



Hydraulics Research
Wallingford

HEAVY METAL DETERMINATIONS ON SEDIMENTS

Particle size dependence II.

Liverpool Bay river inputs

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ABSTRACT

Previous work has shown that the distribution of heavy metals on river and estuarine sediments is not confined to the fine fraction where surface adsorption from solution takes place. Metals present in the coarser sediments can sometimes greatly exceed in quantity those present on the clay minerals. Because of the continuing work on the disposal of sludge and dredging spoil in Liverpool Bay, the metal concentrations in the sediments of rivers flowing into the bay were determined in order to compare these metal sources which are in addition to those of sludge and spoil.

Bed sediments were sampled from thirteen rivers with input directly or indirectly into Liverpool Bay. A further sediment sample was taken from the west of the sludge dumping ground. These sediments were divided into up to 27 separate size fractions and each fraction was analysed for the heavy metals, mercury, copper, zinc, lead, nickel and chromium.

The concentration of each metal in each size fraction for the thirteen rivers was determined and plotted as a size-concentration histogram. The concentration and distribution of metals throughout the various size fractions was examined and the relative inputs to Liverpool Bay discussed. Results showed that the Mersey tributaries and the R Alt contained the highest concentrations of metals both adsorbed on to the fine fraction of the sediments and as particulate minerals within the bed sediments. The presence of metals in high concentrations in the coarse grained sediments provides a metal input to Liverpool Bay which will persist, even if future discharges to the rivers are reduced or eliminated. The possibility of cleaning up these rivers will depend on the ability to remove or otherwise nullify the presence of these metals.

Inputs from North Wales show the influence of natural metal containing minerals within the Welsh mountains. The metals present in the Liverpool Bay sediments themselves show low but sometimes clear peaks in certain size ranges, but the majority of the metals present are in the fine fraction and have been adsorbed from solution or have been transported from the source on the fine fraction of the suspended sediment.

Using metal distributions as tracers for sludge is not likely to be successful because of the restricted size range and fragile nature of sludge particles, but the possibility of using metals distributions as a dredged spoil tracer may be worth further investigation.

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1 INTRODUCTION

The input of heavy metals to the marine environment from coastal sources is an addition to the metals originating from the dumping of sewage sludge, dredging and industrial spoils. Whether or not these coastal sources are of anthropogenic or natural origin is not always easy to ascertain or define. Natural river-borne minerals serve as an upstream source of metals, both in solution and in particulate form. Man's disturbance of top soil by agriculture, mining, civil engineering construction etc can increase the availability of such minerals to erosion and transport to the sea. Industrial wastes, urban and rural drainage all contribute to the heavy metals found in river sediments.

A qualitative estimation of the input of heavy metals from the rivers flowing into the Liverpool Bay area has been attempted. Samples were taken from thirteen rivers and an additional sample recovered from the western side of the the sludge disposal area in the bay (Fig 1). Nine of the samples were taken by grab from road bridges, four samples from the Manchester area, were taken from the bank at water level at the points indicated. The Liverpool Bay sample was taken by grab in the course of a routine bed sediment survey (Ref 1). The aim was to take a typical sample of the river sediment at a point where sufficient mobile fine material was present (below 2mm) to allow as far as possible an analysis of each sieve size fraction of the sediment. If the maximum size was below 2mm then that was accepted as the limit. If grains greater than 2mm were present then they were discarded and the concentrations determined on the fraction below 2mm.

All of the nine coastal river grab samples were taken from below the tidal limit, although the influx of off-shore sediments was expected to be minimal with the exception of possibly the R. Weaver. To define a point in a river where only naturally occurring metals could be found is impossible in most cases as some anthropogenic input occurs in all but the remotest areas. The presence of coastal towns affects the quality of the water and sediment in the rivers on which they stand and this was the chief reason for sampling at the described points.

2 METHOD

The bed sediment samples were split into up to 27 size fractions by a combination of wet and dry sieving and decantation. Classification above 38 μ m was made with stainless steel sieves to BS 410:1969. Classification in the 10 and 20 μ m sizes was made by wet sieving through polyester gauze and the final 2 μ m split was made by repeated decantation from a deionised water suspension assuming a fall velocity of 0.0036 mm/sec for particles of SG 2.65. The accuracy of the limits of these lower size fractions is not so good as that of the larger sizes. Weights of sediment in each size fraction were recorded and sub-samples taken, oven dried at 50°C for heavy metal analysis.

The heavy metal concentrations were determined by a contract laboratory. The method used was based on an atomic absorption spectrophotometric determination on a hydrochloric acid solution of a nitric/perchloric extraction of the sediment size fraction. Mercury was determined by a cold vapour absorption technique and was reported quantitatively up to a limit of 2 μ g/g and as greater than 2 μ g/g. Precision was quoted as $\pm 10\%$.

Because the method is essentially a surface extraction procedure, total metals are determined on the finer fractions whereas on the coarser fractions, only those metals which can be reached by the mixed acids are dissolved. Also, because the quantities of each fraction analysed are low (0.2g) sampling errors are greater in the larger sizes. It is in these larger sizes too, that individual metal containing mineral grains are found so that large variations can occur between adjacent size fractions due to the presence or absence of such grains. In one case, a comparison was made between analysing samples of uncrushed grains and grinding a further sample to a fine powder. The results showed little variation in sizes up to about 1mm but above the metal concentrations were generally higher on the crushed grains due to the metals in the interior being made available for extraction.

Results are expressed as micrograms of metal per gram of sediment in the particular size fraction. This is shown in the solid line histogram in Figs 3 - 8. Because of the different size distribution of the sediments from the various rivers, a further histogram (broken line) has been added to the figures. This is defined as the weight of metal in each size fraction per gram of total sediment. In other words, it shows the relative proportions of metal in the total sediment.

In addition, the mean concentration of metal in the mud fraction is quoted, C_m ; the mean concentrations of metal in the total sediment, C_t , and the percentage of metal in the mud fraction of the sediment, P .

The histograms for the Liverpool Bay sediments K, L and T are taken from previous work (Ref.2) and at that time, no size gradings were determined and so no weights of individual size fractions were obtained. These samples and the LB(G) sample were bulked from sediments taken along the grid lines G, K, L and T as defined in Ref.1. Line G is to the west of the sludge dumping ground and is taken as unpolluted. Line K and L cover the dumping area and line T includes the area adjacent to the Mersey outflow and the dredged spoil ground to the north.

Three samples of Davyhulme sludge were also analysed. The first, untreated, proved impractical to classify into size fractions as the organic materials continually broke down during sieving. The second analysis was made on the sludge residue after treating with hydrogen peroxide. This was intended to simulate the normal oxidation processes leading to the decomposition of sludge. Again, this was difficult to classify into size ranges as nearly 90% of the resultant material was below $38\mu\text{m}$ in size and this contained 98% of the metals. The third samples was ignited at 550°C to burn off all the organic matter. The resultant ash was easier to classify but difficult to disperse but still contained over 90% of the metals below $38\mu\text{m}$.

The sludge analysis showed that essentially all the metals are present in the fine material and these will mix and become adsorbed by the mineral sediments. Thus peak concentrations in the higher size ranges (above $38\mu\text{m}$) are not associated with sludge.

The distribution of the metals on the sludge residues is shown in Fig.2. The mercury is not included as losses occurred on ignition and the values on the peroxide treated sludge were all in excess of $2\mu\text{g/g}$.

3 RESULTS

The histograms shown in Figs 3 - 8 give the concentrations of metals in each size fraction and in the total sediment. Where there is a negligible quantity of metal in the sand fraction and a high concentration in the fines, then the metal does not originate locally but arises outside the area.

All the four Liverpool Bay sites show high concentrations in the fines and low in the sand indicating a source outside the sampling area. This however, does not differentiate between local sludge dumping and metals transported by water. Sludge contains high metal concentrations almost all in the mud size range (below $63 \mu\text{m}$) and thus would be found in the mud and not in the sand fraction of the sediment. The Liverpool Bay mercury histogram (below $20 \mu\text{m}$) shows a declining concentration roughly inversely proportional to the distance from the Mersey estuary. Similarly, zinc shows a slight increase towards the Mersey and lead a somewhat greater increase. Nickel and chromium do not change significantly. Copper alone shows a higher level of concentration adjoining the sludge dumping zone although the peak in the $50 \mu\text{m}$ size range could account for this. These results are not dissimilar to those of the latest more intensive sampling survey reported in 1986 (Ref 3).

There is a high concentration of copper, and also zinc and nickel at the LB(K) position at about $50 \mu\text{m}$. This is repeated for copper on each site, LB(G) and LB(L), but not for the other two metals. Also, there is a copper peak in the same size range for the Conwy sediments but again no zinc or nickel. All these metals are chemically similar and would be expected to behave in a similar manner whether originating naturally or as a manufacturing waste product. Although no metal peaks were present in our sludge sample in this size range, the variability of sludge is large and the origin in sludge cannot be entirely ruled out. Nevertheless, the origin from natural sediments seems more likely.

Of the North Wales rivers, the Ogwen is low in mercury and chromium and relatively high in copper, zinc and nickel both on the fines and in the sand fraction. This is consistent with the metal sources in the Welsh mountains. The Conwy concentrations of copper and lead in the mud are higher than the Ogwen, possibly because of the larger catchment area containing metal ores. The Clwyd and Dee are similar and fairly low in metal concentrations. The only differences are the high

concentrations of zinc present in the mud and in the 0.4mm size range of the Dee. A lead peak in the same size was also found indicating possibly the presence of a lead-zinc ore. The chromium peak at about 50 μm was identified as the resistant mineral chromite.

The Mersey and its tributaries are considerably more polluted. Mercury was found in the Weaver sediments, both fine and coarse, the mud concentration being similar to that found previously in the Mersey estuary (Ref 4). The Mersey, Medlock and Irk only contain metal in the fine fractions indicating input to the sampling area as solution or adsorbed on to fine particles. The Irk and Irwell are very high in lead, zinc and copper on both fine and coarse sediments with peak concentrations of over 2000 $\mu\text{g/g}$ on the fines. Nickel and chromium are also above average.

Moving northwards, the Alt shows the highest zinc contamination found anywhere in these surveys, over 10,000 $\mu\text{g/g}$ (1%) on the finest fraction and a similar amount on the 1mm size grains. This very high concentration on the coarser sizes will be the source of much zinc in suspension for years to come regardless of any diminution of the quantities input to the area. High copper contents were also noted as were above average nickel and chromium concentrations.

The Douglas and Wyre had low concentration of all metals and although the Ribble was slightly above average for metals on the coarser sediments, the concentration on the fine fractions were low.

A summary of the relative concentrations of metals on the river sediments is shown in Table 2.

4 DISCUSSION

The scatter exhibited by many of the results necessarily means that only large differences may be taken as significant. The principle adopted has been to note the major variations between rivers and between metals and to correlate them with their situation and to identify any significant differences between the river sediments and those of the offshore Liverpool Bay area.

The presence of heavy metals in coarse sediments is mainly due to the presence of metal containing minerals. These may be natural or may be particulate residues from anthropogenic activity. In the long term, these coarser particles degrade, either by abrasion and reduction in size and/or by the dissolution of the various individual minerals comprised in each grain. Both the rate of abrasion and dissolution depend on the quantity, velocity and chemical properties of the water in which they exist. The main factors controlling the rate of dissolution of metals are the pH of the water, the oxygen content of the water surrounding the sediment (often measured as the redox potential, eH) and to a lesser extent the concentration of the metal already present in the water.

The metals that are dissolved in the water can in turn be adsorbed on to the surface of the clay minerals present in suspension and on the fine fraction of the surface bed sediments. The concentration of metals present on these clay minerals (nominally below $2\ \mu\text{m}$ but in aggregates up to about $20\ \mu\text{m}$) can be very high. The highest metal concentrations are often associated with the low mud concentrations in the sediments. This arises because of the relatively uniform concentration of metals in solution reacting with varying amounts of clay minerals. The same quantity of metal being presented to a small quantity of clay will give a high concentration and to a large quantity will give a low concentration. Nearer to the source of the metal where the solution concentration is higher or where flow rates or turbulence causes rapid mixing of water and sediment both high concentrations of metals and high mud concentrations are found. This is noticeable in the R. Weaver where a high mud concentration (60%) still contains a high metal concentration.

Precipitation of metals as hydroxides depends on the pH of the water (Table 1). Sea water has a pH of about 8 and river water usually less so there is a tendency for soluble metals to be precipitated on reaching the sea. Metal hydroxides form loosely flocculated suspensions and behave, from the adsorption aspect, in a similar manner to that of metals in solution, the particles being adsorbed on to the clay particles by electrochemical attraction. Thus, in practice, in marine conditions, whether the metals is in true solution or present as flocculated particles in suspension does not affect its distribution in sediments.

In sediments below the bed surface where oxygen deficiencies can occur due to bacterial action, the pH can fall, metals come into solution, diffuse into the surface layers, reoxidise and precipitate again and may well become concentrated in the process. These processes could result in some of the high concentrations found in individual layers or areas of bed sediments.

5 CONCLUSIONS

The natural input of metals to Liverpool Bay from coastal sources is either from solution or from the transport of fine sediments containing adsorbed metals. The source of these metals can be anthropogenic or natural. Once in solution or deposited on sediment and mixed with saline water, the sources are indistinguishable except for a few cases when resistant mineral grains in specific size ranges can be identified (eg. chromite).

The major sources of fresh water inputs of heavy metals are from the Irk and Irwell and with the Medlock and Weaver contribute to the high metal content of the Mersey estuary sediments (Ref 4). The Alt also has a high metal input to the Bay, particularly of zinc.

The remaining rivers show minimal concentrations of metals, the North Wales sediment showing the natural inputs of copper, lead and zinc.

The Liverpool Bay offshore sites show that the coarse sediments are relatively free from metals and the fine fractions (below 50 μ m) contain the adsorbed metals. Copper peaks at 50 μ m in three of the four sites would be included in the mud fraction if the samples had been split at the normal 63 μ m size level. The concentrations of mercury increase toward the Mersey as do lead and zinc to a lesser extent. Chromium and nickel show little change.

The restricted size range of sludge particles precludes the tracing of sludge itself by monitoring the metal concentrations of specific size fractions. All metals that are attached to the organic fraction of the sludge transfer eventually to the clay minerals of the suspended and bed sediments as the organics are naturally oxidised.

This general study of river sediments has indicated the presence of metal containing grains in sizes up to 2mm. Very high concentrations have been found in some rivers. The transport of these coarse fractions well offshore can only be through dredging operations and the tracing of such spoil is possible providing that the metal distributions are sufficiently different from the background sediments. Further studies on selected spoil sources and disposal grounds would be needed before this could be quantified.

6 REFERENCES

- 1 HYDRAULICS RESEARCH. Sludge dispersal in Liverpool Bay. Twelfth bed monitoring survey. December 1984 - March 1985. Report No. SR 71, January 1986.
- 2 HYDRAULICS RESEARCH. Heavy metal determinations on sediments. Particle size dependence I. Report No. DE 72, October 1984.
- 3 HYDRAULICS RESEARCH. Sludge disposal in Liverpool Bay. Thirteenth bed monitoring survey. December 1985. Report No. SR 97, July 1986.
- 4 HYDRAULICS RESEARCH. Heavy metals in shoreline muds of Liverpool Bay and its estuaries. Report No. SR 29, February 1985.

Tables

TABLE 1

Heavy metal precipitation - pH

<u>Ion</u>	<u>pH</u>
Fe ³⁺	2.0
Cr ³⁺	5.3
Cu ²⁺	5.3
Fe ²⁺	5.5
Pb ²⁺	6.0
Cd ²⁺	6.7
Zn ²⁺	7.0
Hg ²⁺	7.3
Mn ²⁺	8.5
Co ²⁺	9.6

From Dean, Bosquir and Lanovette (1972). "Removing heavy metals from waste waters". Environ Sci & Technology, 6, 518-522.

TABLE 2 Summary of metal concentrations

River	Hg		Cu		Zn		Pb		Ni		Cr	
Ogwen	-	-	+	++	+	++	-	+	+	+	-	-
Conwy	-	+	++	-	-	-	++	-	-	-	-	-
Clwyd	-	-	-	+	-	-	+	+	-	+	-	-
Dee	-	-	+	-	++	++	-	-	-	+	+	-
Weaver	+	+++	-	+	-	-	-	-	-	+	+	-
Mersey	+	+	+	-	+	-	++	-	+	-	+	-
Medlock	+	-	++	-	-	-	++	+	+	-	+	+
Irk	+	-	++++	++	++	++	++++	++	+	+	++	+
Irwell	+	+	+	++	++	++	+++	++++	+	++	++	++
Alt	-	+	+++	++	+++++	+++++	++	++	++	+	++	+
Douglas	+	-	-	-	+	-	-	-	+	-	-	+
Ribble	+	++	-	+	-	+	-	+	-	-	+	++
Wyre	-	+	-	-	-	+	-	-	-	-	-	-
LB(G)	-	-	-	-	-	-	-	-	-	-	-	+

The first column under each metal shows the fine fraction of the sediment (< 63µm) and the second shows the coarse fraction. Concentrations are indicated as above or below the median concentration (+ or -) or with factors of 2, 5 and 10 times the median (++, +++, +++ respectively).

Figures

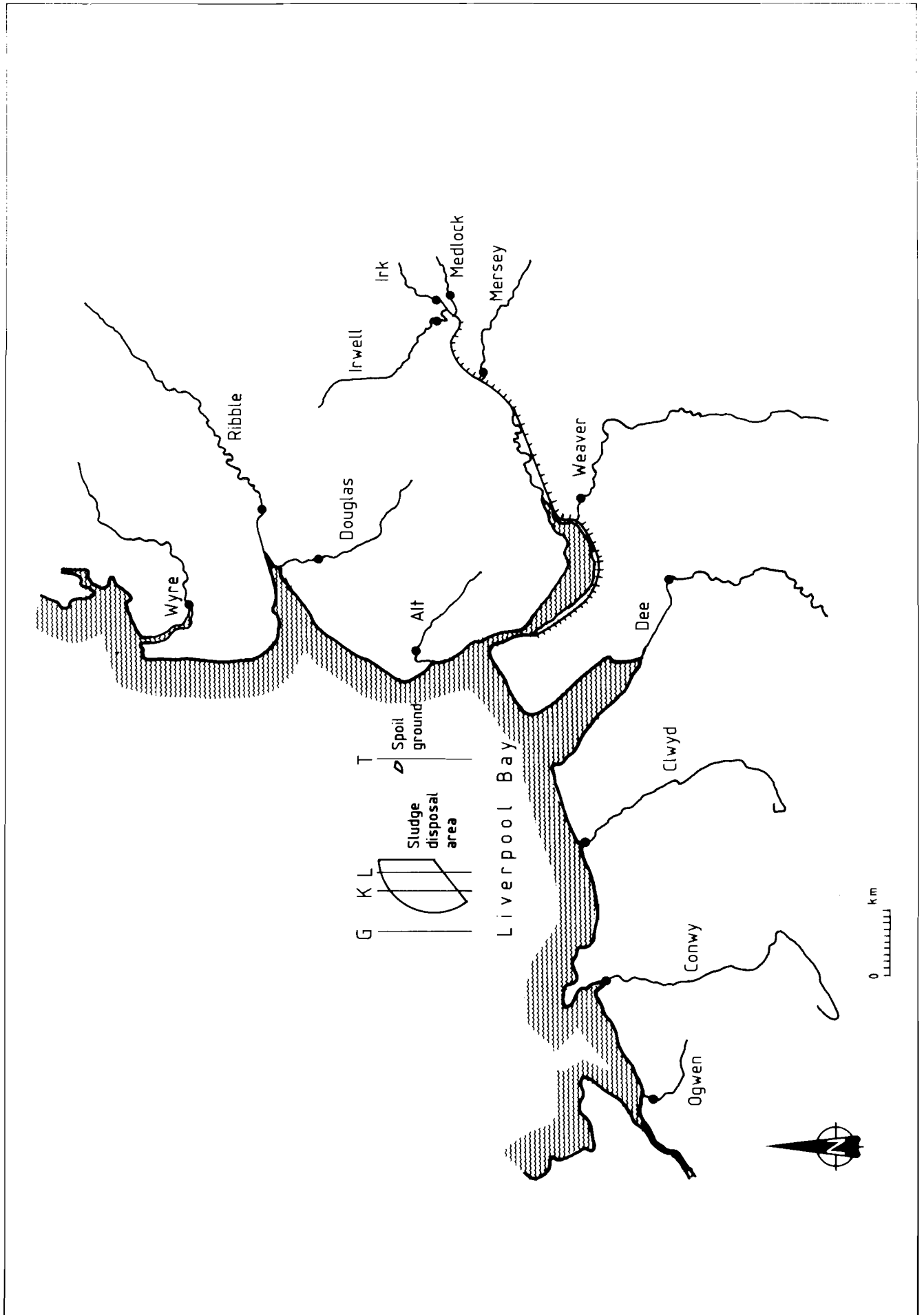


Fig 1 Sampling positions

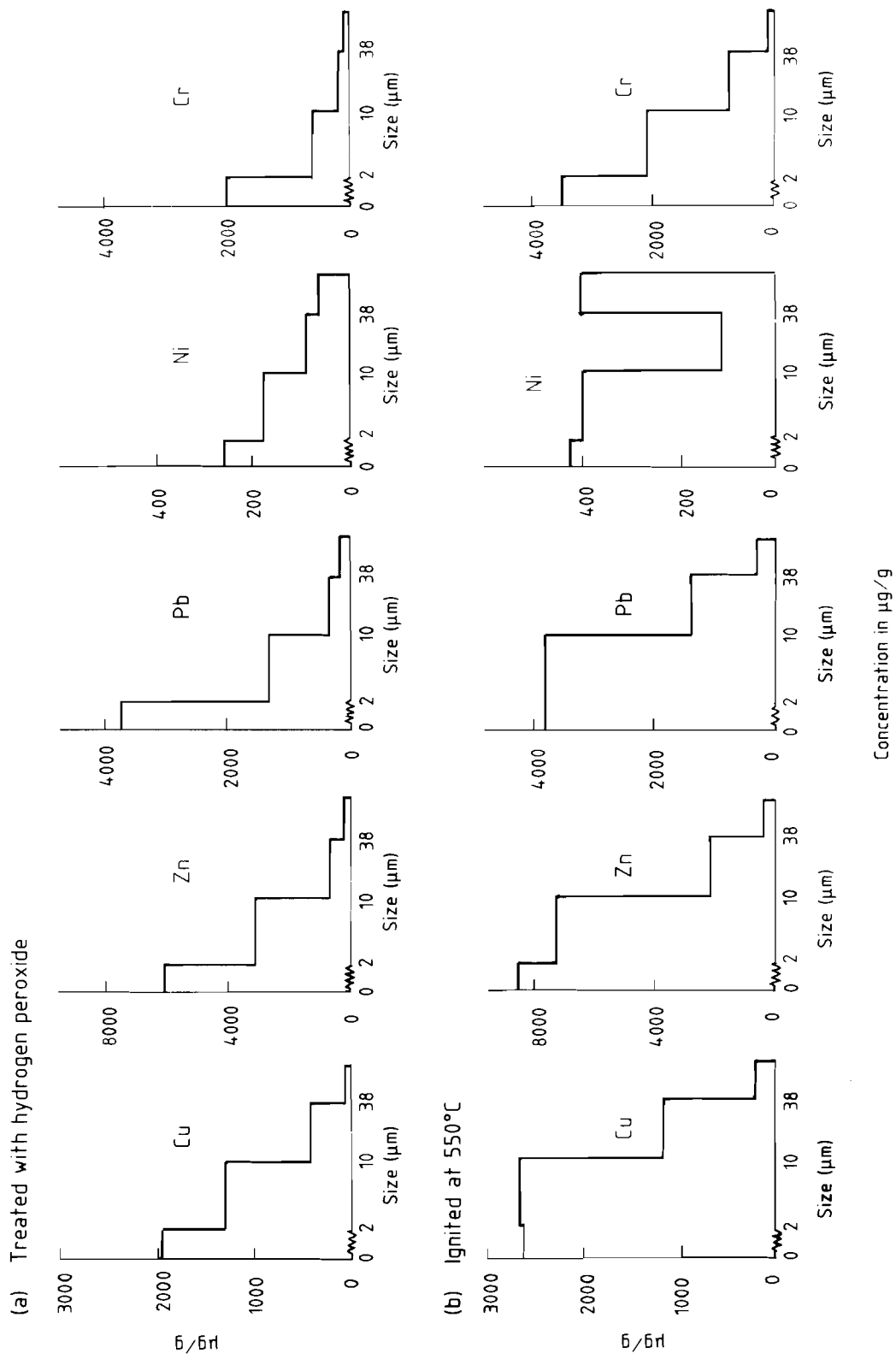
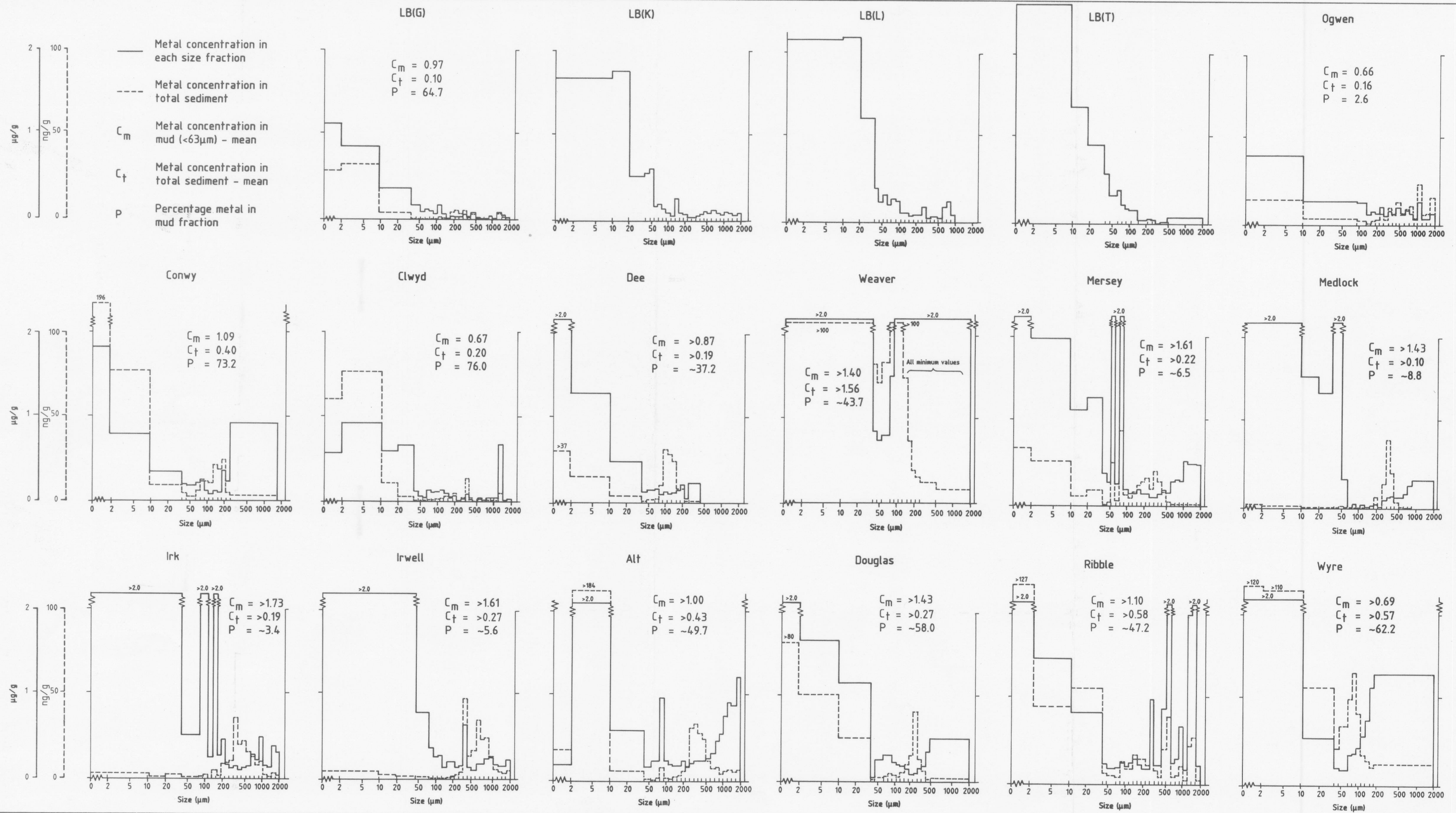
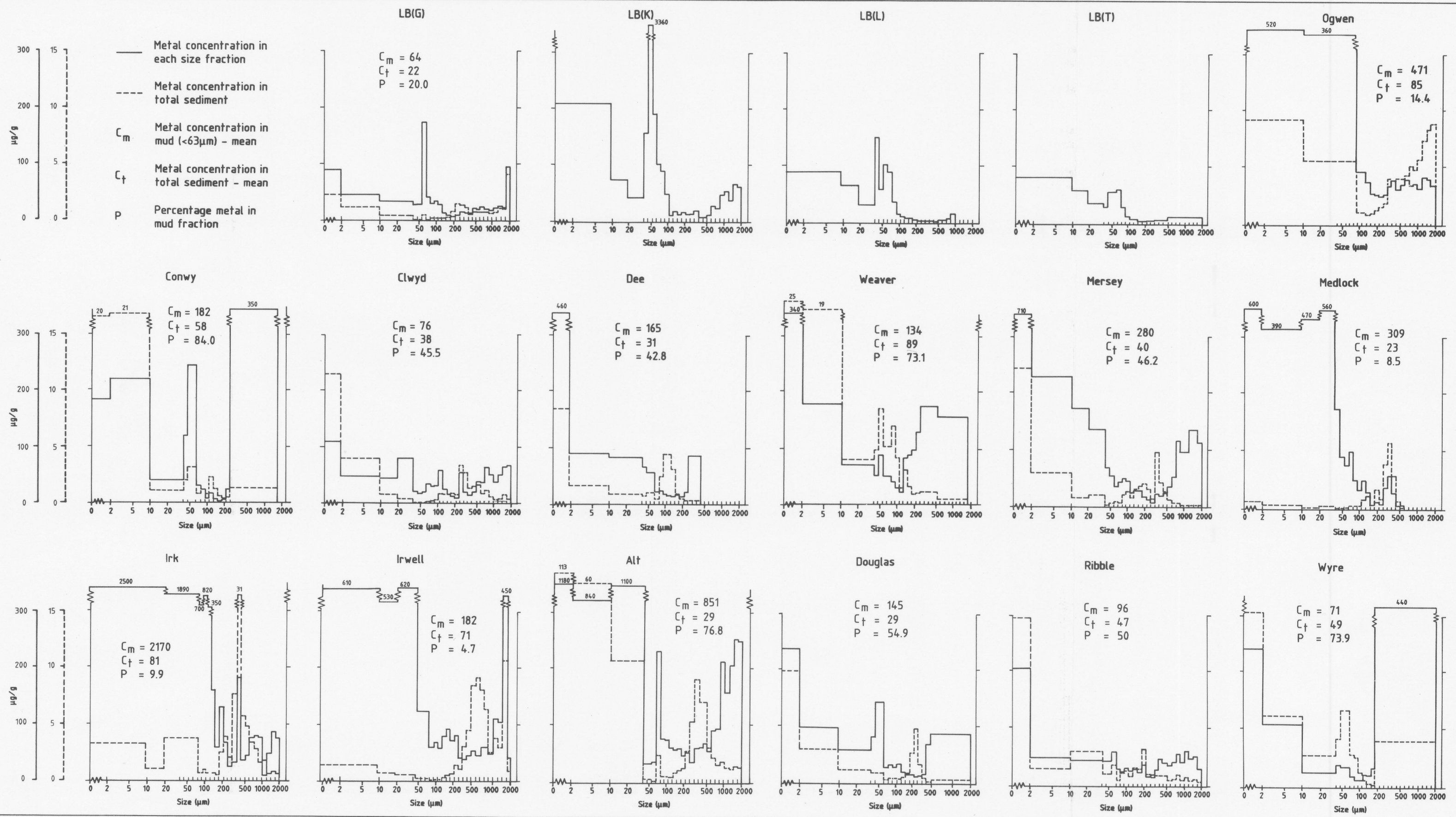


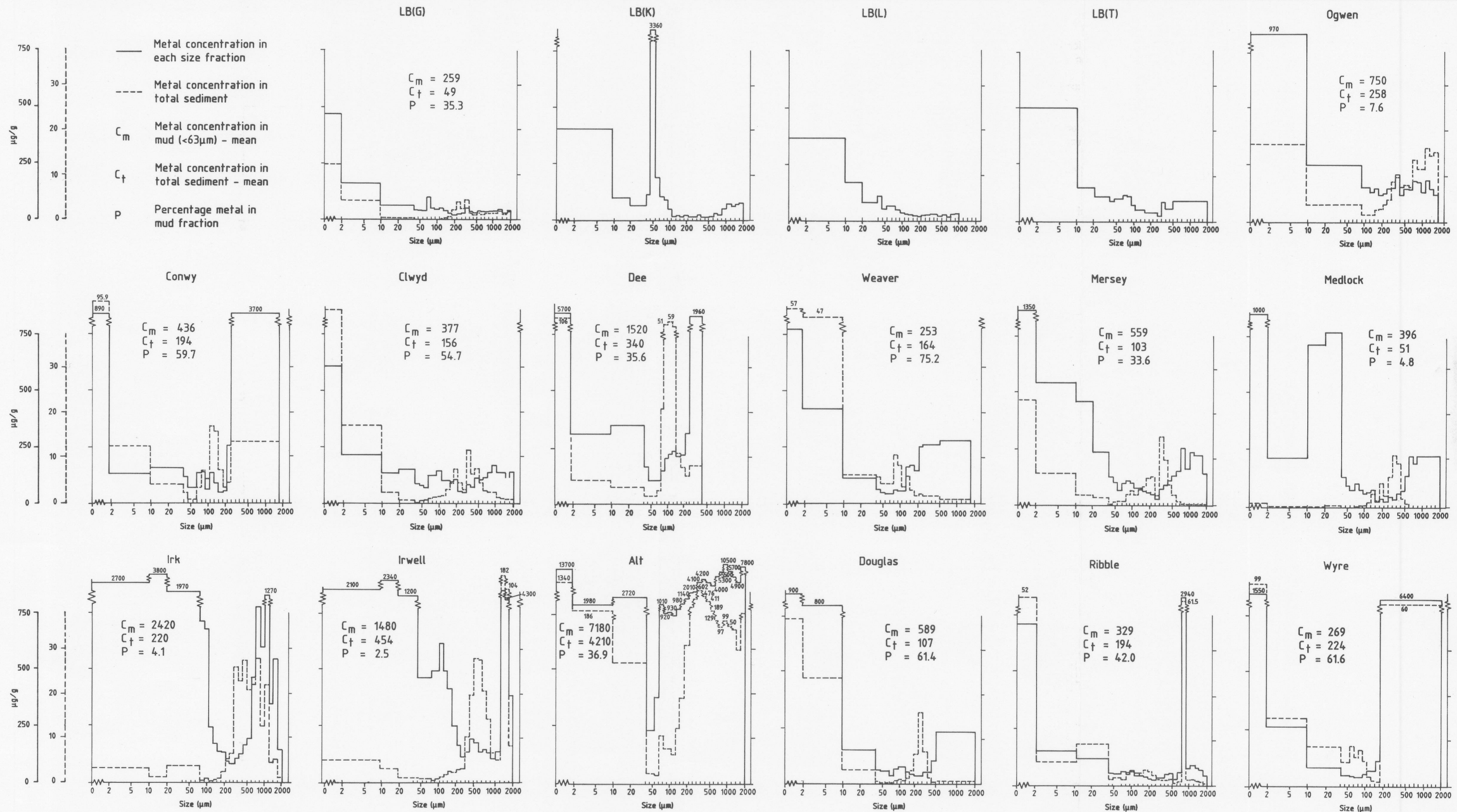
Fig 2 Metal concentration in sludge



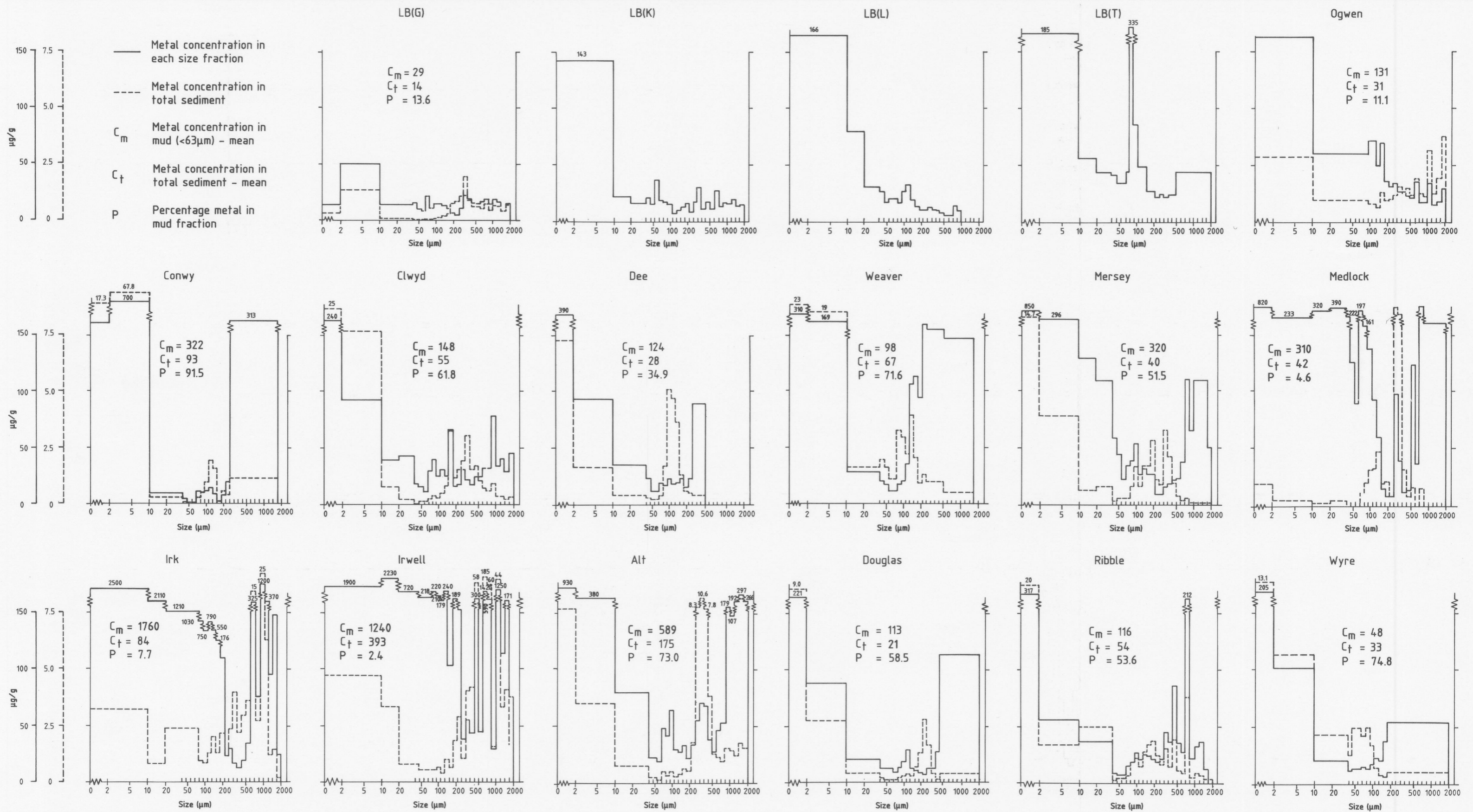
Mercury concentrations



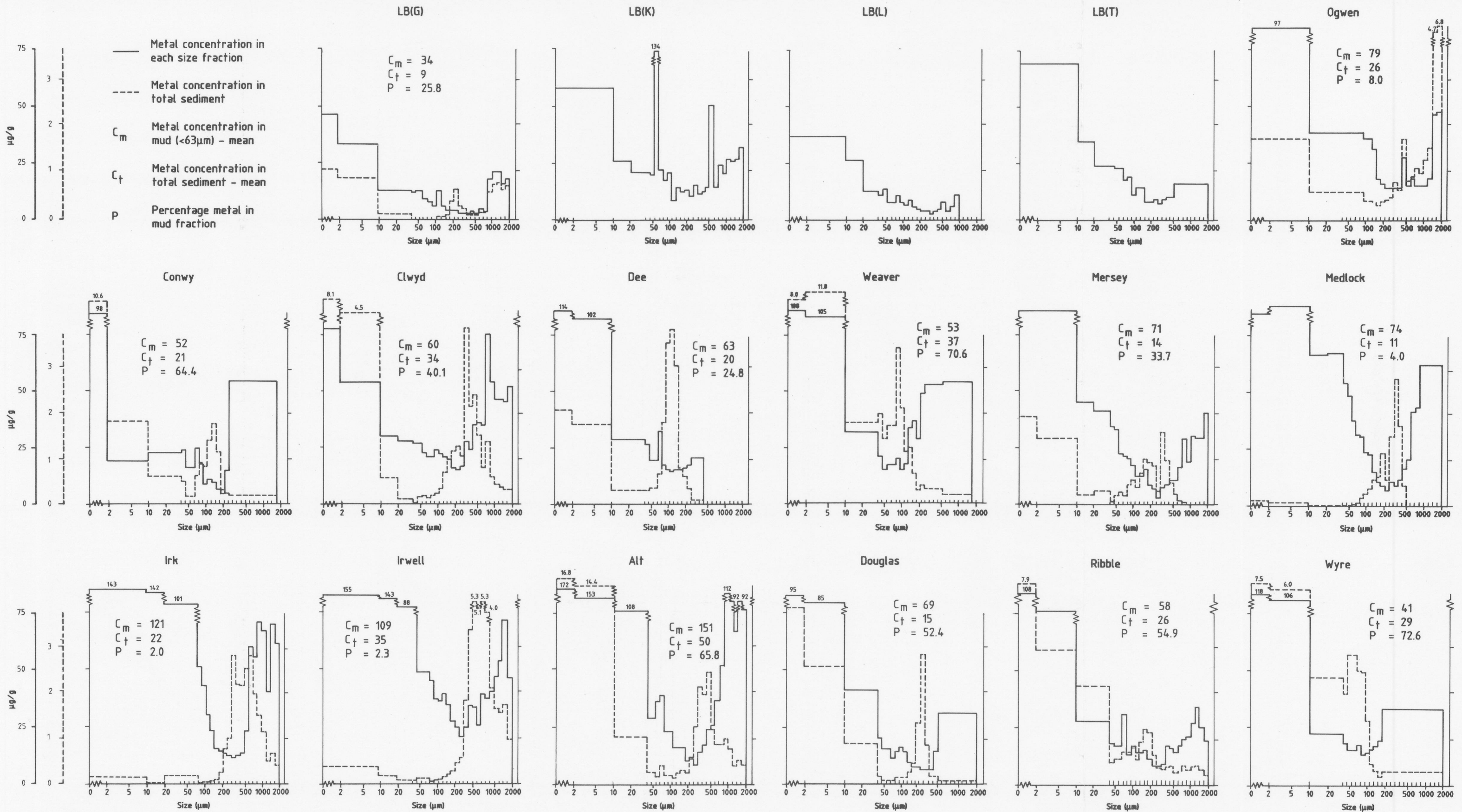
Copper concentrations



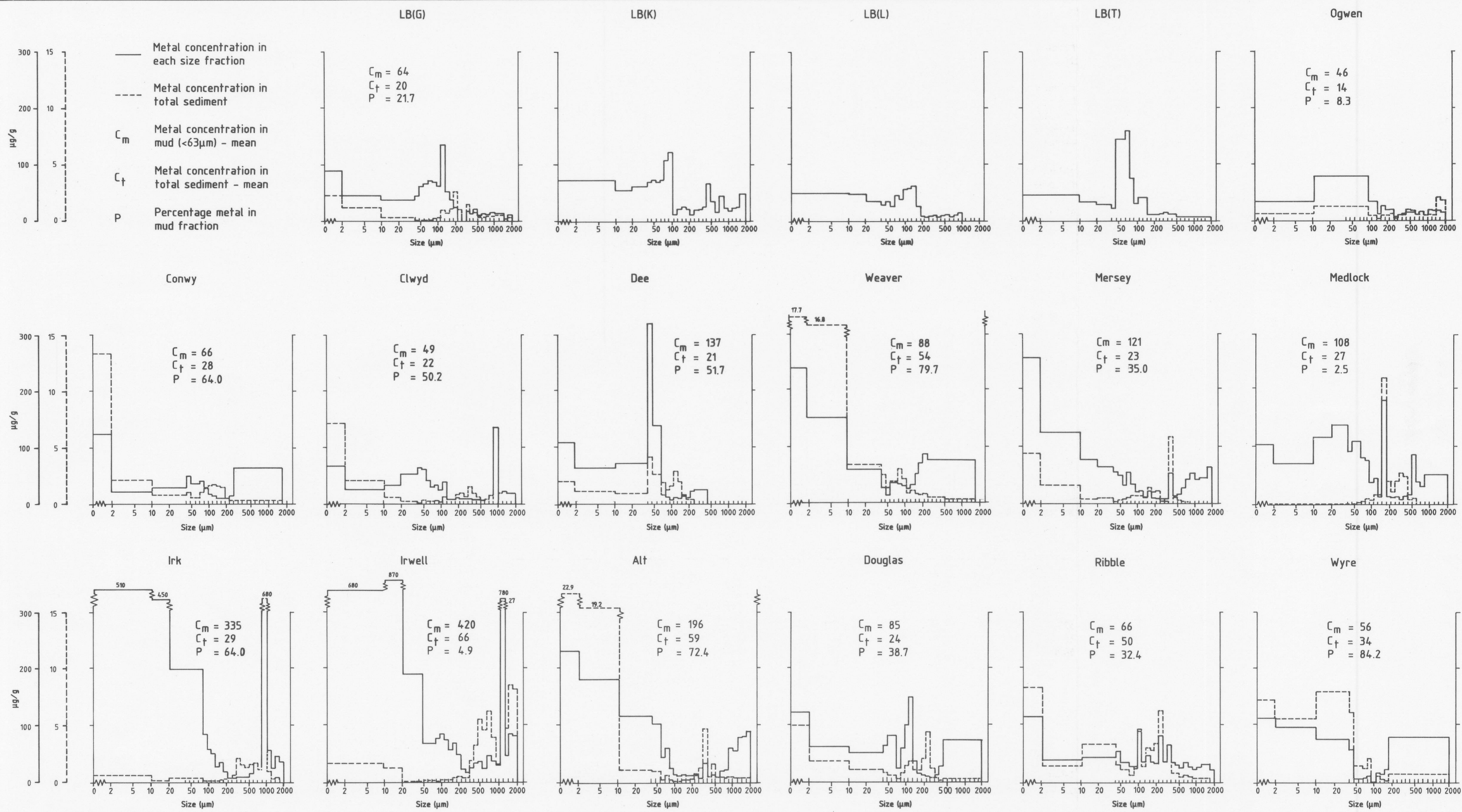
Zinc concentrations



Lead concentrations



Nickel concentrations



Chromium concentrations