

# The perturbation of historical pollution records in aquatic sediments

John G. Farmer

*Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, UK*

## Abstract

It is often claimed that coastal marine and freshwater lake sediments preserve temporal records of anthropogenic input of heavy metals to the environment since the onset of the Industrial Revolution. Growing evidence of perturbatory factors such as physical and biological mixing, other redistributive processes and the early post-depositional diagenetic release and mobility of some elements is reviewed. Fundamental requirements of future studies are outlined.

## Introduction

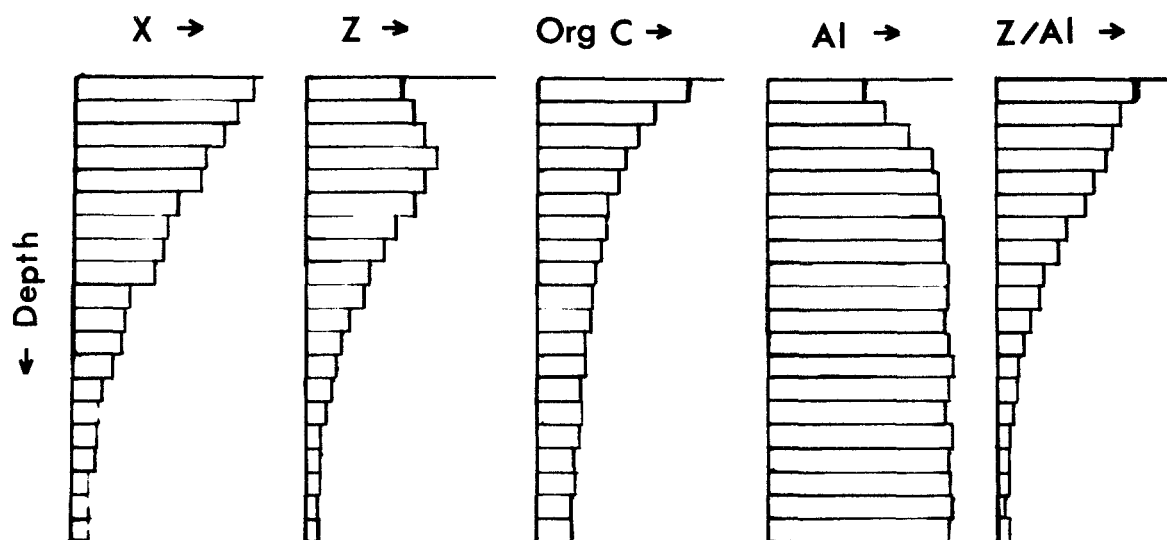
The chemical and biological analysis of preserved remains of living organisms in sediment cores from locations as diverse as the deep oceans and freshwater lakes have yielded evidence of environmental change, ranging from major climatic and atmospheric carbon dioxide trends over hundreds of thousands of years (Shackleton and Pisias, 1985) to the acidification of lakes resulting from the industrialisation and growing energy demands of the last 200 years (Battarbee, 1984). The purpose of this brief review, however, is to examine developments over the last two decades or so with respect to the use and interpretation of vertical profiles of *heavy metal* 'pollutants' and other elements in *recent* sediments (<200 years old) from freshwater lakes and the coastal marine environment. Initial expectations of straightforward pollution record preservation must now be considered over-optimistic. Natural physical and biogeochemical processes and man's impact upon the status of aquatic systems can not only disturb the record of anthropogenic inputs but also, in some cases, considerably modify the traditionally-held perspective of sediments as sinks for pollutants.

## Historical Records

Several factors contributed to the proliferation of studies in the 1970s and early 1980s on historical records of heavy metals in sediment cores. As a consequence of environmental concern there was a need to establish historical perspectives of the extent of current environmental pollution. Heavy metals were of special concern, particularly in the light of well-publicised environmental disasters connected with heavy metals (*e.g.* Minamata and mercury, Itai-Itai and cadmium) and growing unease over the use of lead additives in petrol (Patterson, 1965; Bryce-Smith, 1976; Smith, 1986). A comparatively inexpensive technique, atomic absorption spectrometry, capable of determining heavy metals in a

wide variety of matrices, had recently been launched (Walsh, 1955; Koirtzohann, 1980). In addition, a means of dating sediment over the 100–150 years of major industrialisation, via the radioactive decay of the highly appropriate naturally-occurring isotope ( $^{210}\text{Pb}$ ,  $t_{1/2} = 22.3$  years) of a heavy metal, had been developed (Krishnaswamy *et al.*, 1971; Robbins, 1978). This was bolstered by the use of fallout radionuclides (*e.g.*  $^{137}\text{Cs}$ ,  $^{239,240}\text{Pu}$ ) from nuclear weapons testing to identify time horizons in the sediment column corresponding to the major period (1954–1963) of testing in the atmosphere (Pennington *et al.*, 1973).

The net result was a series of papers on vertical profiles ('historical records') of lead, zinc, copper, cadmium and other heavy metals in dated sediment cores from coastal zones and freshwater lakes, especially from North America and Europe. Typical interpretations assumed fairly rapid transport of metals associated with settling inorganic particulates and/or biotic detritus from water column to bottom sediments, and little or no post-depositional disturbance of the sediments. The general upwards increase in metal concentrations (often to values an order of magnitude greater than baseline concentrations) could then be attributed to temporal variations in input via atmospheric deposition, catchment run-off, effluent inflow and dumping of metals from industrial, transportation, mining, agricultural and waste disposal sources (Figure 1). Superimposed on this trend, occasional near-surface decreases in concentration were linked to reductions in environmental release or, more commonly, to significant changes in bulk sediment composition (*e.g.* greater content of undegraded organic matter). Normalisation of concentrations to the content of aluminium, a major constituent of clays, was sometimes invoked to 'straighten out' profiles and, indeed, to permit calculation of enrichment factors, one of the principal objectives of the studies. Alderton (1985) has comprehensively reviewed the literature of that period.



**Figure 1** Typical concentration profile of a heavy metal (X) in recent freshwater lake or coastal marine sediments. Although the upper part of the profile for Z could reflect decreasing anthropogenic input, the effect of normalising concentrations of Z to concentrations of aluminium, to correct for the influence of higher organic carbon levels in near-surface sediment, is shown in the Z/Al profile.

### Record Perturbation via Sediment Disturbance

It was soon realised that this picture of undisturbed sediment accumulation was somewhat idealised and atypical. Even some of the coring techniques, especially small-diameter gravity devices, employed to collect intact, representative sediment cores, were of highly dubious validity because of their susceptibility to losing surface sediment, smearing, distorting profiles, *etc.* Indeed, the radionuclide information for such unintentional disturbance – *i.e.* the profiles (distorted) and inventories (diminished) of fission products such as  $^{134}\text{Cs}$  and  $^{137}\text{Cs}$  in gravity cores compared with reliable cores collected simultaneously by alternative devices (Baxter *et al.*, 1981) – has also been used extensively to demonstrate the existence, and to quantify the rate and extent, of *natural* mixing (physical, biological) and other important redistributive processes (Benninger *et al.*, 1979; Nittrouer *et al.*, 1984).

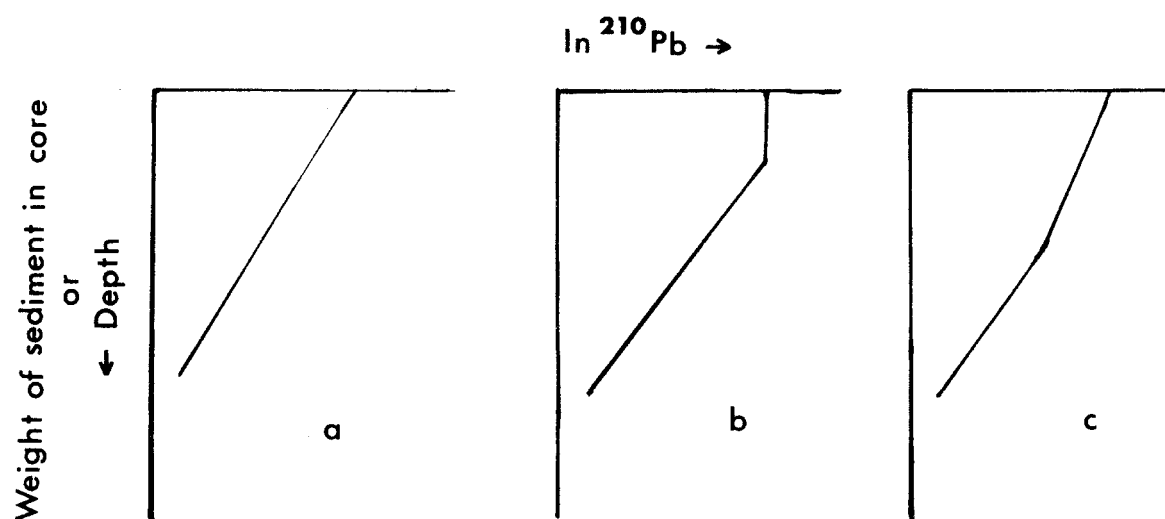
Naturally occurring  $^{210}\text{Pb}$  and, more recently,  $^{234}\text{Th}$  ( $t_{1/2} = 24.1$  days), in conjunction with nuclear fallout or effluent  $^{134}\text{Cs}$  (2.1 yr),  $^{137}\text{Cs}$  (30.2 yr),  $^{239,240}\text{Pu}$  ( $2.4 \times 10^4$  yr;  $6.6 \times 10^3$  yr) and  $^{241}\text{Am}$  (432 yr), are now used primarily to garner information on these processes, as well as sedimentation rates, rather than act as markers for the inference of deposition dates for specific layers of sediment (Santschi, 1989; Santschi and Honeyman, 1989) (Figures 2 and 3). Even so, acknowledgement of the influence of bioturbation, in particular, on sediment profiles, sedimentation rates determined by  $^{210}\text{Pb}$  and, therefore, metal fluxes to sediments, has not always been readily forthcoming or without controversy (Santschi, 1980; Goldberg and Koide, 1980).

In the apparently simpler case where there has been no post-depositional disturbance of sediment, a calculated sedimentation rate based on the assumption of a constant initial concentration (CIC) of unsupported  $^{210}\text{Pb}$  per unit weight of sediment will not be reliable if the actual rate of

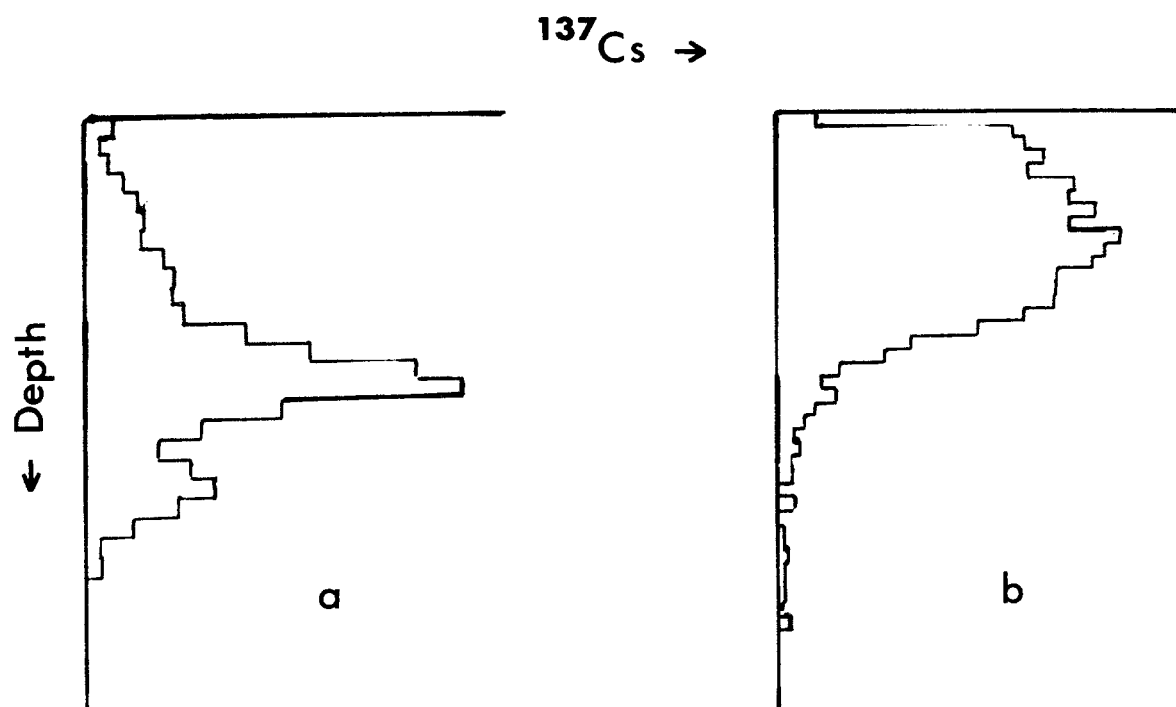
sedimentation has varied with time and so produced irregularities in the decline of unsupported  $^{210}\text{Pb}$  with depth (Figure 2). The adoption of a model based on a constant rate of supply (CRS) of unsupported  $^{210}\text{Pb}$  to the sediments (Oldfield *et al.*, 1978) can be useful in such circumstances as can the profiles of fallout radionuclides (*e.g.*  $^{137}\text{Cs}$ ) for which atmospheric deposition patterns are well known. In freshwater lakes in particular, however, sediment  $^{137}\text{Cs}$  profiles may be distorted by delayed input of  $^{137}\text{Cs}$ -bearing sediment from the drainage basin, focusing of resuspended epilimnetic sediments to the interiors of depositional basins and some downwards diffusion of  $^{137}\text{Cs}$  through pore waters in the sediment column (Davis *et al.*, 1984; Kada *et al.*, 1989; Robbins, 1989) (Figure 3). Appleby *et al.* (1990) have even suggested that the latter process could perhaps restrict the potential usefulness, at least in areas of high fallout, of the recent injection pulse of  $^{137}\text{Cs}$  (and  $^{134}\text{Cs}$ ) from the 1986 Chernobyl accident. Perhaps a more fundamentally important point is that it illustrates differences in the post-depositional biogeochemical behaviour of  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  in the sediment column.

### Record Perturbation via Diagenetic Mobility

Bulk sediment disturbances notwithstanding, post-depositional diagenetic remobilisation and diffusion along pore-water concentration gradients are now the focus of research effort on the behaviour of metals, metalloids and other non-metals in aquatic sediments. Redox-controlled cycling and, under appropriate conditions, near-surface enrichment of sedimentary manganese and iron are well known (Farmer and Lovell, 1984). The driving force is the microbiological decomposition of organic matter through bacterial utilisation of  $\text{O}_2$  and inorganic oxidising agents (*e.g.*  $\text{NO}_3^-$ ,  $\text{MnO}_2$ ,  $\text{Fe}(\text{OH})_3$ ,  $\text{SO}_4^{2-}$ ) in thermodynamically-favoured sequence (Berner, 1980). Upon dissolution of oxides and oxyhydroxides of



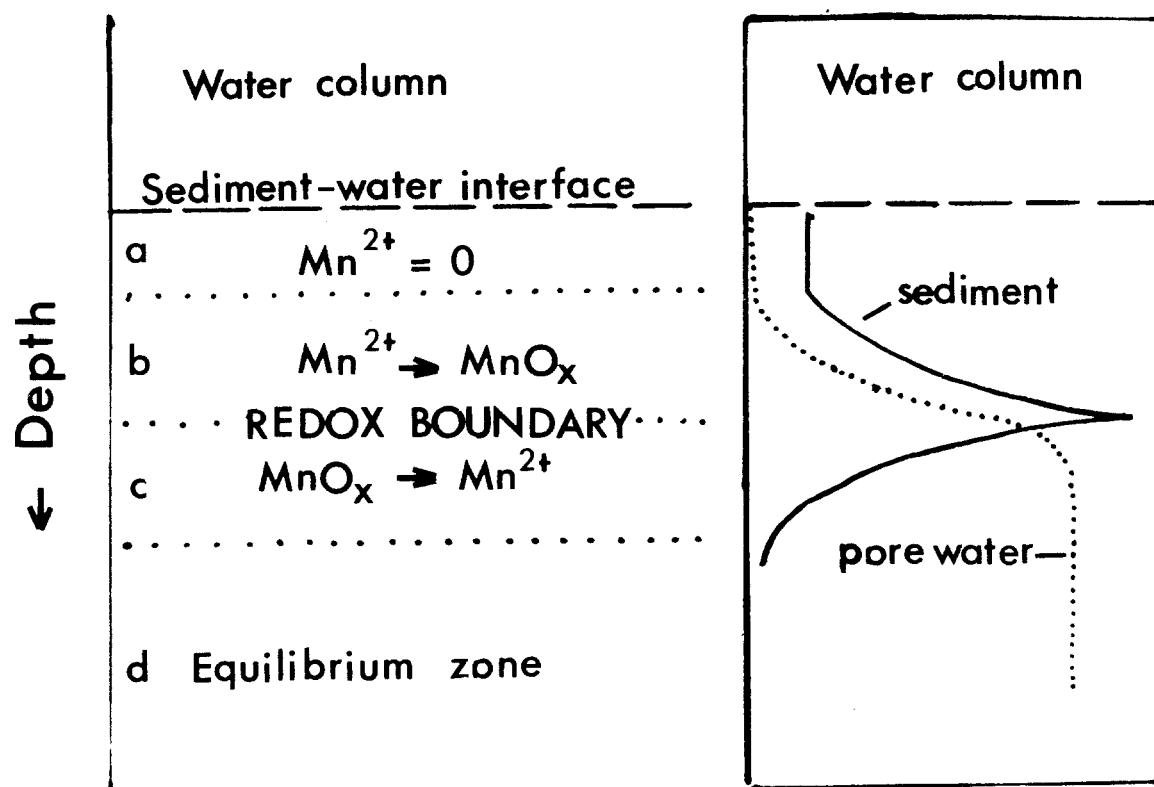
**Figure 2** Typical profiles of  $\ln$  'unsupported'  ${}^{210}\text{Pb}$  specific activity versus depth in recent freshwater lake or coastal marine sediments (after Schell and Barnes, 1986). A plot of  $\ln {}^{210}\text{Pb}$  against weight of sediment accumulated corrects for the effects of compaction in highly porous sediment. Example (a) is the classical first order decay profile, (b) shows the effects of complete mixing in upper layers and (c) results from a change in sedimentation rate. For conditions of varying rates of sediment accumulation, the CIC model of  ${}^{210}\text{Pb}$  dating, based on specific activities of  ${}^{210}\text{Pb}$  ( $\text{dpm g}^{-1}$ ), is often discarded in favour of the CRS model, based on cumulative integrated inventories of  ${}^{210}\text{Pb}$  ( $\text{mCi km}^{-2}$ ) with depth.



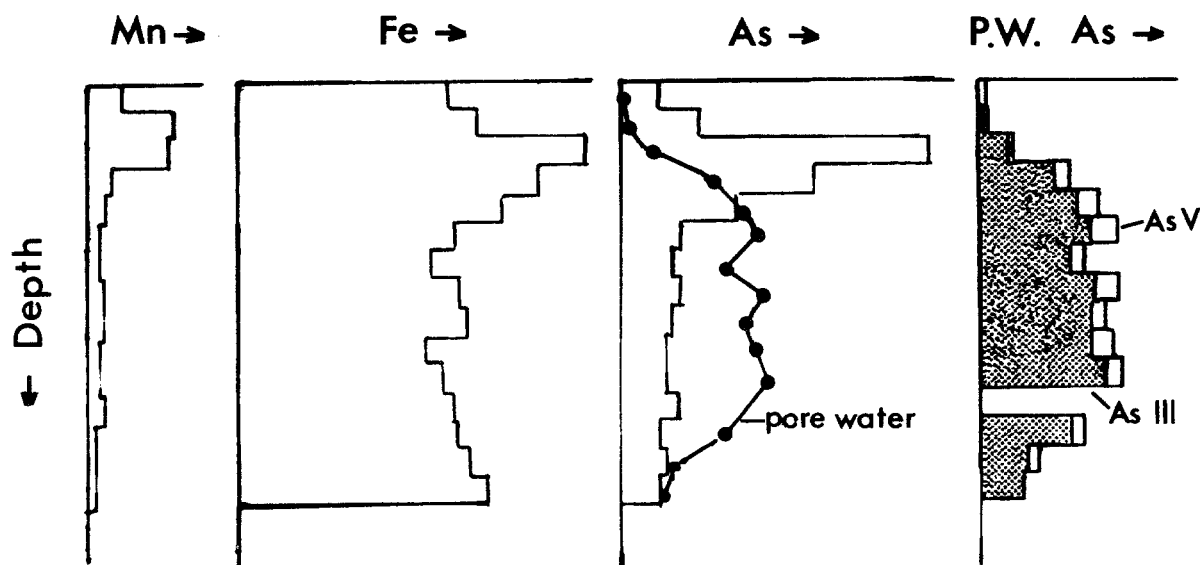
**Figure 3** Examples of  ${}^{137}\text{Cs}$  specific activity ( $\text{dpm g}^{-1}$ ) or sectional inventory ( $\text{mCi km}^{-2}$ ) profiles with depth in recent freshwater lake sediments (after Heit and Miller, 1987). Profile (a) closely resembles the pattern of atmospheric deposition of  ${}^{137}\text{Cs}$  resulting from atmospheric nuclear weapons testing, with the major peak corresponding to the early 1960s. Profile (b) does not retain this pattern, exhibiting instead the effects of possible influences such as significant subsequent catchment run-off, mixing, resuspension and focusing. The tailing with depth may be due to some downwards diffusion of  ${}^{137}\text{Cs}$ .

manganese and iron under reducing conditions at depth, divalent cations of these elements can migrate upwards through the pore waters to be oxidised and precipitated in near-surface oxic layers. The cycling and enrichment processes yield sediment and pore-water profiles which are now well-explained by general conceptual models for transport at a redox boundary (Burdige and Gieskes, 1983; Davison, 1985) (Figure 4).

The classical work of Mortimer (1941) on phosphorus in English Lake District sediments, and more recent investigations in both marine and freshwater systems on its chemical analogue, arsenic (Farmer and Lovell, 1986; Peterson and Carpenter, 1986; Johnson and Farmer, 1987), have shown that elements other than manganese and iron can be recycled. With phosphorus and arsenic, however, it is the negatively charged *anions* which are released into



**Figure 4** Zones of manganese diagenesis and resultant pore water and sediment profiles in aquatic sediments overlain by oxygenated waters (after Burdige and Gieskes, 1983; McKee et al., 1989) (see text). In the equilibrium zone, the concentration of manganese in the pore waters is controlled by equilibria with mineral phases (e.g. carbonates, sulphides) other than manganese oxides.

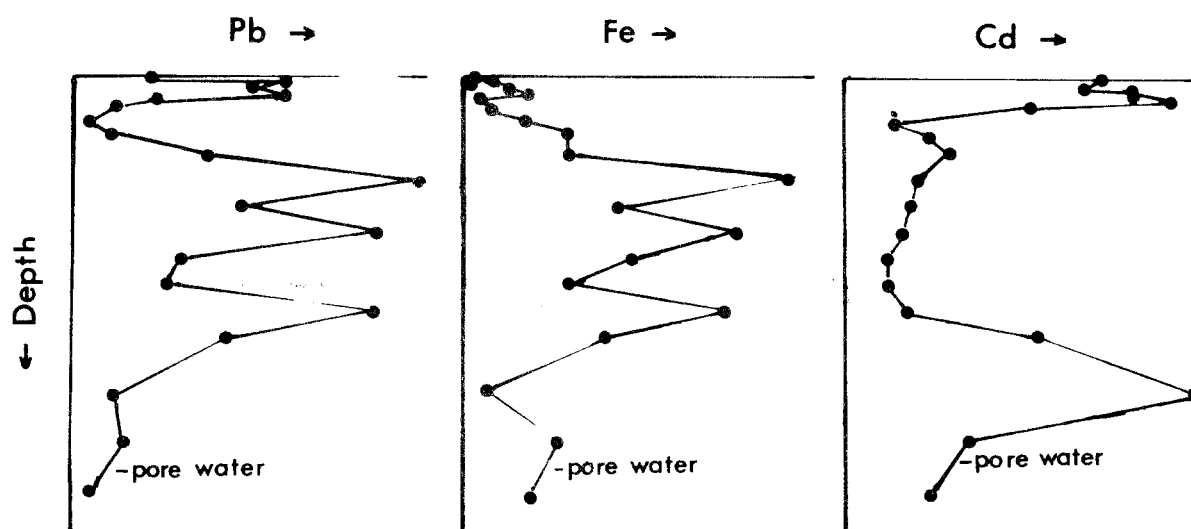


**Figure 5** Profiles showing diagenetic enrichment of manganese, iron and arsenic in upper layers of sediment from the southern basin of freshwater Loch Lomond, Scotland (after Johnson and Farmer, 1987). The pore-water profile confirms the mobility of arsenic leading to near-surface enrichment via internal cycling. Arsenic (III) is the predominant species in the reduction zone and, with the exception of the uppermost section, even in the oxidised zone, due to preferential adsorption of arsenic (V) on iron oxyhydroxides.

solution from an association with solid phase ferric oxyhydroxides which dissolve under sufficiently reducing conditions. Upward migration of reduced species leads ultimately to surface enrichment via oxidation and co-precipitation or adsorption of phosphate and arsenate on

iron oxyhydroxides in surface layers (Figure 5).

Further evidence has recently emerged to show or suggest that selenium, molybdenum, cobalt, barium, radium and some rare earths in locations as diverse as Arctic lakes, the Great Lakes, eastern equatorial Pacific,



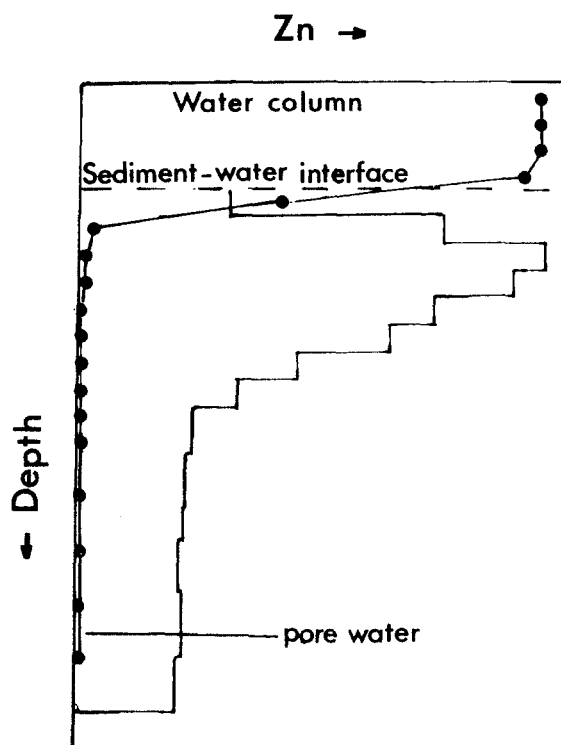
**Figure 6** Pore-water profiles of lead, iron and cadmium in sediments from the Laurentian Trough, St Lawrence Estuary, Canada (after Gobeil and Silverberg, 1989). The profiles suggest the release of lead and cadmium from aerobic degradation of organic matter near the sediment surface, the involvement of lead in cycles of redox-controlled iron diagenesis and the possible existence of soluble polysulphide complexes of cadmium in pore waters at depth.

offshore Baja California and Buzzards Bay, Massachusetts, may be intimately associated with and redistributed by manganese/iron cycling (Graybeal and Heath, 1984; Cornwell, 1986, 1987; Shimmiel and Price, 1986; Elderfield and Sholkovitz, 1987; Nriagu *et al.*, 1987).

As far as the heavy metals such as lead, zinc, copper and cadmium are concerned, the traditional view has been that these elements are diagenetically immobile and remain fixed in the sediment after deposition, apparently as a result of the formation of comparatively insoluble sulphides under reducing conditions at depth. For pore waters associated with sediments of sulphide ion activity of  $10^{-9}$  M, Thomson *et al.* (1975) have calculated anticipated maximum concentrations as high as  $2.5 \times 10^{-3}$  M for manganese and  $4.0 \times 10^{-7}$  M for iron, but only  $7.9 \times 10^{-15}$  M,  $2.5 \times 10^{-17}$  M,  $6.3 \times 10^{-17}$  M and  $1.0 \times 10^{-26}$  M for zinc, lead, cadmium and copper, respectively. Recent results from both marine and freshwater studies reveal considerably more complex behaviour. It appears that lead, zinc, copper and cadmium may, to varying degrees, be directly released to pore water by the degradation of organic matter (*i.e.* to which the metals are bound) under aerobic conditions in surficial sediments, giving rise to the possibility of return to overlying water. Gobeil *et al.* (1987) found that, in Laurentian Trough sediments, about 80% of the total cadmium flux to the sediments is so returned to the water column (Figure 6). About one-quarter of the remaining 20% buried with the sediment is accountable through downward diffusion and precipitation, perhaps as a sulphide, below the oxygenated zone. Cadmium concentrations below the surface layer are believed to be much more stable at depth, although there is some evidence for a subsequent release of dissolved cadmium, possibly as a polysulphide complex. At this location, it is believed that some lead is also solubilised near the sediment surface during the aerobic degradation of organic matter, but that another separate fraction is implicated in the

redox-controlled cycles of iron diagenesis (Gobeil and Silverberg, 1989) (Figure 6). For Lake Superior, McKee *et al.* (1989) also reported the loss of lead (and copper) to lake water from degradation of surface organic matter, but did find that some also diffuses downwards to become associated with other phases (*e.g.* manganese/iron oxides) and involved in redox cycling.

Organic matter diagenesis has also been implicated in the vertical distribution of lead, zinc and copper in the sediments of the Scottish coastal sea loch, Loch Etive (Ridgway and Price, 1987). Here, however, it was claimed that the decline in heavy metal content with depth in the solid phase of the sediments is coincident with the zone of sulphate reduction where the diagenetic release of metals from organic matter results from the activity of sulphate-reducing micro-organisms. Subsequent recycling and reprecipitation of the elements closer to the sediment interface was claimed to enhance the profiles for these metals. Such a mechanism is clearly incompatible with the insoluble sulphide theory. There is some evidence from other studies, however, that the precipitation of simple sulphides may not be controlling the concentrations, and therefore diffusion along concentration gradients, of heavy metals liberated in sulphate reduction zones. Elderfield and Hepworth (1975) observed that measured concentrations of zinc, lead and copper in reducing pore water were some  $10^8$ ,  $10^{12}$  and  $10^{21}$  times greater, respectively, than the theoretical maxima calculated for sulphide ion activities of  $10^{-10}$  M. It was suggested that the discrepancies could be due to the formation of stable metal-organic (*e.g.* humic acid) complexes in the pore waters of anoxic-sulphidic regions of near-shore marine sediments where metal sulphide precipitation or, ultimately, scavenging by insoluble iron sulphides, might have been expected to prevail. The polarographic determination of electro-chemically active metal ions in pore waters both before and after UV irradiation may help to identify the presence of originally electro-chemically inactive



**Figure 7** Bottom water, pore water and sediment profiles of zinc in the acid Clearwater Lake, Ontario, Canada (after Carignan and Tessier, 1985). Downward diffusion of zinc from the overlying water and subsequent precipitation of insoluble zinc sulphide in near-surface sediment are believed to account for the pore water and sediment profiles.

dissolved metal complexes, including metal-organic complexes (Gobeil *et al.*, 1987).

In addition, Ridgway and Price (1987) speculated that the release of lead from organic matter during burial of sediments could affect the validity of sediment accumulation rates determined by  $^{210}\text{Pb}$  dating. Benoit and Hammond (1990) have observed the remobilisation of  $^{210}\text{Pb}$ , in association with diagenetic iron cycling, from the sediments of the seasonally anoxic Bickford Reservoir, Massachusetts. Based on observations in Big Moose Lake, New York, it has been suggested that iron cycling, leading to significant iron enrichment of surface sediments, could affect  $^{210}\text{Pb}$  dating via post-depositional changes in bulk sediment composition and dry mass (Gubala *et al.*, 1990). Potential effects of metal mobility on commonly used radiometric dating methods clearly must not be ignored.

It is clear that the nature and relative contribution of biogenic and terrigenous (*e.g.* clays, metal oxides, organic particle coatings) material to the metal flux in the water column, bottom water oxygen concentrations and sediment redox conditions are very important influences on the early diagenetic behaviour of metals in sediments. 'Selective' chemical extraction of solid phases (Kersten and Förstner, 1987) and direct pore water analyses are essential investigative tools.

In such a study of transition metals in a variety of Californian coastal sediments, Shaw *et al.* (1990) observed a wide range of contrasting behaviour. Manganese oxides

were recycled in the surface sediments provided bottom water  $\text{O}_2$  concentrations exceeded  $5 \times 10^{-6}$  M. Nickel and cobalt were scavenged and trapped by manganese oxides, leading thereafter to recycling via remobilisation from reducing sediments and enrichment in oxic surface sediments. Chromium, vanadium and molybdenum were largely transported to the sediments in biogenic material and then released from the sediments by oxidation. The accumulation of these metals would thus be favoured by reducing conditions in the sediments. Copper was enriched in the sediments by transport with detrital biogenic material, followed by adsorption onto sediment solids after release.

The general decoupling of transport processes from burial processes for metals during early sediment diagenesis, as observed in this study, clearly has major implications for the preservation of historical records of metal pollution in sediments and for the re-release of metals to the overlying water. It should be noted, however, that in certain marine sediment systems, over many thousands of years, potentially useful information on past levels of productivity and changes in bottom water oxygen concentrations may be derivable from multi-element signatures in the sediments as a result of differences in behaviour of individual transition metals to redox shifts associated with decomposition of organic matter.

In the totally contrasting system of unproductive freshwater lakes rendered highly acidic by acid deposition from the atmosphere, it has been suggested that heavy metals could be released from surface sections (*e.g.* via pH-dependent dissolution of iron and manganese oxyhydroxides, carbonates, *etc.*) resulting in sub-surface maxima in sedimentary heavy metal concentrations (Schindler *et al.*, 1980).

In a study of zinc behaviour in two Canadian acid lakes, however, Carignan and Tessier (1985) found steep negative concentration gradients of dissolved zinc between overlying waters and the anoxic pore waters (Figure 7). The low zinc concentrations in the latter were explained on this occasion, with sulphide concentrations of the order of  $10^{-7}$  M, as being due to the formation of relatively insoluble zinc sulphide minerals. Downward diffusive fluxes of dissolved zinc, accounting for at least 50–75% of the recent zinc deposition to the sediments, to a depth of 2–3 cm below the sediment-water interface were considered responsible for the pronounced sediment maxima in total zinc. This suggests that for zinc (and possibly other metals such as cadmium, copper and nickel) in acid lakes, the traditional sedimentation model for transport from the water column to the sediments may not be applicable (Carignan and Nriagu, 1985; Carignan and Tessier, 1985; Likens, 1989). As a consequence, historical reconstructions of zinc deposition and of related freshwater acidification processes based on sediment deposition chronologies and total zinc profiles could be highly questionable.

Further work on zinc (Tessier *et al.*, 1989) has illustrated the likelihood of significant differences in the modes of metal transport to, accumulation in, and release from bottom sediments of aquatic systems, depending on their degree of acidification or eutrophication, two major

anthropogenic effects with widely differing impacts upon productivity. There may even be completely unexpected interactions; for example, there is recent empirical evidence which suggests that the sulphate concentration (enhanced by acidic deposition) of lake waters is an important variable in the release of the non-metal phosphorus from sediments (Caraco *et al.*, 1989). Classically, oxygen, through its control on the iron cycle, has long been thought the critical variable controlling phosphorus immobilisation by aquatic sediments.

### Future Approaches

As with phosphorus, understanding of mechanisms controlling the behaviour and biological availability of sediment-bound heavy metals (Luoma, 1989) is of major environmental and ecological importance in an age of considerable anthropogenic input. It is now clear that aquatic sediments must be viewed not solely as a sink (Salomons *et al.*, 1987) but as part of a dynamic system in which temperature-induced physical structure in the water column, biological productivity, water chemistry, physical and biological mixing of sediment, and sedimentary diagenetic processes are capable of influencing transport mechanisms, particle-metal associations, exchange across the sediment-water interface, vertical profiles in the sediment column and water quality itself (Salomons, 1985; Santschi *et al.*, 1990). Modelling of the mobility, cycling and exchange of heavy metals in aquatic systems based on fundamental heavy metal properties, solution characteristics and the scavenging properties of solid biotic and abiotic surfaces, beyond the simple  $K_d$  approach, is at a comparatively early, although promising, stage (Sigg, 1985; Tessier *et al.*, 1985, 1989; Honeyman and Santschi, 1988; Diamond *et al.*, 1990; Santschi *et al.*, 1990). There is a clear need for a comprehensive practical approach to the behaviour of heavy metals in aquatic systems. This must include the investigation of different systems of varying status (*e.g.* oligotrophic, eutrophic, acid, freshwater, coastal marine), seasonal influences, modes of element introduction and transport, element associations in the water column, depositional and redistributive processes and rates (*e.g.* via radionuclide and stable isotope studies) in the sediments, concentration profiles and speciation in the overlying water, solid sediment and pore water, element/solid phase associations (*e.g.* via sequential chemical extraction procedures) and authigenic mineral identification. Demonstrably satisfactory sampling (*e.g.* coring, pore water extraction) and analytical methods must be employed, the latter including techniques for the detection of any biologically-mediated influences on dissolved nutrient status and on metal speciation (*e.g.* methylation of mercury, arsenic) (Wood, 1987).

When judged against the above criteria, claims of historical records of metal pollution in aquatic sediments, many of which are still appearing in the literature today (De Laune *et al.*, 1989; Finney and Huh, 1989a, 1989b; Mueller *et al.*, 1989; Verta *et al.*, 1989; Rippey, 1990), must therefore be viewed at least with caution unless due attention has been paid to potential perturbatory influences.

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