected from the inflowing rivers and an attempt made to estimate the total storage capacity of anthropogenically derived Zn based on estimates of channel width, sediment depth and density. In total, it is estimated that 45 kg Zn are stored in the river channels, approximately 1.5% of anthropogenic excess Zn in the Slough. Thirdly, one of the inflowing streams filters through a wetland before entering the lake. The upper 5 cm of sediment in one core contains in excess of 5.0 $mg\ g^{-1}$ Zn in the sediment, although insufficient data currently exist to calculate total inventories.

CONCLUSIONS

Interpretation of the metal record in lake sediments presents several problems. Reliance on concentration data alone may be misleading, especially at sites experiencing changing sedimentation rates through time. However, interpretations based upon metal influx calculations may also be misleading, especially in areas of changing erosion rate and sediment source. The use of paired lake catchments as illustrated for rural North Warwickshire may, in part, assist in the development of a quantitatively based interpretation of catchment and atmospheric inputs, especially in areas where non-point pollution dominates the environment. Application of similar methodological frameworks to urban lakes receiving point and non-point inputs is further complicated by strong gradients of atmospheric deposition over short distances and by storage of sediment in different parts of the fluvial system.

ACKNOWLEDGEMENTS We thank Coventry City Council and Coventry Polytechnic for funding. Kayzi Ambridge, Karen Bardell, Liam Kelly, Andy Love, Ceri Owen and Trevor Price contributed to the field and laboratory programs.

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