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# Chemical and physical partitioning in contaminated stream sediments in the River Ystwyth, Mid-Wales

Dyfed Evans

*Department of Environmental Science, University of Bradford, West Yorkshire, BD7 1DP, UK*

## Abstract

This study investigates contemporary fluvial contamination of stream sediments by Pb, Zn and Cu from a mine near Aberystwyth, Wales. Of particular interest is the association between metal cations and particulate substrates and which is investigated using a selective extraction procedure. Emphasis is also placed on the difference between adsorptive phases depending on particle size. As particle size decreases the labile phase becomes dominant, with the easily and moderately reducible fraction being the major scavenging agent of soluble cations. Zinc and copper are largely held as residual rock or ore particles and are therefore expected to have a longer residence time in sediments. Recent floodplain development is difficult to interpret due to reworking of upstream metal-rich alluvium. However evidence is presented to suggest that once silt and clay size particles enter the main channel they are largely removed from the system.

## Introduction

The quantity and rate of sediment supply to any fluvial catchment is governed first by the weathering rate of catchment lithologies and second by the climatic conditions which regulate rates of rock denudation and subsequent supply to the fluvial system. Sedimentation and remobilization of the added sediments is ultimately controlled by channel hydraulics and these sediments move through the system either as suspended particles or as bed load. The degree of metal contamination is governed by catchment geochemistry and anthropogenic inputs.

Background metal concentrations will be higher where mineralized veins have been naturally eroded incorporating localized inputs of metal rich sediments to the fluvial system for thousands of years. Historic and contemporary base metal mining activities can increase the concentration of metals within alluvial soils, with the alterations being both chemical and physical (Lewin *et al.*, 1983; Graf, 1979).

Metal mining in Mid-Wales dates from the Roman occupation, although the peak period was during the nineteenth century. Ore recovery was very inefficient and as a result, both fine ore particles from mine tailings, crushed rock fragments, and solutes from the water flotation process have been incorporated into the fluvial system.

Alluvial sedimentary environments are usually size selective. For example, point bars incorporate progressively finer sediments downstream from bar-head (Bluck, 1971), whilst overbank gravel splays may have interdigitate fine fills (Lewin *et al.*, 1983). Consequently, particle sizes should be divided into fractions possessing similar transport properties and similar chemical sorption properties. However the possibility of chemical mobility, local sedimentary environment changes, variability within point bar sediments, and the reworking of metal rich floodplain material may complicate interpretation (Lewin and Macklin, 1987).

Various chemical associations occur between metal ions and the particulate substrate (Gibbs, 1973) and the occurrence of these controls demonstrates the biological and physiochemical availability and mobilization of metals. Conceptually, the solid particles can be divided or partitioned into specific fractions which can be extracted selectively by using appropriate chemical reagents.

Partitioning of trace metal 'pools' was confined to the following 5 fractions.

*Fraction 1: Exchangeable*

Some sediment constituents adsorb trace metals from solution (clays, oxides of iron and manganese, humic acids) with the attractions being a weak ion-dipole or dipole-dipole attraction.

*Faction 2: Specific adsorption or carbonate sorption*

Chemical adsorption is characterised by the formation of a covalent bond or a chemical association between the metal ions and the particulate surface. For example, the condensation reaction with hydroxyl groups on the surface of Si, Fe, Mn, Al compounds, (Calmano and Forstner, 1983). Other workers have associated this fraction with sediment carbonates (Tessier *et al.*, 1979; Salomons and Forstner, 1984).

*Fraction 3: Co-precipitated with iron and manganese oxides*

Jenne (1968) showed that the hydrous oxides of iron and manganese are known to be efficient scavengers of soluble metal ions, and occur as coatings or discrete nodules which are thermodynamically metastable. However changes in

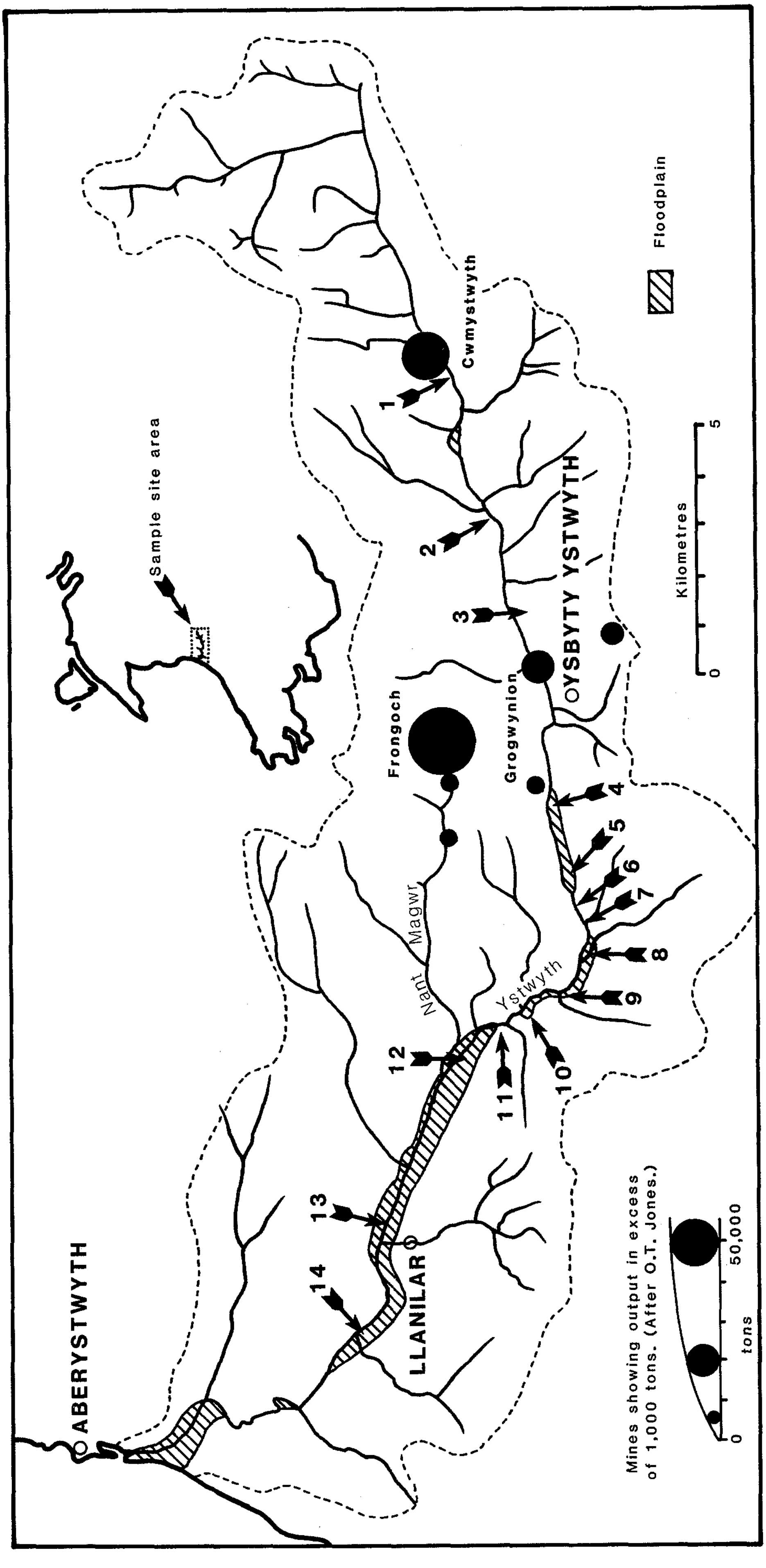

**Figure 1** *The River Ystwyth, mines and sampling points.*

the redox potential may render metals mobile and then these hydrous oxides become a major source of dissolved metals. These oxyhydroxides are common in a mining catchment due to the neutralization of acidic mine drainage. The oxidation of pyrite produces ferrous iron and acidity. In a mining region the acidity maintains dissolved metal cations in solution and ferrous iron undergoes oxidation to ferric iron and subsequent hydrolysis to form ferric hydroxide. This produces more acidity and coats the stream bed with the characteristic 'ochre' (Stumm and Morgan, 1970). Ferric iron can oxidize pyrite and takes over the initial role of atmospheric oxygen in the reaction.

*Fraction 4: Associated with organic matter*

Organic substances available for mobilization can originate in one of two ways, either from plant and animal decomposition, or as sorption of lower molecular weight organic constituents on hydrous oxides or clays. Under oxidising conditions, these can degrade leading to mobilization of metals. In freshwater systems humic acids are the most important products (Nissenbaum and Swaine, 1976) with the attractive forces between metal and the humic substances varying from exchangeable (physical adsorption) to strong metal chelation (Saxby, 1969).

*Fraction 5: Residual* The final step of the sequential fractionation releases primary and secondary minerals, which have metals in their crystal structure. In the Ystwyth catchment, Galena (PbS), sphalerite (ZnS) and chalcopyrite ($CuFeS_2$) are also present as a legacy of poor recovery techniques. It is this fraction that is not expected to be released rapidly into solution, and is resident for the longest time period. This paper deals with the contamination of bed sediment caused primarily by the inefficient mining techniques employed in the last century. Sequential extraction was used to investigate the importance of particular metal-substrate associations within bed sediment and to ascertain how these sediments are incorporated in alluvial soils.

## Study Area

The Ystwyth river drains a catchment area of 193 $km^2$ along the lowest 20 km of its course, with the morphology being divided into discrete floodplains separated by short rock cut channels (Brown, 1952; Figure 1). This is suitable for determining the relative importance of both river flow conditions and chemical changes on the redistribution of metals within river sediments. The present paper deals with the latter process.

## Experimental

Sediment samples were collected from the main Ystwyth channel at fourteen sites below the Cwmystwyth mine, at both chute and floodplain locations, (Figure 1). Floodplain soil samples were also taken at Llanilar (SN 626754), Wenallt (SN 674716) and Grogwynion (SN 721712), and all were dried and sieved to obtain the <2 mm fraction. It was decided to split this into three particle size ranges; 2,000–250 μm, 250–63 μm and <63 μm, the former being obtained by dry sieving and the latter two by settling tubes.

The following chemical extraction scheme was modified from Tessier *et al.*, (1979) and Lindsay and Norvell (1978).

*Exchangeable fraction:* 1M ammonium acetate ($CH_3COONH_4$), pH 7, solid/solution ratio 1:20, 2 hours shaking.

*Specifically sorbed/carbonate fraction:* 1M sodium acetate ($CH_3COONa{\cdot}3H_2O$), pH 5 with acetic acid, dilution 1:20, 5 hours shaking.

*Reducible fraction:* 0.04M $NH_2OH{\cdot}HCL$ in 25% (v/v) acetic acid, 96°C for 4 hours, dilution 1:10.

*Organic fraction:* 0.005M DTPA (Diaminetriethelene-pentaacetic acid), dilution 1:5, 24 hours shaking.

*Residual fraction:* Concentrated HCl and $HNO_3$, ratio 3:1, dilution 1:10.

After each extraction step, all samples were centrifuged for 30 min at 3,000 rpm and the supernatant decanted and filtered for analysis. Between steps, the residue was washed with deionised water (centrifuged at 3,000 rpm for 15 minutes) to remove any traces of the previous extractant solution. The second supernatant was discarded. Analysis for Pb, Zn, Cu, Mn and Fe was conducted using flame atomic absorption spectrophotometry.

## Results and Discussion

Metal concentrations for the five selected fractions are shown in Figures 2–4. The values are expressed as a percentage of total metal content. A discussion of total contamination is not included as this has been reported elsewhere (Lewin and Macklin, 1987; Lewin *et al.*, 1977).

Lead (Figure 2) occurs predominantly in the non-detrital phase; only the <63 μm fraction at the mine site shows residual phase domination. Conversely, both Zn (Figure 3) and Cu (Figure 4) dominate in the residual phase, with the labile phases becoming more important with progressively finer sediments. For instance in the 2,000–250 μm fraction (excluding the mine site) residual Zn ranges from 41–71% of total and Cu from 54–74%, whereas residual Zn in the fine fraction ranges from 19–44%, and Cu from 24–61% of total metal content.

The explanation for this residual phase enrichment for Cu and Zn is to be found in the history of local mining. Before 1870, no large market existed for Zn, and the ore was not separated during processing but was discarded in spoil heaps, with ore particles subsequently entering the main river channel as coarse particles. Therefore a century or more of mining activity passed with Zn as an unprocessed constituent of all wastes. When Zn became used for galvanising steel, spoil was reprocessed to extract zinc at the Cwmystwyth crushing plant, or transferred for treatment from Frongoch mine by aerial ropeway to the Gwaithgoch mine situated on the Grogwynion floodplain (Bick, 1974). Chalcopyrite is also present in the mineralized veins, but not in economic quantities and was also discarded, subsequently to accumulate Cu in the coarse and medium sands.

Within the Ystwyth sediments the most enriched labile phase is the easily and the moderately reducible fraction, *i.e* the Fe and Mn oxyhydroxides (Figures 2–4). Co-precipitation with hydrous oxides is the major control

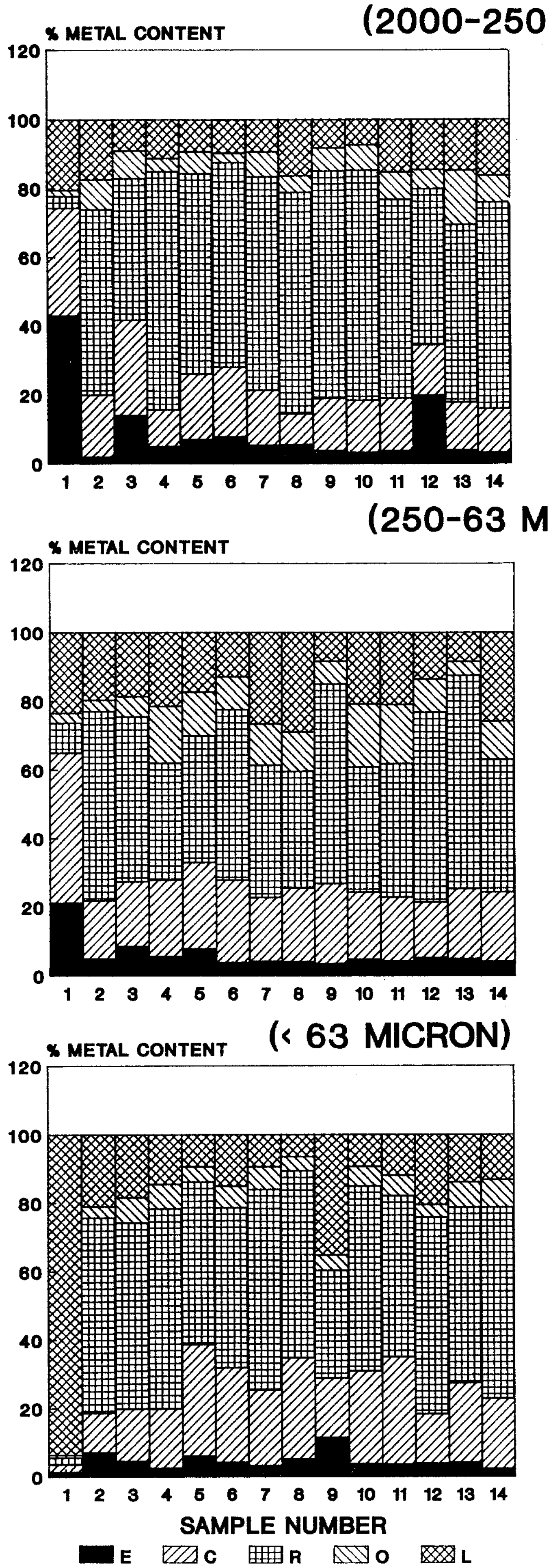

**Figure 2** *Partitioning of lead in bottom sediments from the River Ystwyth. E: exchangeable fraction; C: specifically adsorbed fraction; R: reducible fraction; O: organic fraction; L: lattice or residual fraction.*

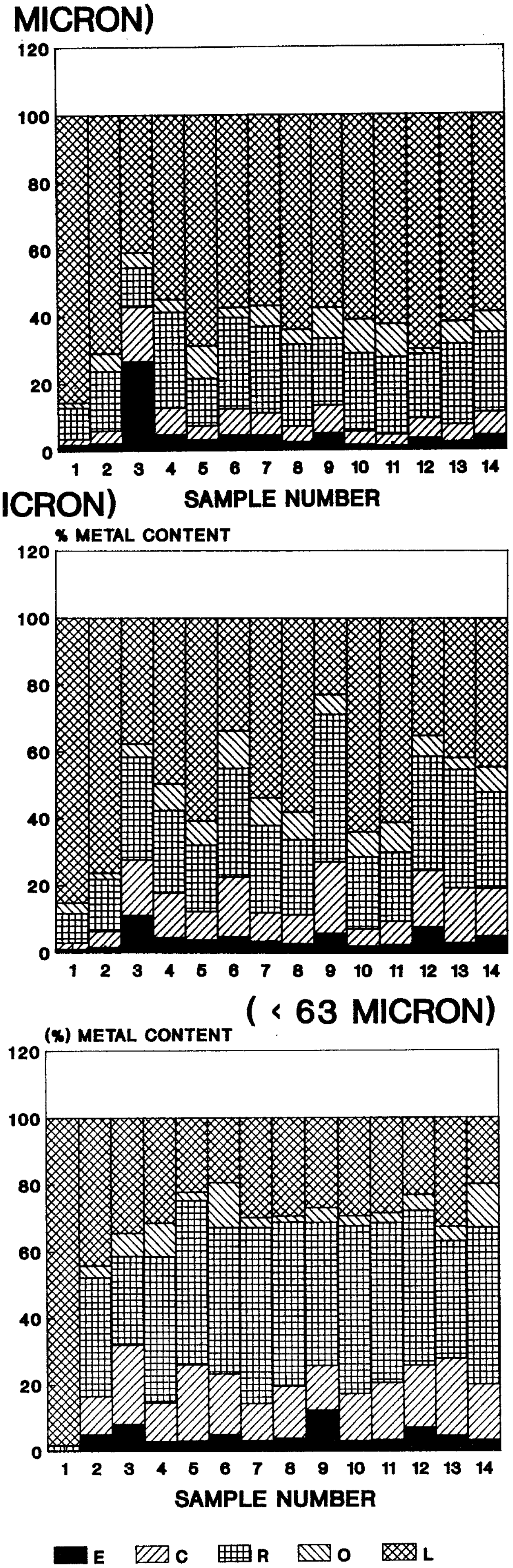

**Figure 3** *Partitioning of zinc in bottom sediments from the River Ystwyth.*

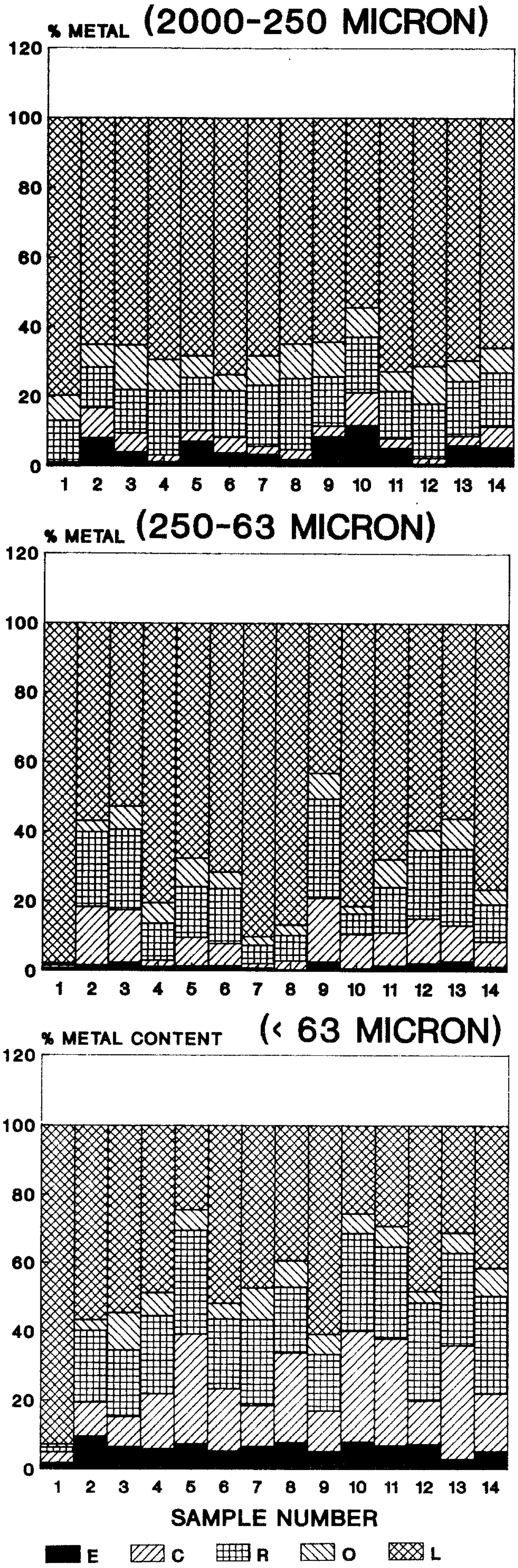

**Figure 4** *Partitioning of copper in bottom sediments from the River Ystwyth.*

**Table 1** *Correlation coefficients between specifically adsorbed metals and metals associated with the reducible fraction.*

| | 250–63 µm | | <63 µm | |
|---|---|---|---|---|
| Pb | $r = 0.94$ | $p < 0.001$ | $r = 0.24$ | – |
| Zn | $r = 0.96$ | $p < 0.001$ | $r = 0.7$ | $p < 0.01$ |
| Cu | $r = 0.70$ | $p < 0.01$ | $r = 0.9$ | $p < 0.001$ |

on the distribution of contaminant metals in the labile phase for all three particle size ranges. This study treats both Fe and Mn as a single phase in an attempt to discover trace element sinks. It is appreciated that hydrous oxides can be operationally separated into easily and moderately reducible fractions. In the 2.000–250 µm fraction, the accumulation order is Pb > Zn > Cu, values range from 3–69% of total Pb, 9–28% of total Zn and 1–20% of total Cu. For the fine sediments (<63 µm) Pb has a similar distribution, whilst the importance of Zn and Cu co-precipitation raises to 26–52% and 16–30% of total Zn and Cu respectively.

This co-precipitation/adsorption phenomenon is largely due to the presence of amorphous fresh oxides (Shuman, 1977) with the pH values of the sediment being critical for adsorption. In this study only Zn is affected by the sediment pH; (correlation coefficient $r = 0.83$ for the 2,000–250 µm size fraction; $r = 0.76$ for the 250–63 size fraction; and $r = 0.82$ for <63 µm sized particles, ($p < 0.01$). Similar results were reported by Stanton and Burger (1967) and Kalbasi *et al.* (1978). Stanton and Burger, (1970) also reported that the sorption capacity of Zn on Fe oxides was related to the amount of phosphate ions adsorbed by the oxides. Pb distribution is dominated by the removal from solution by sorption on hydrous oxides. Pb adsorption by hydrous ferric oxides is greater when Pb is present in solution during precipitation, than if added after. This would accurately reproduce conditions observed with acid mine drainage. Currently, input from such drainage is probably the greatest source of soluble metals to the fluvial system.

Similar results are quoted by Macklin and Dowsett (1989) and Bradley and Cox (1987) for alluvial and stream sediments from base metal mining areas. Other studies on Mid-Wales sediments (Bradley, 1984; Jones, 1986) highlight the importance of association with organic matter on the distribution of metals in the fluvial environment. However a different extractant for the organic 'pool' was used in the present study. The use of hydrogen peroxide as an organic extractant solution will also oxidize metal sulphides, resulting in artificially high levels for this 'pool'. Organic associated Pb, Zn and Cu account for only approximately 10% of total metal contamination, with no difference being observed with varying particle size.

Interactions can occur between the organic constituents and the hydrous oxides with the formation of precipitated complexes (Lamar, 1968) and solid phase changes in metal distribution, (Stumm and Lee, 1961). In the Ystwyth river reducible Fe and Mn only correlate with organic bound Fe and Mn for the finest particle size range, suggesting the formation of a colloidal complex. For Fe $r = 0.93$ ($p < 0.01$) and for manganese $r = 0.65$ ($p < 0.05$).

Physical and chemical adsorption contribute significantly to total metal contamination, in the order Pb > Zn = Cu, (Figure 2–4). Hydrous oxides scavenging of soluble metals by adsorption appears specific between pH ranges 5 and 7 (Gadde and Laitinen, 1974). This is certainly the case for the Ystwyth bottom sediment, downstream from Cwmystwyth.

At the mine site itself, the coarser fractions (2,000–63 μm) are dominated by specific and non-specific adsorption of Pb but by residual fixation of Zn and Cu. Foster *et al.* (1978) suggested that Cu and Zn were not adsorbed by precipitated hydrous oxides until sediment pH values exceeded 4.5 and 6 respectively, and this may explain the observed metal distribution in the main river channel. However Pb is scavenged immediately by freshly precipitated amorphous iron oxides and manganese oxides, with chemical adsorption accounting for 43% of Pb on the 250–63 μm fraction and 31% of Pb on the 2,000–250 μm fraction. Iron and manganese are also mobile in the headwater region of the river due to the presence of upland peat, and this has the effect of providing copious oxyhydroxides as a scavenging substrate for the fluvial system. (Fuge, personal communication).

It has been widely reported that carbonate sorption, or co-precipitation is an important solid phase for metal adsorption (Deurer *et al.*, 1978). Calcite is present as a gangue mineral in the Cwmystwyth ores, but its absence in river sediments suggests that the chemical, or specific adsorption 'pool' is related to hydrous oxide adsorption and not to carbonate co-precipitation.

Further evidence for this is available in the fact that Pb, Zn and Cu values for the specifically sorbed fraction are highly correlated with those for the reducible fraction in the 250–63, and <63 μm ranges, (Table 1). In the 2,000–250 μm fraction only specifically sorbed Pb is correlated to the reducible metal content, $r = 0.78$ ($p < 0.001$). The mine site is an extreme example of this.

## Heavy Metals in Selected Floodplains

Natural river systems ultimately deposit their load as floodplains, which are constructed either by lateral accretion or as overbank sedimentation when bankful discharge is exceeded. The former process is 90% dominant (Wolman and Leopold, 1957). Floodplains are therefore an ephemeral storage site for sediments, but are also a storage site for sediment associated metals. As river meandering proceeds, banks are undercut and lateral bars are constructed causing a cycling of associated metals, and this is little understood.

Total concentrations for Pb, Zn and Cu from three selected floodplains (Llanilar, Wenallt and Grogwynion) are shown in Figure 5; with the contrast between bed sediment metal content and floodplain metal content being of particular interest. Figure 5a–c shows that the finest grained bed-sediments have the highest metal content; for example Wenallt concentrations for Pb, Zn and Cu are 1,200 $\mu g\ g^{-1}$; 650 $\mu g\ g^{-1}$ and 118 $\mu g\ g^{-1}$ respectively. However for the coarsest particulate fractions, concentrations are considerably lower; 750 $\mu g\ g^{-1}$, 450 $\mu g\ g^{-1}$ and 20 $\mu g\ g^{-1}$ for Pb, Zn and Cu.

The distribution of metals within floodplain soils is completely different, with fines (<63 μm) no longer being the most contaminated fraction. Cu shows no appreciable difference between the particle sizes (Figure 5f), whilst Pb and Zn (Figure 5d–e) show metal enrichment on coarse and medium sands. The metal values for fine sand and for the silt and clay fraction show little difference. In terms of metal association observed in floodplain sediments, the reducible fraction is the most enriched labile phase in all the particle size fractions; 32–58% of total Pb, 17–41% of total Zn and 6–25% of total Cu. Similarly, chemical sorption is important for the association of Pb in floodplain soils, but less for Zn and Cu. For the latter two elements the residual phase still remains of considerable importance, this implies a longer residence time in the hydrosystem.

Perhaps more valuable is the comparison between coarse bedload metal loadings (2,000–63 μm) and floodplain metal levels for all particulate size ranges. Pb and Cu have roughly the same values, 900 $\mu g\ g^{-1}$ and 25 $\mu g\ g^{-1}$ respectively. As the river is incising into a contaminated aggradation surface a similarity between bedload and floodplain metal content results. Zn is enriched in contemporary bed sediment due to the reworking of alluvial deposits rich in zinc from upstream sources. Contemporary floodplain fines are likely to be derived largely from a combination of two factors. First, from the weathering of coarser particles, and secondly from the legacy of fine grained interdigitary fills of fines occurring with overbank gravel splays deposited in the late nineteenth century (Lewin *et al.*, 1983).

## Conclusion

Sixty years after the cessation of metal mining in the Ystwyth catchment, reported metal values for Pb, Zn and Cu still remain high in both stream sediments and floodplain soils. Within the labile, phase all metals are controlled by the distribution of Fe(III) and Mn(IV) compounds. The labile phase is also more important for the finest particulate fraction. Within coarse bedload, Zn and Cu remain largely as residual rock particles and are subsequently expected to weather slowly over time adding metals for aquatic redistribution. Pb remains non-detrital for all particulate fractions with the importance of specific adsorption by hydrous oxides stressed as a sorption phenomenon little mentioned by similar studies.

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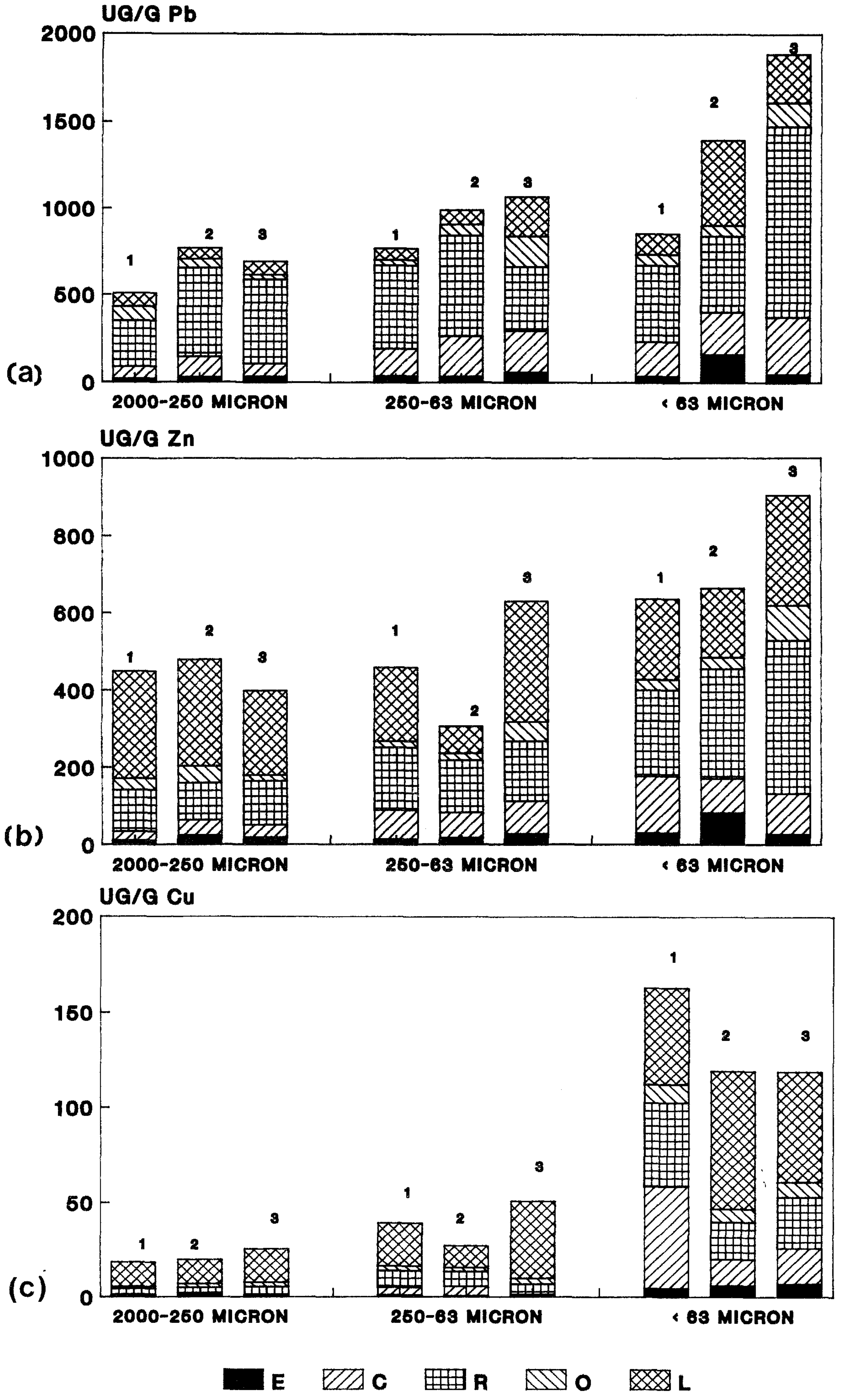
UG/G Pb
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250-63 MICRON
< 63 MICRON
UG/G Zn
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800
600
400
200
0
(b)
2000-250 MICRON
250-63 MICRON
< 63 MICRON
UG/G Cu
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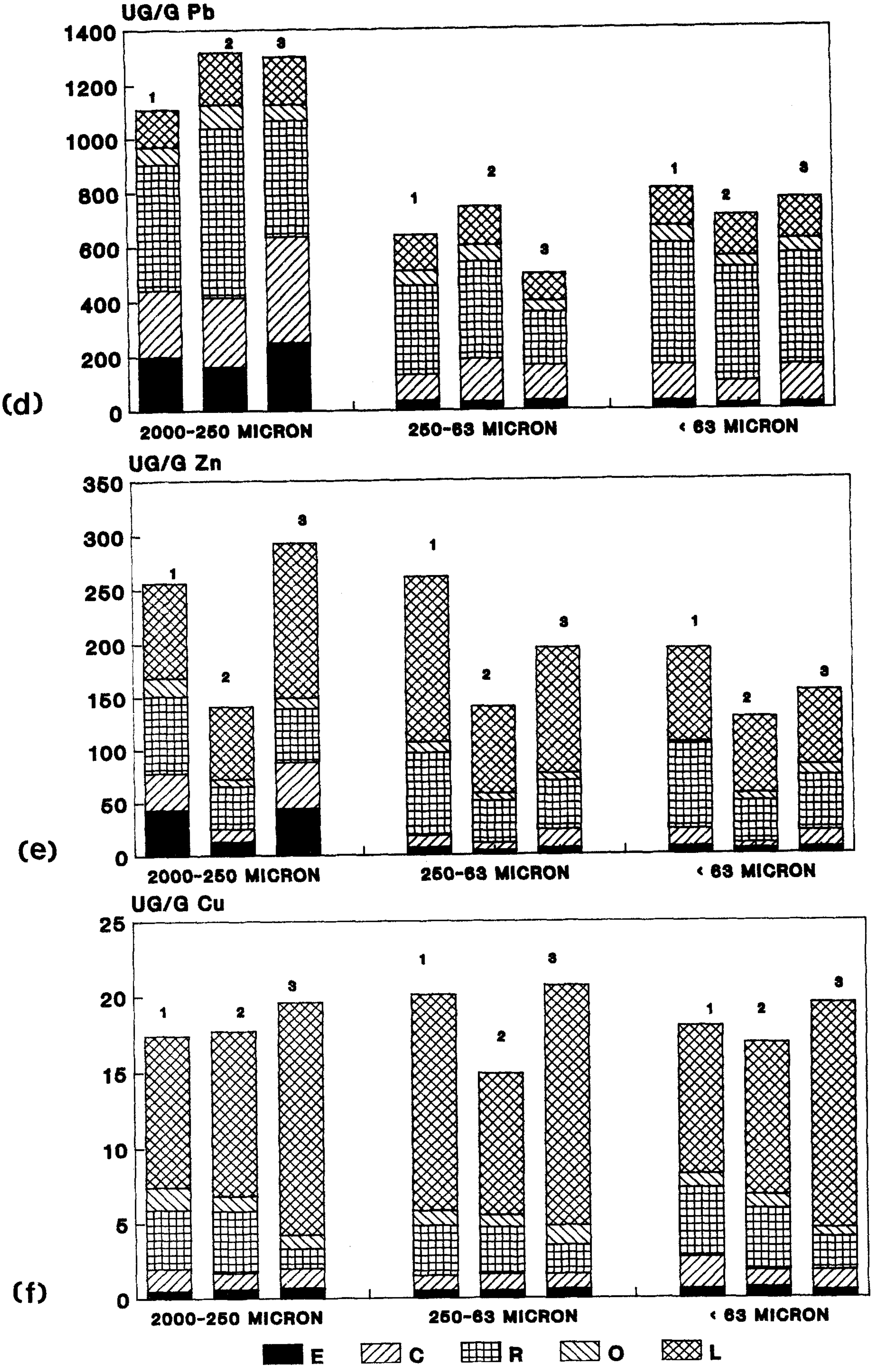

**Figure 5** *Stream sediment and floodplain metal content at selected sites on the River Ystwyth. 1 – Llanilar; 2 – Wenallt; 3 – Grogwynion. (a) Sediment lead content; (b) Sediment zinc content; (c) Sediment copper content; (d) Floodplain lead content; (e) Floodplain zinc content; (f) Floodplain copper content.*

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