Distinguishing between natural and anthropogenic sources of metals entering the Irish Sea

DETR Project CWO 734

Final Report

Coastal Geoscience & Global Change

Commissioned Report CR/01/15

CEFAS
The Centre for Environment, Fisheries & Aquaculture Science

Plymouth Marine Laboratory
NATURAL ENVIRONMENT RESEARCH COUNCIL

BRITISH GEOLOGICAL SURVEY

RESEARCH REPORT CR/01/15

Distinguishing between natural and anthropogenic sources of metals entering the Irish Sea

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Front cover

The city of Liverpool viewed across the Mersey Estuary from Egremont on the Wirral.

Bibliographical reference

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Foreword

This report is the published product of a study by the British Geological Survey (BGS), the Plymouth Marine Laboratory (PML) and the Centre for Environment, Fisheries and Aquaculture Science (CEFAS) concerned with the development of a methodology for distinguishing between natural and anthropogenic sources of metals entering the Irish Sea through major river systems. The work was funded under contract to the UK Department of the Environment, Transport and the Regions as a contribution to its co-ordinated programme of marine research for the North East Atlantic.

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Executive Summary

The OSPAR Action Plan 1998-2003 has an ".. ultimate aim of achieving concentrations in the marine environment near background values for naturally occurring substances ..". This aim requires that metals from anthropogenic sources can be distinguished from those originating from natural sources as a result of geological processes. Whether from natural or anthropogenic sources, high concentrations of metals in sediments are a potential hazard to biota. Environmental assessments and Quality Status Reports thus require a knowledge of the concentrations, sources and bio-availability of metals entering the marine environment. This project set out to address this need through the following objectives:

1. To develop a method of distinguishing between the natural and anthropogenic sources of metals entering the Irish Sea through river inputs.
2. To assess whether metals in estuarine and coastal sediments are biologically available.
3. To establish a means of distinguishing the relative contribution of the anthropogenic and natural sources of metals to any biological uptake or effect that may occur
4. To apply the devised methodology to a number of estuarine and coastal areas of the Irish Sea in order to demonstrate its effectiveness.

For Objective 1, the geochemistry of stream, river and estuarine sediments was used to identify natural background geochemical signatures, related to geology, and modifications to these signatures by anthropogenic activities. The BGS geochemical database, based on stream sediments from 1-2 km^2 catchments, was used to derive the natural signatures. Where mining activity was present, the impact on the signature was estimated by comparison with the geochemistry of sediments from a geologically similar, but mining free, area. River sediment samples taken upstream and downstream of major towns were used respectively to test the validity of using stream sediments to estimate the chemistry of the major river sediment and to provide an indication of the anthropogenic impact related to urban and industrial development. The geochemistry of estuarine sediments from surface samples and cores was then compared with river and offshore sediment chemistry to assess the importance of riverine inputs to the Irish Sea. In addition, a rapid, cost effective method of determining lead isotope ratios in sediments, has been developed. Objectives 2 and 3 were addressed through a programme of field sampling, using the clam *Scrobicularia plana*, known to be suitable and widespread except in the inner Solway (alternatives include another clam *Macoma balthica* and the ragworm *Nereis diversicolor*) as a bioindicator species, and by exposing representative species to sediment cores from estuarine and marine environments in the PML Mesocosm to observe the accumulation of metals over time. Studies were undertaken in the Solway, Ribble, Wyre and Mersey estuaries to meet the requirements of Objective 4.

The results verify that catchment averages of stream sediments and major river samples have comparable chemistry where anthropogenic influences are small. Major urban and industrial development causes easily recognised departures from the natural multi-element geochemical signature in river sediment samples downstream of the development and enhanced metal levels are observed in estuarine sediments with industrial catchments. Existing stream sediment chemistry coupled with limited river and estuarine sampling provides a cost-effective means of identifying anthropogenic metal inputs to the marine environment. Results also demonstrate that Mersey sediments have isotopic signatures between those of local natural lead and anthropogenic lead of imported origin. The highest lead concentrations correspond with the largest anthropogenic component. Data from the Solway catchment show that lead here is of essentially local origin.

Trends in bioavailability, represented directly by body-burdens in the indicator species, resemble patterns of anthropogenic enrichment in sediments, as defined by geological signatures, and decrease northwards, generally, away from the Mersey/Liverpool Bay. Predictions of bioavailability based on sediment chemistry can be made for some metals: weak chemical extracts frequently prove to be a more reliable 'mimic' of bioavailable metal than strong ones. Normalisation with respect to organics or iron oxyhydroxides also improves a number of the relationships, confirming the important role of these sediment coatings in modifying bioavailability. Mesocosm studies are promising as a screening method for bioavailability in sediments, though for estuarine scenarios they are best used to complement field observations, rather than as a substitute for surveys. The mesocosm approach is likely to be most useful and cost-effective with respect to offshore sediments or materials destined for disposal at sea, since *in-situ* measures of bioavailability are usually impractical here: a combination of uptake experiments with species such as the snail, *Turritella communis*, and chemical simulation (e.g. selective extracts), represent the most viable alternative.

1. BACKGROUND

It has been recognised for many years that the concentrations of metals found in rivers, estuaries and coastal waters, whether they be in the dissolved, suspended particulate or sedimentary phase, are derived from a variety of anthropogenic and natural sources. The dissolved load is affected by rainfall and there may be seasonal variations in metal concentrations, whereas the bed load is more likely to represent an integral over time of both suspended and bottom transported sediment and precipitates of dissolved materials (e.g. Fe and Mn hydrous oxides and accompanying sorbed trace elements). Work in temperate climates supports the view that metal concentrations in stream bedload sediments are relatively unaffected by seasonal variations (Chork, 1977; Bolviken *et al.*, 1979). In most circumstances, the major part of the anthropogenic metal load in the sea and sea bed sediments will have a terrestrial source, from mining and industrial developments along major rivers and estuaries. Metals with an anthropogenic origin must be distinguished from naturally occurring metals if contamination is to be properly assessed and the identification of specific sources of metals is desirable in order to facilitate control and monitoring of pollution. Of key importance in this latter respect is the presence or absence of mineralisation in the river catchment which can lead to a substantial proportion of the metal concentration present being unamenable to control. It can also account for major differences between river basins in both concentrations and relative distribution of the metallic elements present.

A considerable amount of data has been accumulated, both very recently and earlier, on the concentrations of a variety of metals in the sediment of the Irish Sea area. The available data relate to both the offshore and estuarine areas and to some extent the sediments of freshwater streams and rivers.

Unfortunately not all the available data are comparable, either because the sampling and analysis procedures used were not identical or because, even when they were, they were not subject to modern analytical quality control and assurance procedures. Furthermore, the different groups generating data have often treated their sediment samples in different ways prior to analysis (storage, drying procedures, sieving, leaching etc.). Even when such variations have been eliminated and a comparable data sub-set has been gathered together, key questions remain. These are: to what extent have man’s activities influenced the concentrations of metals found at a particular location and; do the concentrations found have any significance in biological terms. These two questions in turn give rise to a third question, namely is there a difference in the biological availability and significance to the two components of the concentration found.

This last question is particularly important in DETR terms as it is fundamental to the need, or otherwise, for control of metals discharged in effluents and atmospheric emissions. It is also a major issue in relation to the policies of the Commission on the 1992 North East Atlantic (OSPAR) Convention, by which the UK, as a contracting party to the Convention, is bound. Within the Commission and its committees the tendency continues to be one of assessing total concentrations (whether in total sediment or a sub-fraction thereof) and to consider any concentration above a vaguely defined ‘background’ as being directly attributable to man's activities. Furthermore, any excess above background tends to be assumed to be biologically available and thus detrimental to sedimentary organisms. The establishment of appropriate background values is thus of fundamental importance.

The countries party to the OSPAR Convention are currently engaged, at a regional level, in gathering together material to feed into a Quality Status Report (QSR) 2000, which will cover the entire Convention area. It would be particularly useful to have a clearer understanding of the origin and biological significance of the data on metal concentrations in sediments, gathered as part of the QSR process.

This project is therefore directed at the development of a generic method which will allow a distinction to be made between the natural and anthropogenically derived fractions of the total concentrations of metals present in the sediments of estuaries and their associated coastal waters.

The proposed methodology is based on using:

(A) multi-element sediment geochemical data to relate river, estuarine and marine deposits to natural and anthropogenically overprinted onshore and offshore sediment sources;

(B) lead isotopes to identify local and industrial (largely petroleum product) lead; and

(C) sediment-biota biogeochemical relationships to determine the bio-availability and potential environmental impact of identified contaminants.

The study area incorporates the catchment basins, estuaries and immediate offshore areas of the Mersey, Ribble, Wyre and Solway Firth (Nith, Esk and Eden) drainage systems, along with the smaller catchments of the Waver and Ellen, which drain into the Solway Firth.

After setting out the project objectives and major milestones, existing data is reviewed and then parts A, B and C (above) are described in separate sections, followed by a brief summary of the main conclusions and recommendations arising from them.

2. OBJECTIVES AND MILESTONES

2.1 Objectives

The project objectives, as set out in the tender document, were:

1. To develop a method of distinguishing between the natural and anthropogenic sources of metals entering the coastal zone through river inputs.

This task has been successfully completed, based on the use of existing BGS onshore geochemical data in conjunction with new sampling and analysis of major river, coastal and offshore sediments. The work has demonstrated that is possible to distinguish elevated metal concentrations due to: mineralisation alone; mineralisation subjected to mining activity; industrial and urban development; and other anthropogenic activity such as agriculture and road building. Using Pb isotope ratios it was possible to identify Pb from local sources and Pb related to petroleum products.

2. *To assess whether the metals in estuarine and coastal sediments are biologically available.*

This objective was achieved through a review of the literature backed by data from earlier studies carried out by the contractors. In general it has been shown that higher metal concentrations in sediment are reflected by higher levels in biota.

3. *To establish a means of distinguishing the relative contribution of the anthropogenic and natural sources of metals to any biological uptake or effect that may occur.*

A laboratory mesocosm study was used to approach this objective. Typical sediment dwelling animals were exposed to sediment cores taken from areas affected to varying degrees by anthropogenically derived metal enhancement. This clearly showed metal bioavailability, but the extent varied according the species and also depended on conditions in the sediment. Although anthropogenically enhanced metal levels in sediment are likely to be associated with higher uptake by animals, the relationship is variable.

4. *To apply the devised methodology to a number of estuarine and coastal areas of the Irish Sea in order to demonstrate its effectiveness.*

The procedures developed for assessing sediment metal enrichment were tested in the Solway, Wyre, Ribble and Mersey and their effectiveness demonstrated, fulfilling the requirements of the contract.

2.2 Milestones

Five milestones were built into the project:

Milestone 1 *1 March 1999*	*Completion of a review of existing datasets and check analyses to assess compatibility*

The work for this milestone was completed on time and the results described in an Interim Progress Report in February, 1999. It was concluded that a programme of new sampling and analysis, to complement existing BGS data, was necessary in order to fulfil the project requirements.

Milestone 2 *31 August 1999*	*Completion of the Phase 1 programme, including field collection of biota and sediment samples and chemical analyses*

Some slippage was experienced in achieving this Milestone because sample collection was more comprehensive than originally planned and thus not completed until mid-November 1999, with chemical analysis of sediment samples finishing in December 1999. An Interim Progress Report in December 1999 detailed the results.

Milestone 3 *31 December 1999*	*Completion of the Phase 2 programme, including field collection of biota and sediment samples and chemical analyses*

From the outset Milestone 3 was seen as marking an important progress point only if additional sample collection and analysis were deemed necessary after completion of Phase 1. In practice, the comprehensive and rigorous sampling and analytical programme carried out in Phase 1 meant that further field and laboratory work were not necessary and Milestone 3 was effectively passed during the extended course of Phase 1.

Milestone 4 *31 May 2000*	*Completion of the mesocosm studies*

The laboratory phase of Milestone 4 was completed on time, but full interpretation of the data was carried over to the next and final milestone.

Milestone 5 *31 July 2000*	*All project tasks completed*

Chiefly because of the slippage in the timing of the sample collection programme, a deferment of the project completion date to 31 October 2000 was requested and agreed. A draft of this final report was submitted at the beginning of October 2000.

3. REVIEW OF EXISTING DATA

A review of existing data, their compatibility and fitness for purpose, is a logical precursor to any programme likely to involve the collection of new data. Such a review can help avoid duplication of effort and throw light on the extent and nature of the problems under consideration. It was particularly important for this project, which set out to develop a methodology to distinguish between natural and anthropogenic sources of metals entering the Irish Sea based on the maximum use of existing datasets. Studies not specifically referred to elsewhere in this report are appended as a separate bibliography (Appendix 1)

The following review examines three types of datasets from the eastern Irish Sea region relating to: (1) onshore geochemistry and sources of contamination; (2) offshore and estuarine geochemistry and sources of contamination; and (3) biogeochemistry and sediment-metal availability.

3.1 Onshore geochemistry

The major data source used for onshore geochemistry and the characterisation of natural background geochemical signatures was the BGS stream sediment dataset for north west England and southern Scotland. This dataset, based on the <150 µm fraction of stream sediment samples collected at a density of approximately 1 per 1.5 km^2, was generated using optical emission spectrometry (DR-OES) as the major analytical technique and covers all the catchment basins pertinent to the project. Total concentrations of CaO, Fe_2O_3, K_2O, MgO, MnO, TiO_2, Ag, B, Ba, Be, Bi, Cd, Co, Cr, Cu, Ga, La, Li, Mo, Ni, Pb, Rb, Sn, Sr, V, Y, Zn, and Zr were determined. Two other elements, As and Sb were determined by either atomic absorption spectrometry (AAS) or X-ray fluorescence (XRF) techniques and U was determined using the delayed neutron method. Work in relevant basins took place between 1977 and 1990 and is described in three geochemical atlases covering the Lake District, Southern Scotland and Northwest England and North Wales (BGS 1992, 1993 and 1997 respectively). Details of quality assurance and quality control (QA/QC) procedures are given in these publications, which also provide interpretations of the geochemical distribution patterns. Small headwater catchments of the Mersey and Weaver river systems, not described in the three atlases, are covered by BGS work which has been completed, but not yet published.

The impacts of mineralisation and mining on the onshore geochemistry are discussed in the three atlases detailed above. Mineralised localities, along with the major elements present and commodities mined, were entered into the project GIS from BGS datasets. Urban and industrial sources of contamination were also compiled into the GIS from published sources.

3.2 Offshore geochemistry

Relevant estuarine and offshore datasets for the Irish Sea are listed in Table 1, from which it can be seen that there are significant problems of compatibility in terms of the size fraction, chemical extraction and analytical method used, and also in the range of elements determined. Three surveys, which employed the same sampling and analytical techniques, are of particular interest to this project: the OSPARCOM baseline survey of 1990-91 (OSPARCOM, 1994); the NRA estuarine survey of 1995; and the National Monitoring Programme (NMP) survey of 1997-98.

Sediment samples were collected at the stations shown in Figure 1, which shows the total coverage of the three surveys. Most samples from the initial OSPARCOM survey were collected between May 1990 and December 1991 from the MAFF ships RV CORYSTES and RV CIROLANA. Samples from the NRA survey were collected in 1995 using an NRA boat. Samples in the NMP survey were collected in 1997/98 from MAFF ships.

Samples were collected using a Day grab fitted with stainless steel jaws or, where the substrate was either too hard or too gravelly for the effective use of this device, a stainless steel Shipek grab.

For metals analysis, approximately 1 kg of the surface (0-1 cm) layer of sediment was taken using a polyethylene scoop and stored in a polyethylene container at -18°C. On return to the laboratory the samples were defrosted, sub-sampled wet and about 150 g freeze dried, the remainder being returned to an archive freezer. Each freeze-dried sub-sample was sieved at 2 mm to remove gravel particles and any large detritus. The sub-sample was then split to yield a 30 g sub-sample which was ground to a powder using a mechanical agate mortar and pestle.

Table 1. Estuarine and Offshore datasets relevant to the present study. See text for further information. References not in the main reference list can be found in Appendix 1. Continued……

Date	Area	Sites	Sampling Method	Fraction	Extraction	Determinands	Anal. Method	References	Notes
1967	Central NE Irish Sea	115	Bottom sediments by grab	<2mm	Total	B Ba Co Cr Ga Fe Mn Mo Ni Sn Sr Ti V Zr Cu Zn P K	Emission Spec. AAS Colorimetry Flame photometry	Cronan, 1970.	CO_2 also determined. Precision mentioned but no other QA/QC
Pre 1980	Coast and estuaries of NE Irish Sea		Intertidal sediments by hand	Whole sediment		Hg	Ref. in paper	Rae and Aston, 1981	Organic C also determined. Reference to QA/QC given.
1973-82	Liverpool Bay	18-100	Bottom sediments by grab	<80 <63 90-500	HNO_3/H_2O_2 $HNO_3/HClO_4$	Cd Cr Cu Hg Ni Pb Zn	AAS	Norton and Rowlatt, 1982a Norton and Rowlatt, 1982b Norton *et al.*, 1984a Norton *et al.*, 1984b Rowlatt, 1986	Organic C also determined. Data from two laboratories (MAFF & HR) using different methods compared.. Some QA/QC details
1974-83	Liverpool Bay, Dee and Mersey estuaries	92-408	Bottom sediments by grab, intertidal by hand, <1m-30m cores	Whole sediment	Aqua regia	Cd Co Cr Cu Mn Ni Pb Zn Hg	AAS Cold vapour AAS	Taylor, 1986	Organic C also determined. Mainly Mersey. Analytical QA/QC and sampling variability considered.
1980	Solway Firth	41	Intertidal surface sediment	Whole sediment	Total	Ba Cu Mn Nb Ni Pb Rb Sr Ti Y Zn Zr CaO Na_2O SiO_2 MgO Al_2O_3 K_2O Fe_2O_3 P_2O_5 LOI	XRF Beta Probe	Jones *et al.*, 1982	No QA/QC details. Part of a radiometric survey
1980-81	Mersey estuary and Liverpool Bay	23	Suspended sediment			Hg	Cold vapour AAS Ref. in paper	Campbell *et al.*, 1986	No QC details.
1980-84	N. Wales, Dee and Mersey estuaries to Cumbrian coast	44	Intertidal sediments by hand	<100	HNO_3 plus weaker leaches	Ag Cd Cr Cu Fe Mn Ni Pb Zn As Sn Hg	AAS Hydride gen. AAS Cold vapour AAS	Langston, 1986	Organic C also determined. No QA/QC.details. Temporal trends and speciation studied. Mainly Mersey.
1982-83	E Irish Sea	216	Bottom sediments by grab	<80	HNO_3/H_2O_2	Cu Ni Pb Zn	AAS	Rowlatt, *et al.*, 1984	No QA/QC details
1982-84	Mersey estuary	1	Suspended sediment and water			As Cd Cr Cu Hg Ni Pb Zn		Whitelaw *et al.*, 1985	No analytical method or QA/QC details given
1983-84	Liverpool Bay	63	Bottom sediments by grab	<63 Whole sediment		Total organic carbon Total carbohydrate	Ref. in paper	Vivian, 1987	Some QA/QC details
1984	Liverpool Bay	4	Sewage sludge	Whole sediment	$HClO_4/HF$	La Ce Pr Nd Sm Eu Gd Dy Ho Er Yb Lu	ICP	Vivian, 1986	No details of QA/QC
1984	Liverpool Bay	50	Bottom sediment by grab	Whole sediment	Aqua regia	Al Cd Cr Cu Hg Pb Zn	AAS	Rowlatt *et al.*, 1986	No QA/QC details given
1985	Liverpool docks, Mersey estuary and approaches	36	Bottom sediments by grab, dredge and core	Whole sediment	Aqua regia	Al Cd Cr Cu Fe Hg Mn Pb Zn	AAS	Rowlatt, 1988	No QA/QC details
1984-88	Liverpool Bay	60-67	Bottom sediments by grab, 30-80cm cores	<80 <63		Cr Cu Hg Ni Pb Zn	AAS	Kiff, 1986 Kiff and Crickmore, 1987 Kiff and Crickmore, 1989	Organic C also determined. Some QA/QC details.

Table 1. Continued.

Date	Area	Sites	Sampling Method	Fraction	Extraction	Determinands	Anal. Method	References	Notes
1988	Liverpool Bay	70	Bottom sediments by grab	<100 100-500	HNO_3/H_2O_2 Aqua regia-HF	As Cd Cr Cu Fe Mn Ni Pb Zn Hg Al	AAS Cold vapour AAS AAS	Wrench, 1989	LOI determined also C and N using a Carlo Ebra C-H-N analyser. Some QA/QC details
1988	Morecambe Bay	203	Bottom sediments by grab, beach and intertidal by hand	Sand Mud		Cd Cr Cu Ni Pb Hg	No details of methods or QA/QC given	Rostron and McLaren, 1989	
1988	Liverpool Bay	70	Bottom sediments by grab	<100 100-500 <500	HNO_3/H_2O_2 Aqua regia-HF	As Fe Mn Hg Al	AAS with graphite furnace for As and cold vapour technique for Hg	Camacho-Ibar *et al.*, 1992	LOI determined also C using a Carlo Ebra C-H-N analyser. QA/QC details given.
1989	Morecambe Bay	144		<63 <500	HNO_3/H_2O_2 Aqua regia-HF	Cd Cr Cu Ni Pb Hg Al	AAS Cold vapour AAS AAS	Wrench and Loney, 1989	Some QA/QC details. C, N, LOI and stable carbon isotopes ^{13}C and ^{12}C also determined
1989	Liverpool Bay	70	Bottom sediments by grab	<100 100-500	HNO_3/H_2O_2	Cd Cr Cu Ni Pb Hg	AAS Cold vapour AAS	Wrench and Crow, 1990	Organic C also determined.. No QA/QC details
1972-91	UK estuaries on Irish Sea	~250	Surface sediments	Whole sediment to 1976 <100 post 1976	HNO_3	Ag As Cd Co Cr Cu Fe Hg Mn Ni Pb Se Sn Zn	AAS with hydride generation and graphite furnace as appropriate	Burt *et al.*, 1992	Some QA/QC details
1990-91	Irish Sea	~90	Bottom sediments by grab	<2mm	Aqua regia-HF (Ex. Hg)	Al Cd Cr Cu Fe Hg Li Mn Pb Zn	AAS	OSPARCOM, 1994 Rowlatt and Lovell, 1994a	Part of wider survey of OSPAR region. Some QA/QC details given.
1991	Liverpool Bay	16	Bottom sediments by grab	<63	Aqua regia	Cd Cr Cu Hg Ni Pb Zn	AAS	MAFF, 1993	No QA/QC details given
1991	Dee estuary and Irish Sea	~50	Intertidal, subtidal (by grab) and SPM	<63 <1mm SPM	Acetic acid	Al Ca Cd Cr Cu Fe Mn Pb Zn	AAS with graphite furnace for Cd and Cr	Turner *et al.*, 1994	C and N determined using a Carlo Ebra C-H-N analyser. QA/QC details given.
1992	NE Irish Sea	4	Box core	<63	HCl	Cu Fe Mn Pb ^{206}Pb ^{207}Pb	AAS ICP-MS	Williams *et al.*, 1998	Some QA/QC details.
1994	NE Irish sea	30	Box core	Whole sediment	Aqua regia-HF HNO_3	Al Cd Cr Cu Li Pb Hg	AAS with graphite furnace	Nixon, 1995	$CaCO_3$ and organic C also determined. QA/QC details given.
1995	Solway Firth	45	Intertidal surface sediments	Whole sediment	Total	Al_2O_3 CaO Ce Cr Cs Fe_2O_3 K_2O MgO MnO P_2O_5 SiO_2 Th TiO_2 U Zr	XRF	Jones *et al.*, 1995	No QA/QC details. Part of radiometric survey
1995	UK estuaries on Irish Sea	~10	Bottom sediments by grab	<2mm	Aqua regia-HF (Ex. Hg)	Al Cd Cr Cu Hg Li Pb Zn	AAS		NRA estuary survey. Techniques same as for OSPARCOM, 1994
1997-98	UK estuaries on Irish Sea	~16	Bottom sediments by grab	<2mm	Aqua regia-HF (Ex. Hg)	Al Cd Cr Cu Hg Li Pb Zn	AAS	MPMMG, 1998	Part of National Monitoring Programme. Techniques same as for OSPARCOM, 1994

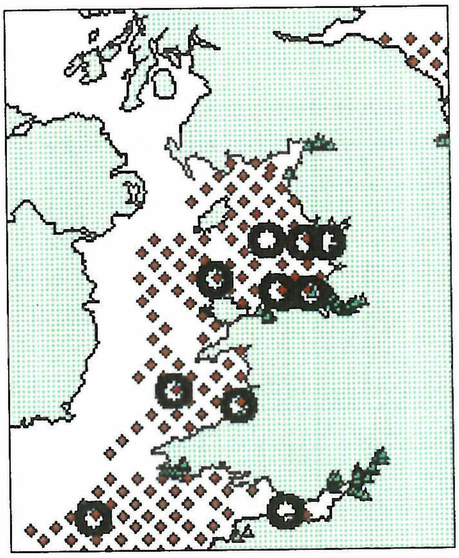

Figure 1. Samples stations for the OSPARCOM (red diamonds), NRA estuary (green triangles) and NMP (open circles) surveys mentioned in the text

500 mg of the powder was completely digested in a microwave furnace using a mixture of hydrofluoric acid and aqua regia (Jones & Lazlett, 1994). The resulting solution was treated to minimise matrix effects before being analysed for a range of elements (Al, Li, Cd, Cr, Cu, Pb and Zn) using flame and furnace atomic absorption spectrophotometry or ICP. Mercury was measured, using an atomic fluorescence technique.

The collection and analytical methods used in these studies followed ICES advice (ICES, 1989).

3.2.1 Results

Sediments have often been used to assess environmental quality as they reflect and integrate contaminant inputs to the marine environment and often allow sources and sinks to be identified (e.g. Hanson *et al.*, 1993). Detailed analysis of sediment information is only possible after compositional variations due to mineralogical and grain-size differences have been taken into account. Clay minerals, a major component of many fine-grained sediments, have a relatively high natural metal content compared to sand and also a greater active surface area which may sorb metals. This causes sediment metal concentrations to be generally higher in areas of mud than in sandy regions. Such mineralogical and grain-size effects can confound attempts to compare metal concentrations throughout a given area but may be taken into account by using a normalisation procedure (ICES, 1989, Loring, 1991). In the present context, normalisation is best achieved through the use of a non-contaminant element associated with clay minerals to account for grain size variations.

Various authors have favoured different grain size proxies as normalisers. For example, Windom (1986), working in Florida, preferred aluminium, while Grant and Middleton (1990), working in the Humber, used rubidium. Loring (1991) recommended the use of lithium in areas with sediments derived by glacial processes where aluminium may be present in feldspars in the sand-sized sediment fraction.

Rowlatt and Lovell (1994b) showed little difference in the North Sea in the final results obtained using lithium and aluminium as normalisers, indicating that any such effect is only minor.

The situation in the Irish Sea is demonstrated in Figures 2 and 3, where the muddier coastal and estuarine samples, particularly of the mud belts off the Cumbrian coast and in the NW Irish Sea (BGS, 1987), can be seen to contain higher concentrations of aluminium, a significant component of clay minerals. Normalising the dataset can thus be achieved using aluminium concentration as a proxy for grain size.

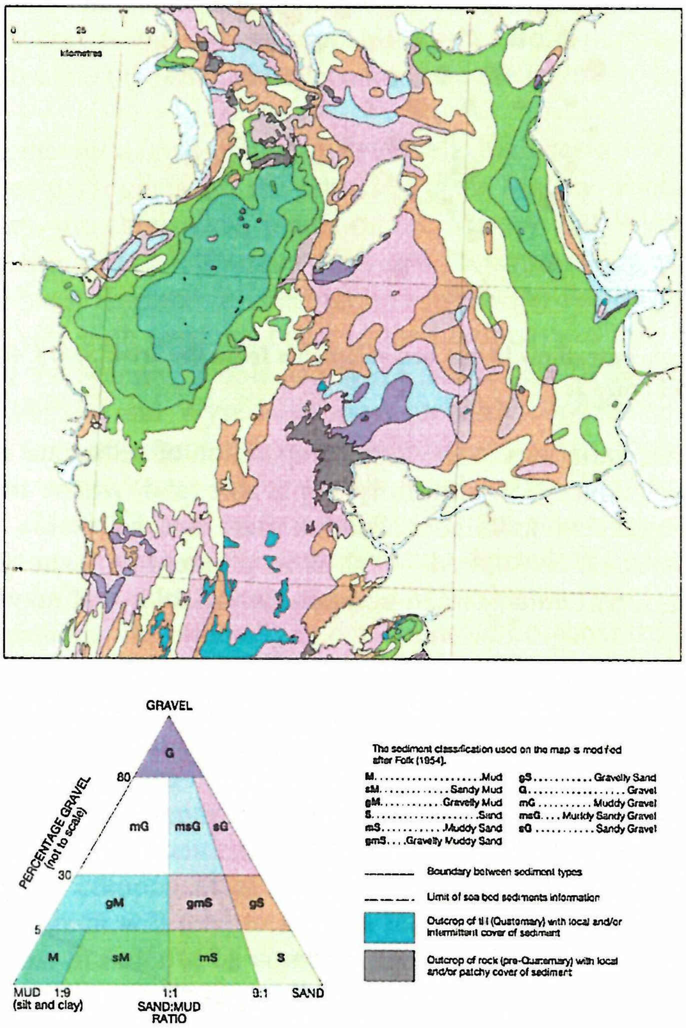

Figure 2. Distribution of sea bed sediment types in the Irish Sea (taken from BGS, 1987). Note the distribution of muddy areas for comparison with Figure 3.

Several methods of normalisation are possible, ranging from the use of simple metal/normaliser ratios to more complex methods based on regression analysis. As some of the metal/normaliser regressions in the OSPARCOM dataset have significant intercepts on the metal axis, the simple metal/aluminium ratio can lead to spuriously high values at low normaliser concentrations. A common technique is based on a metal/normaliser regression model with calculation of residuals about the regression

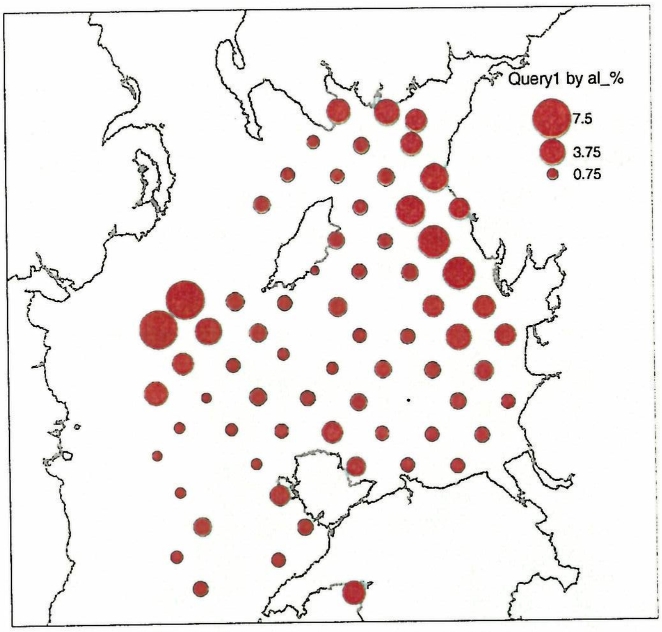

Figure 3. Aluminium concentrations in sea bed sediments from the Irish Sea. Compare with the distribution of muds in Figure 2.

line (Fig. 4). However, variations in the bulk composition of sediments mean that not all normalisation techniques are uniformly applicable and where the aluminium content of the sediments is low, normalisation may not be viable and the raw concentration data must be considered. Work is in progress to identify and employ alternative normalisers, particularly multi-component variables that may be applied to the whole dataset.

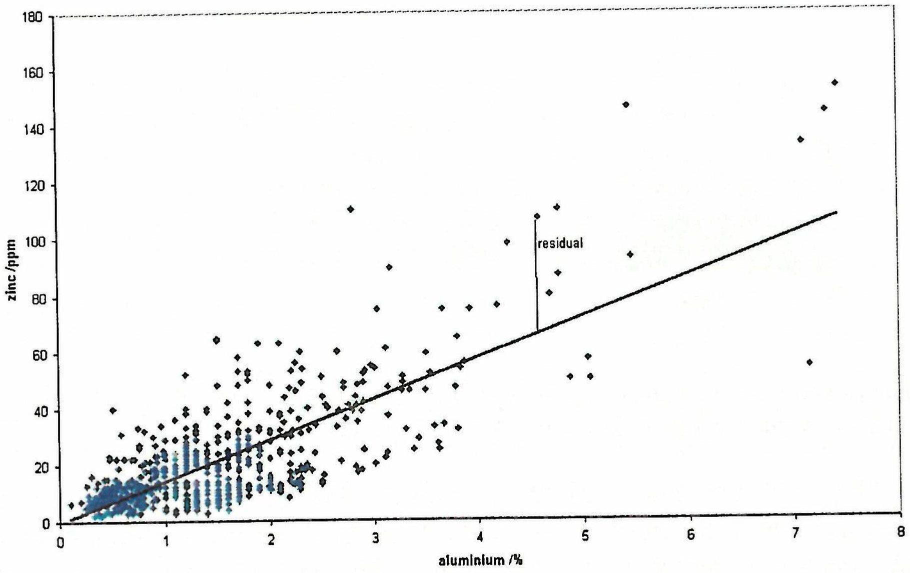

Figure 4. Method of calculation of residuals about metal/aluminium relationships using data on zinc and aluminium concentrations in sea bed sediments from the western North Sea

Some results of the application of normalisation to the 1990/91 OSPARCOM data for eastern Britain are illustrated in Figure 5 a-f. These results, coupled with the NRA and NMP data, show that in the coastal zone and around estuaries, sediment metal concentrations are generally higher than offshore, suggesting that river inputs from the land are significant sources of sediment metals. It is probable that contaminants released to the rivers as a consequence of anthropogenic activity are a significant component of these inputs. Information on the natural (pre-industrial) concentrations of metals in sediments is required to quantify the natural and anthropogenic components of sediment metals. The question of differentiating natural and anthropogenic material is particularly relevant to areas where rivers drain naturally mineralised zones and also flow through industrialised areas. In such cases high sediment metal concentrations are probably due to both natural and anthropogenic effects, the natural metal enrichment depending on the nature of the local geology.

For cadmium, mercury, lead and zinc, relatively high residuals occur in the north-eastern Irish Sea particularly off the estuaries of the Mersey, Ribble and Wyre. In the case of mercury, the chlor-alkali plants on the Mersey and Wyre have undoubtedly contributed to this effect. The other elements to some extent reflect the industrial nature of north-west England. It is difficult to assess the For cadmium, mercury, lead and zinc, relatively high residuals occur in the north-eastern Irish Sea particularly off the estuaries of the Mersey, Ribble and Wyre. In the case of mercury, the chlor-alkali plants on the Mersey and Wyre have most probably contributed to this effect. The other elements to some extent reflect the industrial nature of north-west England. It is difficult to assess the source of the metals in all areas, although it is clear that the sediments off industrial areas contain relatively high concentrations of trace metals, the metal which is enriched in any particular case depending on the nature of the local industry. Table 2 shows the contrast in metal levels between the heavily industrialised Mersey catchment and the relatively uncontaminated Solway Firth.

French (1993) reported Cu, Pb, Zn and Rb concentrations in pre-industrial salt marsh sediments from the Severn Estuary. It is quite likely that further 'background' data sets could be obtained from pre-industrial coastal and estuarine sediments around the UK and they should be representative of the non-anthropogenic component of sediments being deposited at the present time. They should be of more relevance in determining the anthropogenic component of recently deposited sediments than data sets from offshore cores, which will tend to give an integrated picture from a wider variety of sediment sources. In order to be comparable, new data sets will need to be generated using the same or directly comparable techniques.

3.3 Biogeochemistry

The concept of using biological samples as indicators of metal contamination is now widely regarded as an essential component of monitoring schemes, to complement the traditional methods of assessment provided by water and sediment analyses. The major argument supporting the inclusion of indicator organisms in such schemes is that they reflect and integrate only biologically available forms. In contrast, analysis of water and sediment usually provides information concerning the total concentration of the contaminant in the environment, without defining its accumulation potential - and thus its biological impact. Since Environmental Quality Targets are most frequently aimed at the protection of biological resources, the use of indicator

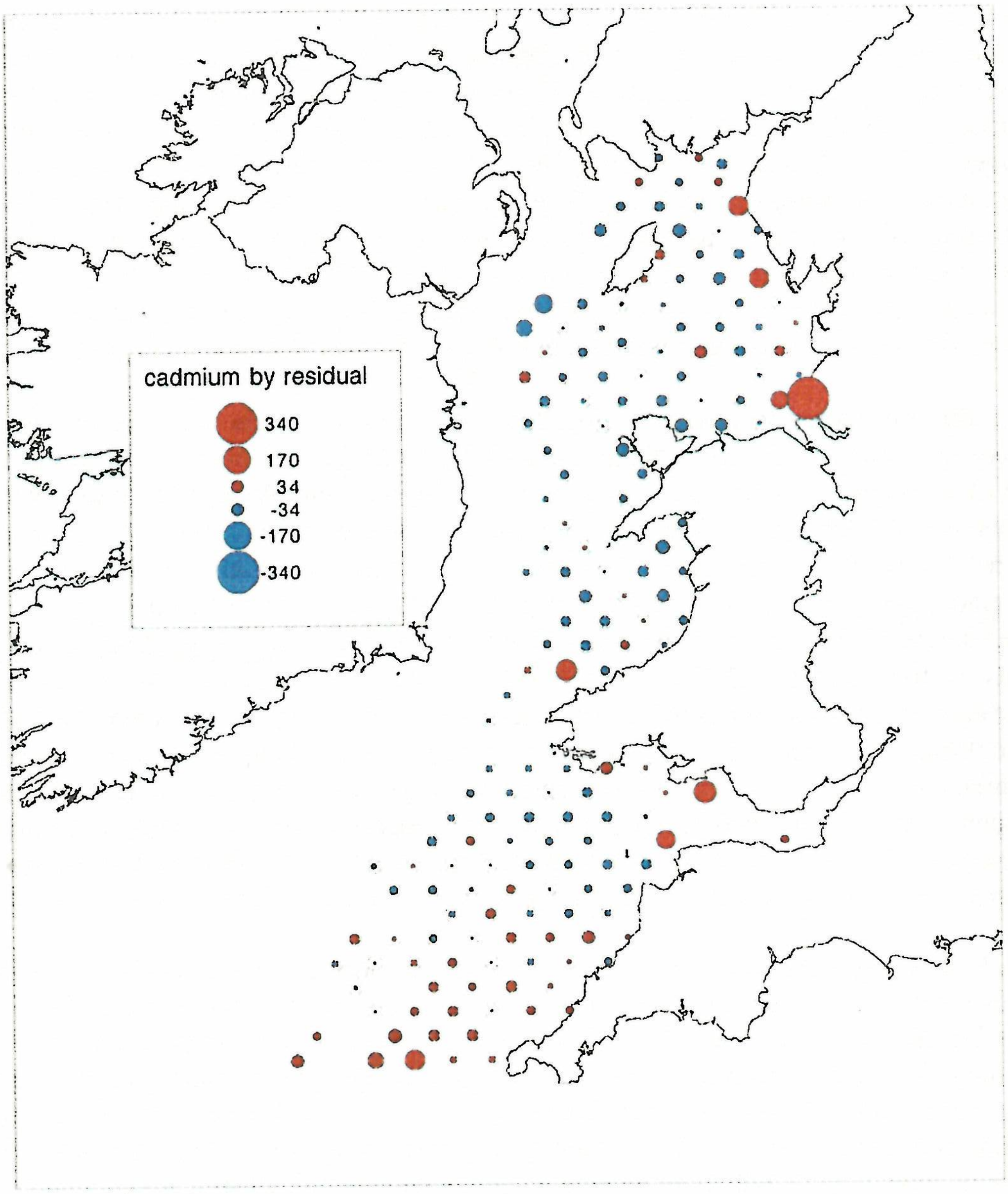

Figure 5a. Cadmium

Residual values around the relationship between various metals and aluminium in sediments from the Irish Sea region. Data shown are graduated by a square-root law with larger circles representing greater residual values, positive values in red and negative values in blue

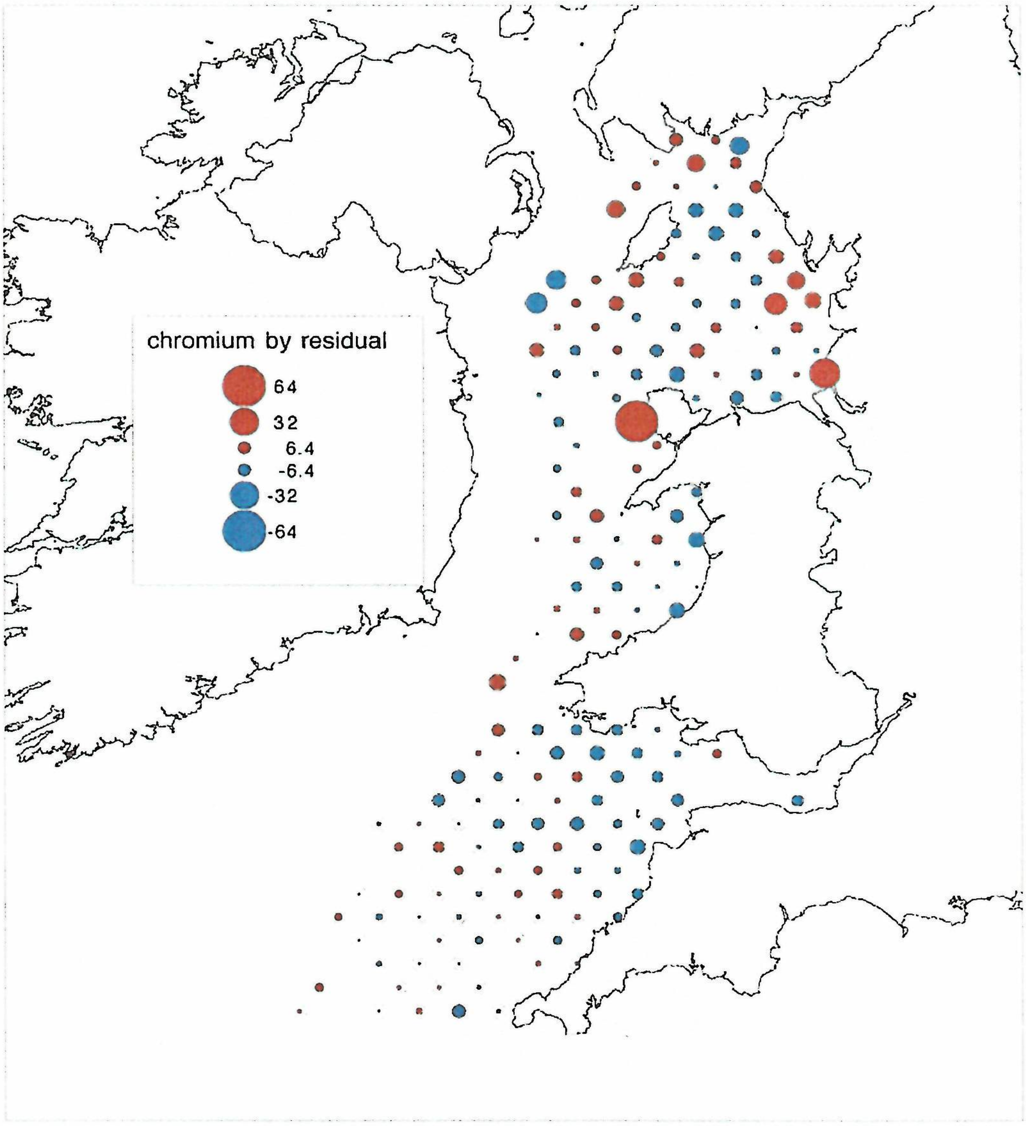

Figure 5b. Chromium

Residual values around the relationship between various metals and aluminium in sediments from the Irish Sea region. Data shown are graduated by a square-root law with larger circles representing greater residual values, positive values in red and negative values in blue.

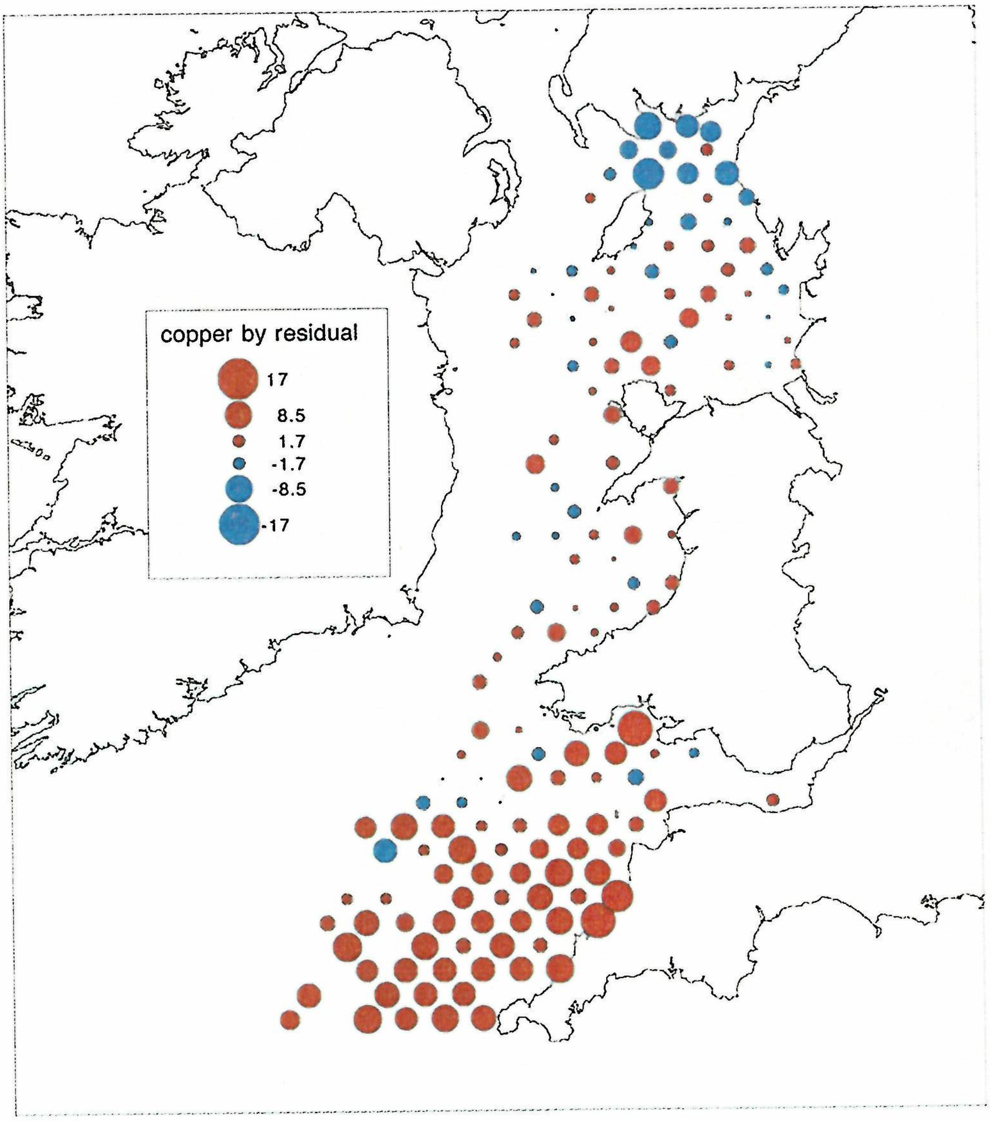

Figure 5c. Copper

Residual values around the relationship between various metals and aluminium in sediments from the Irish Sea region. Data shown are graduated by a square-root law with larger circles representing greater residual values, positive values in red and negative values in blue.

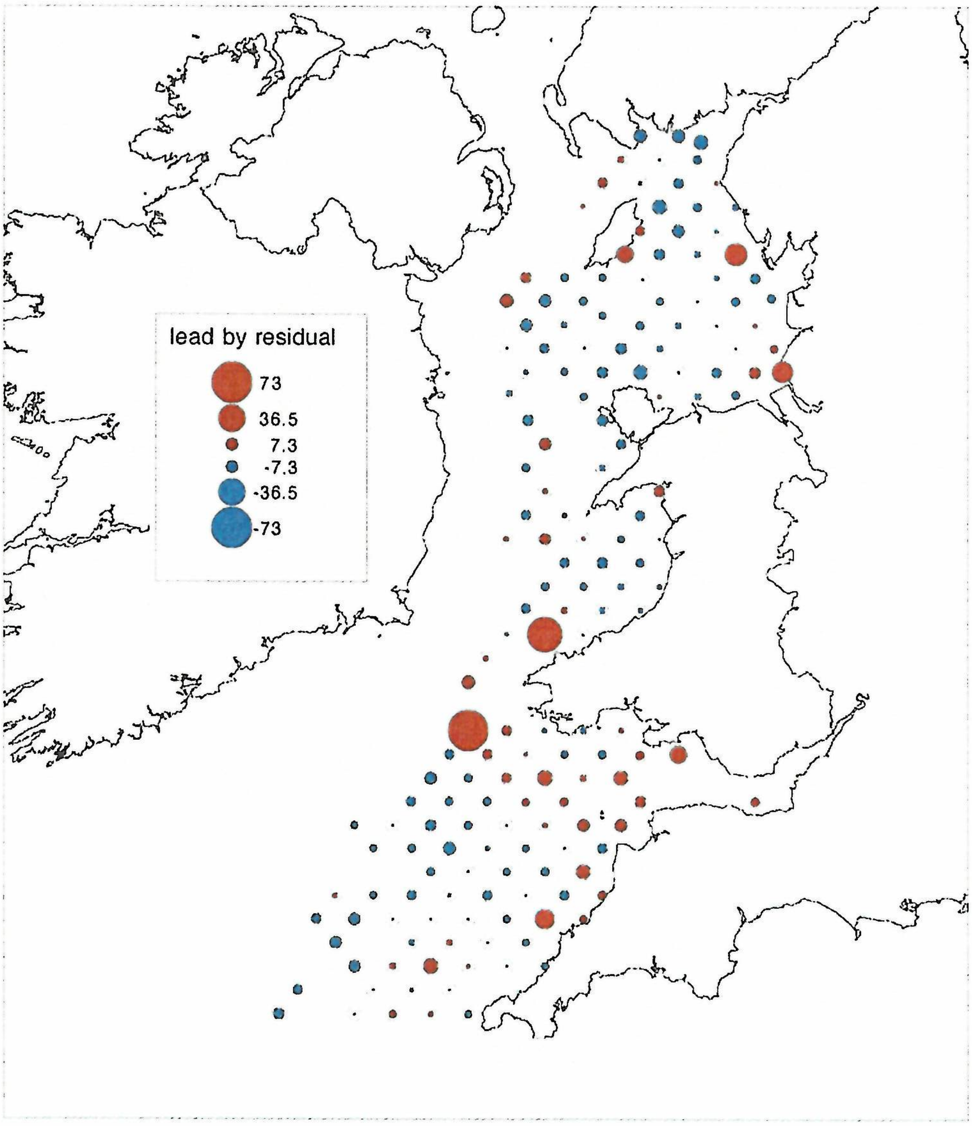

Figure 5d. Lead

Residual values around the relationship between various metals and aluminium in sediments from the Irish Sea region. Data shown are graduated by a square-root law with larger circles representing greater residual values, positive values in red and negative values in blue

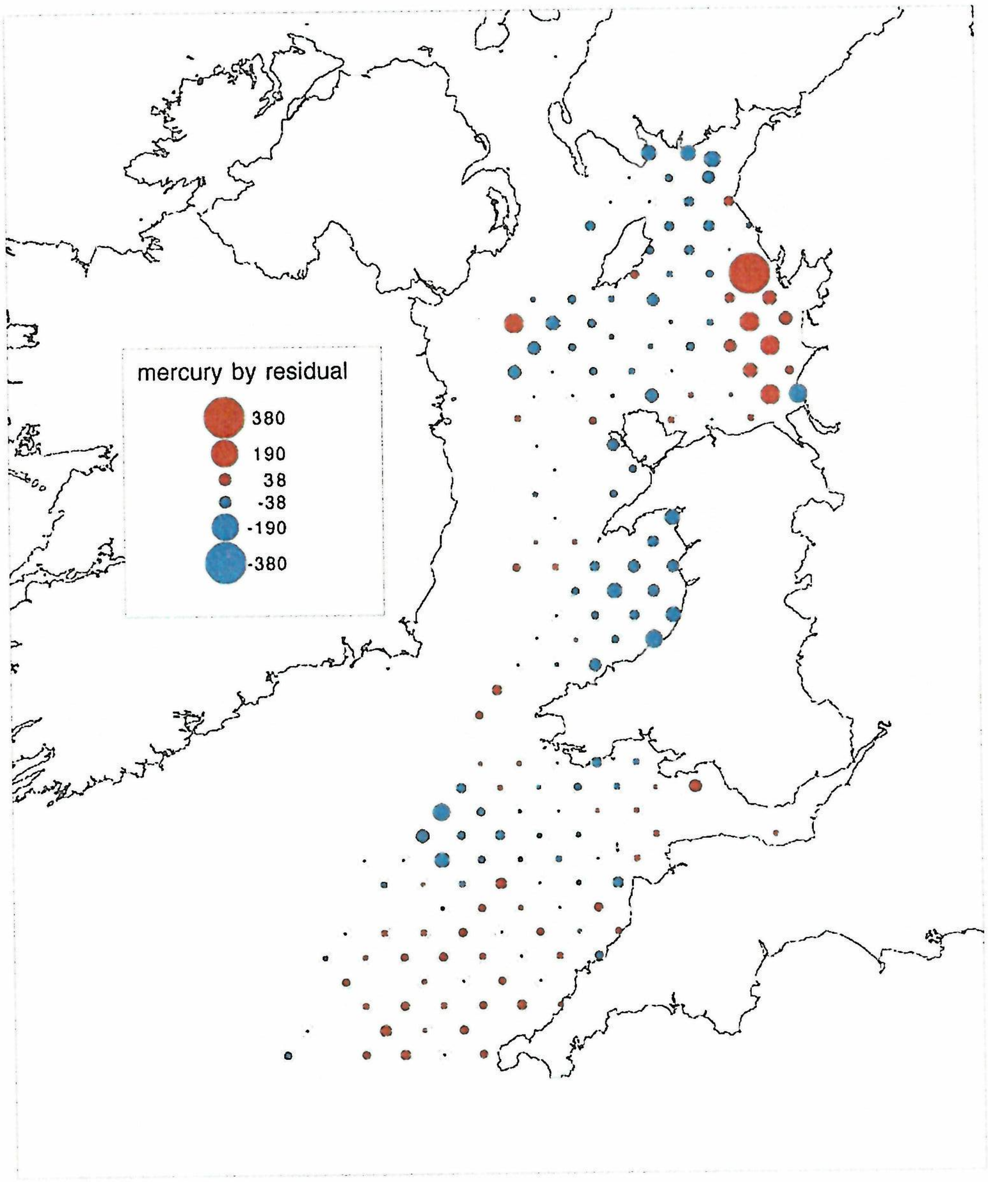

Figure 5e. Mercury

Residual values around the relationship between various metals and aluminium in sediments from the Irish Sea region. Data shown are graduated by a square-root law with larger circles representing greater residual values, positive values in red and negative values in blue

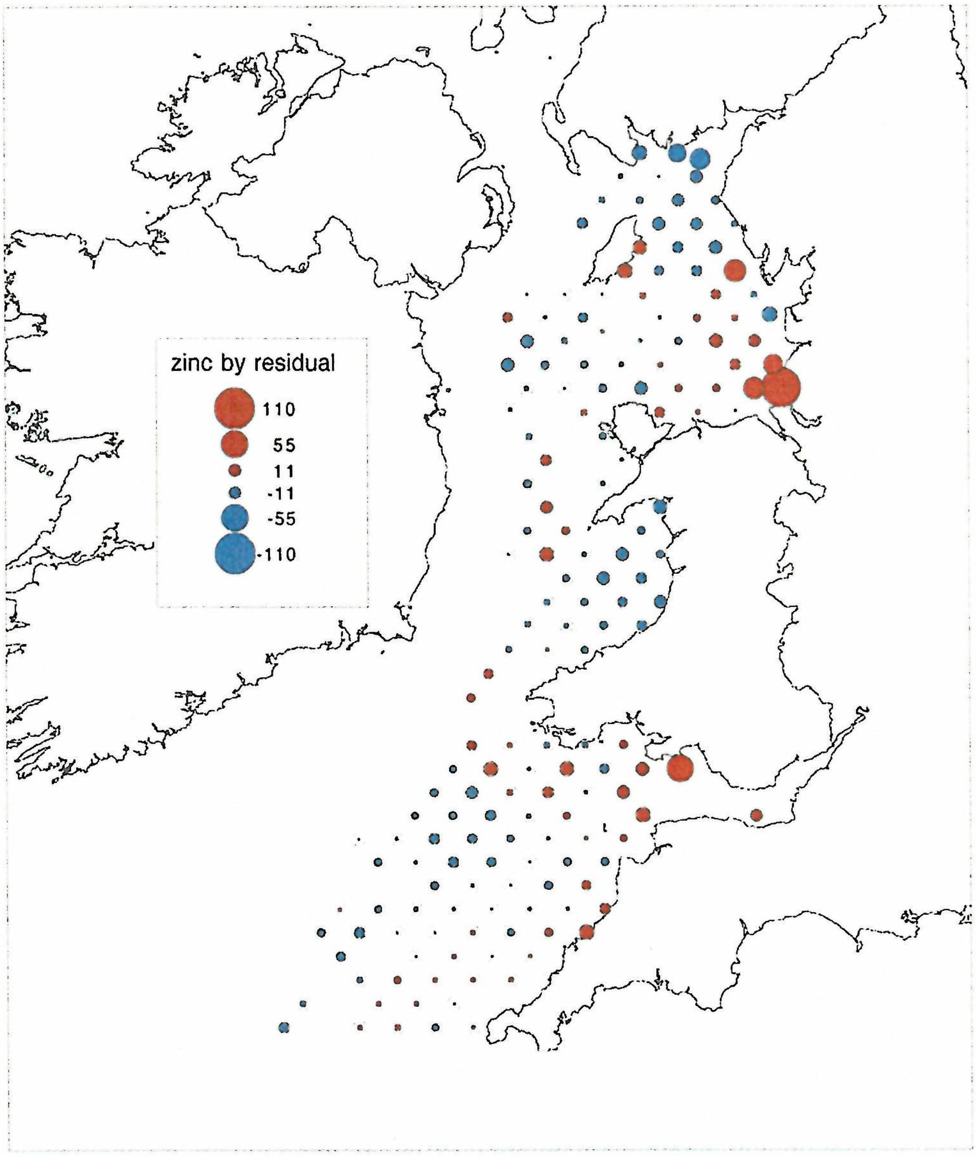

Figure 5f. Zinc

Residual values around the relationship between various metals and aluminium in sediments from the Irish Sea region. Data shown are graduated by a square-root law with larger circles representing greater residual values, positive values in red and negative values in blue.

Table 2. Comparison of metal concentrations in sediments from the Mersey Estuary and Solway Firth. Values in ppm except for Al and Fe which are in weight percent.

ESTUARY	SUBSTATION	Al	Rb	Cd	Cr	Cu	Fe	Hg	Li	Ni	Pb	Zn	As	V
MERSEY	GARSTON CHANNEL	4	69	742	102	50	3	1380	44	26	101	295	20	70
MERSEY	GARSTON CHANNEL	1	23	173	16	4	1	67	11	8	19	54	15	16
MERSEY	GARSTON CHANNEL	1	29	127	15	3	1	36	10	7	14	46	5	13
MERSEY	MIDDLE DEEP	1	19	450	20	6	1	52	11	7	21	59	19	18
MERSEY	EASTHAM CHANNEL	1	26	80	12	4	1	19	10	4	15	40	9	13
MERSEY	EASTHAM CHANNEL	1	22	142	12	3	1	41	11	6	18	45	13	14
MERSEY	EASTHAM CHANNEL	4	54	971	92	48	2	1415	36	24	94	294	24	60
MERSEY	LANGTON LOCK ENTRANCE	5	69	758	106	49	3	1439	49	31	107	281	22	77
MERSEY	GLADSTONE LOCK ENTRANCE	3	50	645	73	32	2	857	31	20	65	218	15	49
MERSEY	GLADSTONE LOCK ENTRANCE	6	89	859	127	78	3	1720	62	43	126	334	23	93
MERSEY	NEW BRIGHTON	1	21	11	9	1	1	19	10	5	13	29	9	13
MERSEY	ALFRED LOCK ENTRANCE	3	47	572	64	28	2	1042	27	18	59	301	14	43
MERSEY	TRANMERE	6	95	1194	140	107	4	2430	70	48	177	471	24	107
MERSEY	MANCHESTER SHIP CANAL	6	82	1319	137	82	4	4044	60	41	278	405	29	95
MERSEY	MANCHESTER SHIP CANAL	6	88	1365	152	103	4	6051	66	48	812	465	29	105
MERSEY	MANCHESTER SHIP CANAL	5	79	933	113	72	3	1610	55	39	167	358	23	87
MERSEY	MANCHESTER SHIP CANAL	5	64	1534	133	88	3	15041	44	40	599	344	20	70
MERSEY	MANCHESTER SHIP CANAL	5	62	2555	119	99	3	19609	49	42	187	356	39	64
MERSEY	C16 BUOY	1	24	83	22	3	1	75	9	5	13	25	6	17
MERSEY	C10 BUOY	6	81	658	121	56	4	1709	63	41	129	288	24	98
MERSEY	C23 BUOY	3	43	348	50	22	2	641	28	19	58	135	16	42
MERSEY	MOUNT MANISBY	1	26	144	24	3	1	20	10	7	14	39	7	17
MERSEY	STANLOW POINT	1	25	42	36	3	1	9	10	6	14	47	6	21
MERSEY	OGLET	2	34	223	29	7	1	98	12	7	21	107	8	17
MERSEY	HALE	1	30	97	14	5	1	41	10	7	16	59	8	13
MERSEY	WOODYARD	2	34	387	21	8	1	159	13	9	25	132	7	16
MERSEY	HEMPSTONES POINT	3	48	1210	72	44	2	1001	28	21	79	312	15	41
MERSEY	MONKS HALL	3	46	1336	85	48	2	1125	29	25	85	319	17	43
SOLWAY	1	2	40	10	19	5	1	27	10	24	11	13	4	22
SOLWAY	2	2	39	2	25	11	1	<0.02	10	26	11	14	7	22
SOLWAY	5	2	33	51	21	9	1	62	22	15	9	11	6	23
SOLWAY	4	2	46	50	19	11	1	65	16	11	10	28	10	20
SOLWAY	5	2	42	26	8	100	1	41	23	15	9	19	8	18
SOLWAY	6	2	47	146	22	10	1	59	17	11	10	21	9	21
SOLWAY	7	2	42	31	7	31	1	44	23	16	9	14	5	19
SOLWAY	8	2	44	101	8	46	1	113	27	26	97	33	14	25
SOLWAY	9	3	20	57	18	3	1	<14	15	8	12	26	4	51
SOLWAY	10	2	19	65	20	3	1	<17	13	5	11	29	3	44
SOLWAY	11	2	18	93	20	3	1	<17	13	5	11	36	4	44
SOLWAY	12	2	17	156	18	3	1	<15	11	6	10	31	3	38
SOLWAY	13	2	19	84	19	4	1	<16	13	7	11	32	3	43
SOLWAY	14	2	47	146	19	13	1	58	17	10	10	24	9	20
SOLWAY	15	2	20	29	23	3	1	<16	12	4	10	18	3	39
SOLWAY	16	3	44	163	21	16	1	63	17	11	9	20	8	20
SOLWAY	17	3	44	67	13	31	1	112	25	20	11	24	5	21
SOLWAY	18	3	46	76	12	14	1	52	27	18	11	26	5	23

organisms which reflect the presence of bioavailable metals is often a preferable means of assessing contamination. The alternative, which is under investigation in the current work, is to attempt to mimic or predict bioavailability of anthropogenic metals through geochemical measurements

An initial review of existing data on sediment metal bioavailability, relevant to the objectives of the current proposal, has been carried out. In addition to a literature search of published studies on metals in biota, the review process has drawn extensively on PML's own previous surveys in the region (mainly in estuaries and coastal zones in NW England) and related studies in UK estuaries. Though by no means comprehensive, this probably represents one of the most extensive and unified sets of data. In the context of the assessment of sediment-metal bioavailability, it is certainly most relevant and will be used extensively to complement new data in order to meet the specified objectives of the current project:

contamination in estuarine and marine environments. Though many, such as the Mersey and Cumbrian surveys, superficially represent a series of "stand-alone" projects, they nevertheless integrate fully with continuing broader based research interests on metals in British Estuaries and Coastlines, a programme which has been developing during the last 20 years. Some of the principle objectives of this long-term research are:

1. To determine which ubiquitous estuarine/marine organisms are most suitable for analysis as indicators of heavy metal contamination

2. To study factors controlling the availability of metals in waters and sediments to these organisms

3. To determine the effects of metals on estuarine species

4. To use indicators to identify contaminated areas around the United Kingdom, and thereby to assess the capacity of these areas to accept inputs without excessive build-up of contaminants in biota.

5. To evaluate long-term trends in contamination, i.e. the possible advent of new risks and also the effectiveness of control measures to reduce impact in known 'hotspots'.

Thus although surveys were not designed as a monitoring exercise *per se*, PML has, in the course of its long-term research programme, built up a sizeable data-set. The data, comprise measurements of up to 13 metals in sediments and a dozen indicator organisms - not only for the Irish Sea region but encompassing more than 100 estuaries and coastal regions around the UK. Publications referring to the Irish Sea estuaries are listed in the bibliography.

The Irish Sea Estuaries which have been visited and for which PML holds 'historic' metals data are indicated in Figure 6. It should be stressed that many of these represent single sampling surveys. Therefore, rather than being a continuous record, the results provide snapshots of many estuaries: (1) as a guide to relative levels of metal contamination in different estuaries and (2) as a basis for studies of future trends.

3.3.1 Estuarine sediment data

Earlier examples of sediment data for the Mersey, Wyre and Solway Estuaries, showing the scale and ranges in concentrations for the 13 metals analysed, are illustrated in Table 3.

Table 3. Surface Sediments: metal concentrations (μg g^{-1} dw) in the <100μm fraction following digestion with concentrated HNO_3

Estuary	*site*	*Ag*	*As*	*Cd*	*Co*	*Cr*	*Cu*	*Fe*	*Hg*	*Mn*	*Ni*	*Pb*	*Sn*	*Zn*
Solway	Creetown	0.08	11	0.39	8.1	34	11	19770	0.08	765	23	36	0.3	92
Wyre	Singleton	0.3	9	0.66	9.8	46	34	24210	3.71	696	24	58	4.5	177
Mersey	Stanlow	1.34	63	2.53	15.8	97	131	31330	4.5	1519	44	203	8.7	327

Superficially, contamination entering a water-body will usually be reflected by levels in sediments. In estuaries, scavenging by particulates and removal by deposition means that bed sediments are major contaminant sinks. Not surprisingly therefore, examination of the data for several metals in surface sediments of a number of major estuaries in N W England which drain into the Irish Sea follow expected patterns in relation to recent industrial and population impacts, at least on first impressions. This is most predictable for 'pollutant metals' i.e. those with low natural levels. For example, mercury concentrations are highest in the south of the region - notably in the Mersey and Wyre Estuaries - reflecting previous heavy usage in chlor-alkali plant. Levels in the much less industrialised Solway Firth are considerably lower (by almost two orders of magnitude). Concentrations of the more common metals such as zinc and nickel may display similar trends but tend to be more evenly distributed, with less distinctive ranges, and it is less easy to predict the extent of contamination above background: closer scrutiny of what constitutes anthropogenic loadings is a major objective of the present study.

1 :- Water of Fleet
2 :- Urr Water
3 :- Whitehaven
4 :- Harrington
5 :- Nith
6 :- Derwent
7 :- Ellen
8 :- Solway
9 :- Annan
10 :- Port Carlisle
11 :- Browhouses
12 :- Esk
13 :- Barrow
14 :- Leven
15 :- Wyre
16 :- Ribble
17 :- Lune
18 :- Anglesey
19 :- Anglesey
20 :- Anglesey
21 :- Afon Goch
22 :- Anglesey
23 :- Menai
24 :- Conwy
25 :- Dee
26 :- Mersey

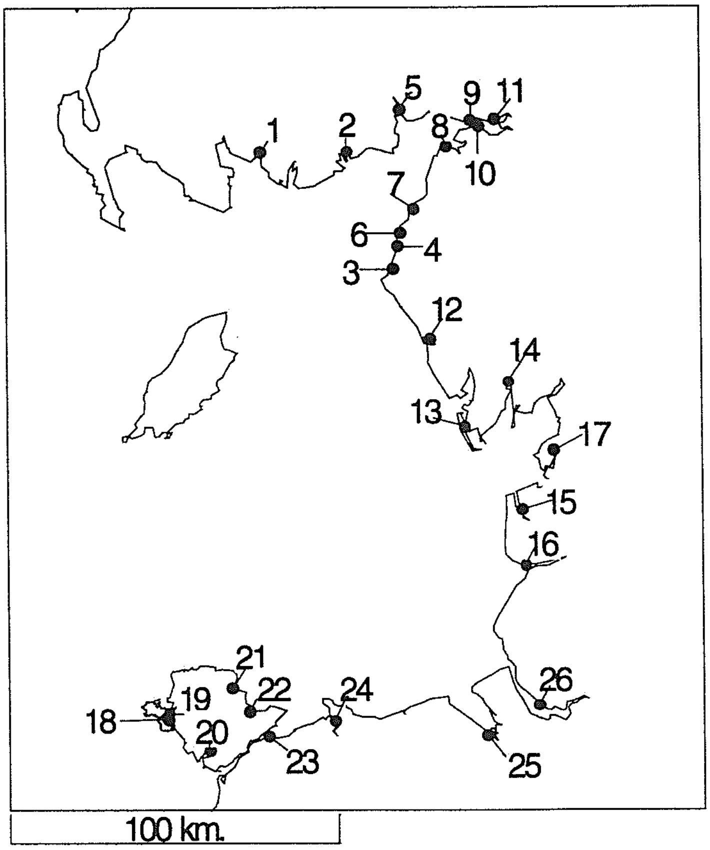

Figure 6. Map showing estuaries sampled by PML staff in earlier surveys

Sediment data may be of potential use in determining whether biological effects might be expected. However, standard measurements of sediments (or water) rarely take account of the existence of metals in different chemical forms having different biological availabilities.

3.3.2 *Biological data*

Earlier examples of biological data for the Mersey, Wyre and Solway Estuaries, showing the scale and ranges in concentrations for 13 metals in the ragworm *Nereis diversicolor*, are illustrated in Table 4.

Table 4. ***Nereis diversicolor*****: metal concentrations (μg g^{-1} dw)**

Estuary	*site*	*Ag*	*As*	*Cd*	*Co*	*Cr*	*Cu*	*Fe*	*Hg*	*Mn*	*Ni*	*Pb*	*Sn*	*Zn*
Solway	Annan	0.35	9	0.33	2.3	0.08	19	397	0.09	21	1.5	0.7	0.1	155
Wyre	Knott End	2.08	11	0.39	2.9	0.37	21	499	0.44	19	2.1	1.7	0.5	148
Mersey	Stanlow	2.45	26	2.59	4.9	1.3	64	895	1.79	25	9	18.1	1.1	294

Intuitively, the best way of assessing the presence of bioavailable metals is by measuring their concentrations in indicator organisms. These are species in which the accumulation of metals in tissues reflects their availabilities in sediments or waters. Few organisms are ideal indicators for all metals. For example, some species control their body concentrations of certain metals by excretion or exclusion: others are poor accumulators of some metals and are thus more difficult to analyse. Nevertheless, support from biological data can be important in determining what should or should not be regarded as a contaminated sediment. To return to the example of Hg in Irish Sea estuaries, evidence of contamination of Mersey sediment is generally confirmed by the gradients in body burdens in benthic organisms such as *Nereis* (Table 4).

Relationships between sediments and biota are not always straightforward, and modifying factors may influence bioavailability, sometimes in a predictable fashion. In the case of mercury, the availability of sediment Hg may be influenced by the sediment-organic content at some sites; high levels of iron oxyhydroxide in sediments can reduce bioavailability of metals such as As and Pb; whilst other modifying factors include the competition for uptake between metals e.g. Cd and Zn, Cu and Ag (Langston, 1985, 1986; Bryan and Langston, 1992). These aspects were investigated further in the current project in attempting to establish the most viable options and methodology for predicting the bioavailability of metals in Irish Sea sediments. This involved the use of both previous data and validation with new material.

The dozen or so indicator species examined in previous work may be divided into three categories reflecting biovailabilities of metals in: i) Water mainly; ii) Water and suspended particles; iii) Sediment mainly. The latter are the chief concern of this project. The three most ubiquitous species which are likely to prove useful in assessing sediment-metal bioavailability in Irish Sea estuaries, and their general bioindicator characteristics, based on earlier work, are :

1) *Scrobicularia plana (deposit-feeding clam).* Relationships have been observed in some UK estuaries between metal levels in these clams (Ag, As, Cd, Co, Cr, Hg, Pb, Zn) and concentrations in sediments (see review by Bryan and Langston, 1992). The relationships may sometimes not necessarily be direct, as suggested above for Hg. In

particular, bioavailability of Cu to *S. plana* does not appear to be a simple function of sediment loading. Correlations between Cd in sediments and clams appear to be reasonably good, although, since Cd tends to remain in solution, the high clam concentrations observed in estuaries such as the Severn probably also reflect a degree of accumulation of the dissolved metal.

2) Macoma balthica (deposit-feeding clam). In a few estuaries the small (10-20 mm) clam *Macoma balthica* is more common than *Scrobicularia plana* and can be used with or instead of the latter. Both clams belong to the Superfamily Tellinacea and appear to accumulate metals in the same way – at some (but not all) sites they possess similar concentrations of Ag, As, Cr, Cu, Fe, Hg, Mn and Zn. Concentrations of Cd, Co and Pb tend to be higher in *Scrobicularia* and it is regarded as the superior indicator. In contrast, *Macoma,* though less than ideal as an indicator of Cu, may be preferable to *S. plana*. The fact that adult *Scrobicularia* live at greater depth in sediment than *Macoma* may be partly responsible for these variations, though in fact both species feed on oxidised surface material.

3) Nereis diversicolor (sediment-dwelling worm; ragworm - see sample results for estuaries in NW England in Table 4). Of the estuarine sediment-dwelling species considered here, the ragworm usually penetrates farthest upstream. As a whole, very significant relationships are observed between ragworm-tissue concentrations (e.g. Cu, Cr, Pb, Ag) and levels in sediments, but again these relationships may be modified by factors such as Fe or organics - as indicated for As and Hg, respectively (Langston 1985, 1986). It should be noted that, compared with bivalves, tissue concentrations of Zn do not respond markedly to environmental changes and thus the worm is a doubtful indicator for this metal. If sediment-metal levels are low but the overlying water is contaminated, relationships can occur between concentrations in the worm and dissolved metals (using seaweed *Fucus vesiculosus* as surrogate measure of dissolved concentrations): data for Cd in the Severn Estuary again provide a good example .

It is clear that no single species is the ideal 'universal bioindicator organism' though between them the above candidates are likely to provide a reasonable picture of bioavailable metals in Irish Sea Estuarine sediments and are most relevant to the current project.

3.3.3 PML surveys of the Mersey Estuary and Cumbrian coastline

Field sampling over the years has concentrated on the more heavily contaminated estuaries and coastal sites. Two regions of particular interest, the Mersey Estuary and Cumbrian coastline, have been the subject of long-term programmes. Details of completed PML reports of Cumbrian and Mersey surveys and related publications are included in the bibliography. A description of the type of data included in these programmes and a summary of recent trends is given below:

3.3.3.1 Mersey Estuary

Surveys have been carried out by MBA/PML staff since 1980 (see, for example, Langston, 1986). These mainly involve measurements of 13 metals (Ag, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, Sn, and Zn) in seven indicator organisms (*Scrobicularia* *plana, Macoma balthica, Nereis diversicolor,* together with *Fucus vesiculosus, Littorina littorea, Mytilus edulis* and *Cerastoderma edule*). Although metal concentrations rarely approach those encountered in estuaries in mineralised regions of SW England, the Mersey is fairly unique among UK estuaries in being moderately contaminated with such a wide range of metals. One notable feature, however, is mercury, which up until recently at least, has been consistently high in Mersey biota – ranked among the highest for this metal in the UK. Concern has also focused on bioavailability of lead in the estuary, because of suspected environmental damage caused by discharges of alkyl lead in the late 1970's and early 1980's (Wilson *et al* 1986). Following some significant reductions in inputs during the early 1980's, Hg and Pb concentrations now appear to be reaching steady state, though these and other metals still show considerable anthropogenic enrichment, particularly at some individual sites. This is reflected in tissue burdens at these 'hotspots' which, in a number of examples, are still close to their upper limits in UK estuaries.

Results of these studies provide a platform for observations of long-term trends in contamination (and species abundance and occurrence) along the Mersey. They will help to assess the effectiveness of previous controls on industrial discharges, major improvements in sewage treatment and inputs to the estuary, and changes in sludge dumping practices in Liverpool Bay. They also help to highlight factors (other than metal inputs) which modify tissue burdens in the estuary (speciation, redox conditions, salinity, major ligands,).

3.3.3.2 *Cumbrian coast and its estuaries*

During the early 1980's small scale sampling along the Cumbrian coastline had suggested some important anomalies with regard to metal concentrations in inter-tidal organisms. A series of surveys has subsequently taken place whose primary object was to judge the impact of industrial discharges on biota. Initially, concern focused mainly on the area between Silloth (at the mouth of the Solway) to St Bees, though this has been extended considerably in the latest survey to cover almost 200 km of shoreline, including some estuaries.

The majority of inter-tidal sites provided substrates for typical "rocky shore" communities and, where present, representative dominant species were sampled. These included macroalgae, *Fucus* spp.; mussels, *Mytilus edulis*; limpets, *Patella vulgata*; winkles, *Littorina littorea*; and dogwhelks, *Nucella lapillus*. Not all species were found at certain locations. At several sites it was possible to collect fine sediments and infaunal bioindicators, namely, *Nereis diversicolor*, *Scrobicularia plana* and *Macoma balthica*. The inclusion of these samples, and analysis of the same suite of metals as indicated above, enables comparisons to be made with other estuaries, including the Mersey.

Metal concentrations in some rocky shore organisms especially those from close to major industrial discharges in the region represent considerable enrichment relative to UK baselines (see, for example, Langston *et al.,* 1997). As with Mersey surveys a long-term goal is to evaluate the success of clean-up policies.

Metal burdens in Cumbrian estuarine sediments do not appear exceptional by UK standards, though some hotspots have been identified. This is thought to be generally reflected in the tissue burdens measured in infaunal organisms. However, the nature and extent of metal bioavailability in Cumbrian and Solway sediments is evaluated further in the current project.

3.3.4 Other surveys

During the review stage searches of other bioaccumulation data for the Irish Sea were made. A reference list of material assembled is included in the bibliography of Appendix 1.

Surprisingly, little of this directly addresses the issue of the bioavailability of sediment-bound metals, or the related topic of separating anthropogenic and natural metal loadings. Much of the work described relates to monitoring of metal-burdens in edible species of fish and shellfish. Nevertheless it is interesting that the conclusions on distributions are similar, in general terms, to PML findings on benthic invertebrates. Thus, areas impacted by discharges from chlor-alkali industries and other sources, including the Mersey, Wyre, (Ribble and Dee) estuaries, are most significant in terms of Hg accumulation in fish. Concentrations decline significantly with distance from these 'hotspots' in Liverpool and Morecambe Bay, towards minimal values at sites in the Western and Northern Irish Sea (CEFAS, 1987, 1990; Leah *et al.*, 1991a, 1992a). Similarly, Pb and As are, in addition to Hg, indicated as being high in eels (*Anguilla anguilla*) and flounder (*Platichthys flesus*) from the Mersey estuary, relative to those from the Solway Firth (Collings *et al.*, 1996). It is not surprising therefore that livers of stranded or entangled marine mammals sampled opportunistically throughout the Irish Sea had highest Hg and Pb burdens - presumably transferred along the food chain – in the Liverpool Bay area, (Law *et al.*, 1992).

In contrast to the general pattern of distribution of these metals, industrial discharges on the Cumbrian coast invariably account for the largest anomalies in bioavailable Cd in mussel-watch surveys of the Irish Sea coastlines (e.g. CEFAS, 1990), again consistent with PML observations in the area.

Most time-series studies are in agreement that clean-up procedures (and, in the case of organolead compounds, a reduction in demand for the product) have had the desired effect of reducing residues in fish and shellfish. This is best documented for Hg in the Mersey (Langston, 1986: Leah *et al.*, 1993) where efforts to reduce inputs began more than 20 years ago. The question remains, given the persistence of most chemicals in sediments, will this reservoir slow down any further amelioration?

In assessing bioavailability of metals across the Irish Sea as a whole, most studies to date would support the notion that anthropogenic/industrial inputs from NW England are most significant. This may be so, however, when considering data for the western Irish Sea alongside those for English coastal and estuarine sites, it becomes evident that the choice and availability of bioindicators, and different sampling protocols, could, to some extent, influence comparisons a basin-wide scale. For future environmental quality programmes, there is a good case for greater harmonisation of sampling of sediments and, particularly, infauna, if assessment of sediment metal bioavailability and anthropogenic impact is a goal.

Previously, mussels and other benthic organisms such as oysters, winkles and seaweed, have been employed in a number of national monitoring programmes (on both sides of the Irish Sea) mainly to ensure suitability for human consumption rather than for sediment biomonitoring. Most of these organisms have characteristics (widespread distribution, sedentary, ease of collection, size etc) which make them reasonable *general* bioindicators: *Mytilus edulis* was used in this capacity by Gault *et al.,* (1983), for example, to monitor metal trends in Northern Ireland (NI - Lough Foyle, Belfast Lough, Strangford Lough, Carlingford Lough). These earlier data for NI – together with contemporary data published by Davies and Pirie (1980) for Scottish waters – appear to confirm that levels of metals (particularly Cd and Pb) were generally lower than in mussels for England and Wales (Murray, 1982). However, though most sites in NI were relatively low in metals, two sites in Strangford Lough were fairly high in Cr and Hg (means 150 and 15 times baselines, and attributable to tannery discharges and antifouling paints, respectively). Concentration ranges for Pb, Cd, Ni, Cu and Zn varied by less than five-fold, making separation of possible anthropogenic or natural sources difficult to establish for these metals (see Gault *et al.*, 1983). Partial regulation of Cu and Zn in *M.edulis* may contribute to this problem

Additional studies with mussels have been performed at individual sites in Belfast Lough, (suggesting some enrichment in Zn -Manga, 1980) and, together with winkles *Littorina littorea* and seaweed *Fucus vesiculosus*, in Carlingford Lough (Manga and Hughes, 1981). *Littorina rudis* has also been used to depict a declining gradient of Cu concentration emanating from the mining-impacted Avoca Estuary, northwards along the Irish coast (Wilson, 1982). Our own results, e.g. for the Cumbrian coast, support the use of such species on rocky shores (Langston, *et al.,* 1997). However as specific indicators of sediment-metals they are inferior to species such as *Nereis diversicolor, Scrobicularia plana*, and *Macoma balthica.* To achieve compatibility with the eastern Irish Sea data, it would be particularly valuable to investigate the possibility of extending coverage, for these or equivalent infaunal species, to the Irish estuaries.

In addition to the above surveys on estuaries and loughs, information on metal burdens in coastal waters of the western Irish Sea is held by Governmental Departments and generally conforms with JMP guidelines on monitoring (oriented towards edible species). This includes the Department of Agriculture, Northern Ireland (DANI) and the Department of Agriculture and Fisheries (Department of the Marine, Fisheries Research Centre), Dublin. The latter has published data for metals (Hg, Cd, Cu, Pb, Zn, together with limited information on Cr and Ni) in mussels, oysters, fish, waters and sediments (<63 µm) selected from coastal and estuarine sites round Ireland, from the Boyne estuary to Mulroy Bay (O'Sullivan *et al.*, 1991). Based on these samples, collected between 1978 and 1988, Irish waters were generally classified as low in contamination: elevated concentrations sometimes occur but are generally small in scale. Of the estuaries sampled those on the East coast (Irish Sea) were considered to be most at risk from environmental stress - those most regularly monitored include the Boyne, Lower Liffey (Dublin Bay), Slaney (Wexford harbour), Barrow and Suir (Waterford Harbour). Data is also available for Carlingford Lough and the Dublin Bay sewage sludge dumping ground.

To summarise the data: waters were acknowledged by O'Sullivan *et al.* (1991) as being somewhat difficult to assess due to analytical uncertainties and temporal variation, though some contamination with dissolved metals was indicated for the

Boyne (Cd), Waterford harbour (Cd and Hg) and Dublin Bay (Pb, Hg). Few areas of gross sediment metal contamination were identified (one of the most impacted was, in fact Tralee Bay in SW Ireland). Of the Irish Sea Estuaries, sediments of the inner Liffey contained elevated levels of Cu and Cd (see Jones and Jordan, 1979) whilst moderate concentrations of Zn have been observed in the Slaney, and Pb and Zn in the Boyne estuary and Dublin Bay- notably in port areas (O'Sullivan *et al.*, 1991).

There are no chlor-alkali plants in Ireland and mussel data were all lower than the Joint Monitoring Programme (JMP) guideline of 0.3 mg Hg g^{-1} (wet weight) - generally tending to be in the lower-medium range, reflecting relatively small-scale inputs (O'Sullivan *et al.*, 1991). Likewise, Cd in mussels largely fell below the JMP upper guideline value of 5 mg g^{-1} (dry weight) though, occasionally, higher values were recorded in Dublin Bay and the Boyne estuary. Pb concentrations were highest in Dublin Bay (2.6 mg kg^{-1} wet wt). Mussels are thought to regulate Cu and all values were < 10 mg kg-1 wet wt. Partial regulation of Zn is also likely, though values of 50 mg kg^{-1} wet wt in the Boyne estuary, compared to a mean value of less than 20 mg kg^{-1} wet wt, imply a degree of response to contamination. Cod, whiting, plaice, herring and mackerel were the main fish species monitored and there are signs from cod data that Hg levels in Irish Sea catches tend to be higher than those taken from other Irish coastal waters. Temporally, however, there is an overall downward trend for most contaminants and in these fish species values were all within recommended safety guidelines and ICES baselines with the exception of one Cd value in dogfish liver. By-catch species, such as shark, had Hg concentrations > 0.3 mg kg^{-1} wet wt, though these probably are largely a result of the organisms physiology and trophic status (O'Sullivan *et al.*, 1991).

Offshore benthic monitoring throughout the Irish Sea as a whole is limited in extent - due largely to the inherent difficulties in benthic sampling (this is one of the reasons why a mesocosm approach to the issue of sediment metal bioavailability is to be tested in the current project). Published field data suggest that bioavailability in offshore sediments could be increased as a result of anthropogenic activities such as dumping. For example Pb, Cu, Zn and Ni (and to a slight extent Hg and Cd) concentrations in sediments near the Dublin Bay sewage disposal site were found to be elevated, compared with those elsewhere in outer Dublin Bay (O'Sullivan *et al.*, 1991). Measurements of potentially bioavailable metals in these dumping ground sediments are described by Dinneen *et al.* (1988) though it appears that any effects are likely to be extremely localised and of little ecological significance.

A DANI study of metals (Cr, Cu, Hg, Ni, Pb, Zn) in surface fines (<63μm) throughout the NW Irish Sea (approximately a triangular area between the North Channel, Dublin and a point to the south of the Isle of Man) did not reveal any major hotspots. Overall, concentrations in fine sediments from offshore were within the ranges reported for Strangford Lough, inshore, whose metal inputs were largely attributed to local geochemistry (Service 1993, Service *et al.*, 1996). It is intriguing to find, therefore, that some sediment concentrations in the more remote central areas of the NW Irish Sea were comparable to the upper end of the Strangford values. This implies, perhaps, a natural mechanism for retention of contaminated fines, analogous to that suggested for some parts of the central North Sea (see, for example Rowlatt and Lovell, 1994a; Kersten and Kroncke, 1991). However, to place these observations in context, stations with the highest metal content in the NW Irish Sea were those closest to known regions of anthropogenic input and industrial dumping grounds - off Belfast, Dublin and Liverpool Bay (Service *et al.*, 1996).

The contribution of industrial sources in NW England to the sediment-metal loadings of Liverpool Bay are probably the most widely cited examples of anthropogenic enrichment in the Irish Sea (see for example Rowlatt and Lovell, 1994a). Impact on biota is less well documented, though it would seem from one of the few published studies on benthic invertebrates that Hg, Cr and Cd concentrations are enhanced in the deposit-feeding polychaete *Lagis koreni* collected near to dredged material disposal grounds in Liverpool Bay (CEFAS, 1994). Similar observations were made for As is in fish from sludge disposal grounds (Leah *et al.*, 1992b); furthermore, the fact that bottom-dwelling plaice *Pleuronectes platessa* had higher concentrations than a mid-water species such as whiting (*Merlangius merlangus*) implies a sedimentary source, though this needs to be confirmed. Not surprisingly, levels of Hg in plaice were enhanced at the Liverpool Bay sludge grounds compared with 'controls' from Walney (Leah *et al.*, 1993) although this, too, is not definitive proof of a direct sedimentary source.

Diet and physiology are, in fact, crucial in defining Hg burdens in fish. This is the most likely explanation of why dogfish *Scyliorhinus caniculus* from the Liverpool Bay area contain Hg concentrations which are, on average, 5-10 times higher than those in flatfish from the same area (Leah *et al.*, 1991b). To re-emphasise the regional importance of Hg inputs, however, analysis of dogfish showed that three-quarters of the specimens analysed from the NE Irish Sea exceeded the Environmental Quality Standard (EQS-0.3 mg Hg g^{-1}): even more significantly, all of those captured within Liverpool Bay itself exceeded the EQS.

Finally, this review has revealed some areas where there are deficiencies in data, particularly with regard to the assessment of sediment-metal bioavailability. Inevitably, the main problems are that the information is patchy, difficult to compare (due to species or sampling variability), and often historic. Some of the data in PML's own data base is now more than twenty years old and ideally it should, in the near future, be brought up to date - by conducting contemporary, systematic surveys in all of the major estuaries in the Irish Sea region - along the lines of the work undertaken in the Mersey, Wyre, Ribble and Solway as part of this project. There have been some major changes in industrial and domestic inputs in recent years (with the advent of stricter pollution controls and the decline of manufacturing): therefore, estimates of the current scale of anthropogenic impact should be gauged with extreme caution if extrapolated from data which was collected before these changes. They may not be an accurate reflection of present contamination status.

Bearing these caveats in mind, the review of available data is being used to fine-tune the current field sampling programme i.e. to provide necessary contemporary information for the four main estuarine systems under study.

3.4 Compatibility of Datasets

One of the objectives of the review of existing datasets, was to establish the degree of compatibility between them with a view to minimising the requirement for new sample collection and analysis. From the foregoing it is clear that only five datasets merit serious consideration in this respect: (1) BGS onshore geochemical data; (2) OSPARCOM 1990/91 baseline survey data; (3) NRA estuary data; (4) NMP data; and (5) PML sediment data. However, because the proposed methodology requires multi-element data in order to develop characteristic geochemical signatures, the limited element ranges of datasets 2-5 render them unsuitable for use in later stages of the project, except as useful indicators of appropriate sampling sites. In addition, differences in the size fractions used (BGS, <150 •m; OSPARCOM, NRA and NMP, <2 mm; and PML, <100 •m) and times of collection introduce further complications. The time factor is probably of little significance with regard to the BGS onshore stream sediment based data, since temporal variation in stream sediment chemistry is usually small compared with that from other (e.g. geological) sources, particularly in temperate climates (Chork, 1977; Bolviken *et al.*, 1979). However, in offshore and estuarine sediments temporal variations in chemistry, perhaps related to changes in sedimentary regime, are less well understood, but could be significant.

The digestion technique (aqua region/hydrofluoric acid) used in the OSPARCOM, NRA and NMP surveys should produce 'total' values for the elements analysed and in this respect the data for these elements should be compatible with the 'total' values reported in the onshore BGS data. The PML method of digestion, with concentrated nitric acid, does not extract all metals completely (though any remaining metal is unlikely to be bioavailable). Tests have shown that while most metals were almost totally extracted (by comparison with dissolution in hydrofluoric acid), recovery of Mn, Fe and Cr was usually around 90% and could be less.

X-ray fluorescence spectrometry (XRF) has now superseded DR-OES as the preferred method of analysis for routine multi-element geochemistry in BGS and additional analyses of river, estuary or offshore sediment samples within Project CWO 764 were carried out by XRF. In order to better assess the relationships between metal data produced for the different surveys, a small number of samples from the NMP work in the Solway and Mersey, along with representative samples from PML were analysed using BGS XRF facilities. The results are shown in Table 5 and Figure 7. In general there is a reasonable correlation between the XRF and other methods, with occasional aberrant results lowering the correlation coefficient (e.g. Fig. 7: Rb, V, Pb). The OSPARCOM, NRA, NMP, PML and BGS (XRF) data can, therefore, be used with confidence to compare general metal levels.

A more serious concern, is whether BGS XRF and DR-OES data are compatible since the existing onshore geochemical data for north west England was produced by DR-OES, whilst new data from rivers, estuaries and offshore, produced by Project CWO 734, has been generated by XRF techniques. However, as part of the planned change-over from the obsolescent DR-OES technique to the more modern automated XRF system for the analysis of the large numbers of samples and analytes generated by the G-BASE regional geochemical survey, BGS has undertaken a comparative study of the two methods. This was principally to establish the degree of compatibility between existing and future datasets obtained by the different methods and to determine what data processing procedures would be required to render datasets

Table 5. Comparison of BGS XRF and PML/CEFAS acid extractable metals data for selected samples. Hg in both cases is by AAS. A = acid extractable, X = XRF

ESTUARY	Rb		Cd		Cr		Cu		Fe2O3		Hg		Ni		Pb		Zn		As		V	
	A	X	A	X	A	X	A	X	A	X	A	BGS	A	X	A	X	A	X	A	X	A	X
MERSEY	23	28	0.173	<3	16	21	4	1	1.37	1.32	0.07	0.07	8	5	19	18	54	53	15	15	16	16
MERSEY	22	28	0.142	<3	12	15	3	1	1.29	1.31	0.04	0.05	6	4	18	18	45	47	13	15	14	14
MERSEY	54	62	0.971	<3	92	86	48	40	3.25	2.99	1.42	1.00	24	21	94	80	294	283	24	24	60	60
MERSEY	21	24	0.011	<3	9	11	1	1	0.92	0.93	0.02	0.02	5	4	13	12	29	31	9	11	13	14
MERSEY	95	91	1.194	<3	140	148	107	99	5.52	4.50	2.43	3.00	48	37	177	161	471	550	24	36	107	98
MERSEY	34	40	0.223	<3	29	27	7	6	1.09	1.10	0.10	0.15	7	7	21	22	107	114	8	7	17	18
MERSEY	30	36	0.097	<3	14	24	5	2	0.96	1.08	0.04	0.05	7	5	16	16	59	61	8	9	13	15
SOLWAY	47	53	0.146	<3	22	20	10	2	1.32	1.11	0.06	0.01	11	7	10	12	21	20	9	6	21	18
SOLWAY	42	51	0.031	<3	7	24	31	1	1.34	1.13	0.04	0.02	16	8	9	11	14	19	5	5	19	16
SOLWAY	44	53	0.101	<3	8	18	46	3	1.72	1.25	0.11	0.06	26	11	97	21	33	29	14	12	25	21
SOLWAY	20	56	0.057	<3	18	18	3	2	1.39	1.11	0.01	0.01	8	8	12	12	26	21	4	4	51	18
SOLWAY	19	49	0.084	<3	19	22	4	1	1.29	1.02	0.01	0.02	7	8	11	12	32	18	3	6	43	18
SOLWAY	47	56	0.146	<3	19	20	13	2	1.19	1.30	0.06	0.01	10	9	10	13	24	22	9	5	20	22
PML High		209	2.999	5	38	58	2963	2285	8.69	9.08			34	45	272	261	4098	4003	1757	1293		93
PML Med		100	6.544	<3	152	166	56	56	4.78	5.43	0.31		32	39	88	92	225	223	19	27		104
PML Low		64	0.408	<3	33	63	10	9	2.76	2.79	0.07		20	21	28	31	80	70	8	12		50

provided by the different methods compatible. The ultimate requirement is that GBase retains the capability to produce 'seamless' geochemical maps of the UK. The changeover between DR-OES and XRF analysis took place between the 'North Wales and North West England' and 'Wales and West Midlands' 1:250,000 scale Geochemical Atlas sheets in 1993. The compatibility exercise was carried out in addition to the existing rigorous error and quality control procedure of the G-BASE programme, which monitors the analytical data for temporal drift and variations in calibration, regardless of the analytical method, using both internal and certified international standards.

3.4.1 BGS Comparison of XRF and DR-OES data

3.4.1.1 Methodology

The BGS analytical laboratories operate two different XRF facilities, one based on wavelength dispersive (WD-XRF) techniques and one on energy dispersive (ED-XRF) techniques. For operational reasons, new data for this project were generated using ED-XRF. This has complicated the comparison because the largest comparability study carried out to date was between WD-XRF and DR-OES data. However, another, more limited, study has compared WD and ED-XRF results, thus allowing the compatibility DR-OES and ED-XRF data to be assessed.

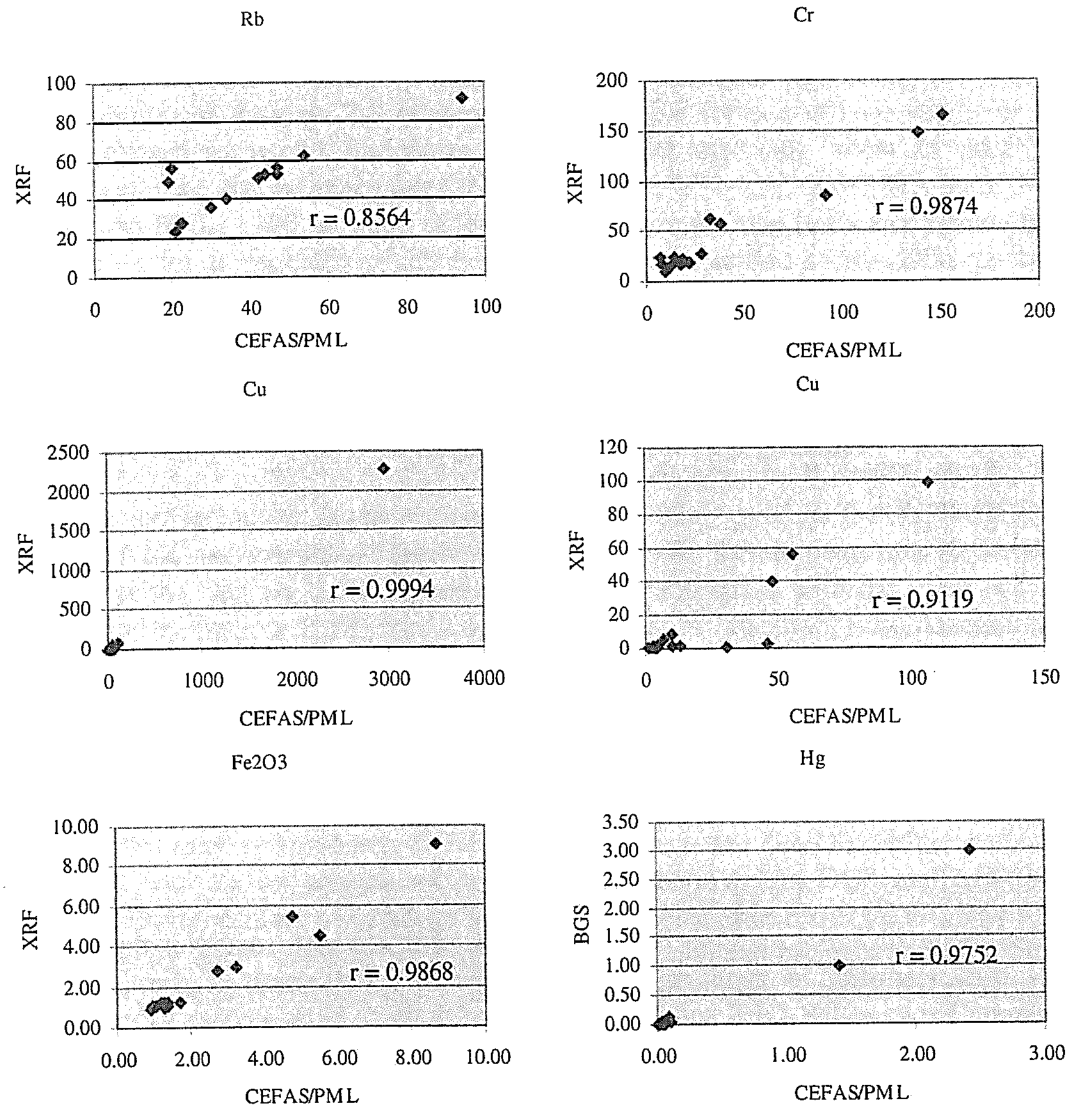

Figure 7. Relationships between BGS XRF and acid extractable metals data for selected samples. See text for further explanation. Continued ……

Some 3301 stream sediments and 854 soil samples were selected from the North Wales and NW England regional geochemical survey dataset for the larger comparison study. These samples, previously analysed by DR-OES, were re-analysed by the WD-XRF method. Both sets of data were subjected to individual and comparative statistical analysis, and used to make colour, percentile-classified gridded geochemical maps, so that statistical, graphical and spatial variations could be observed and determined. StatView 4.5 was used for most of the statistical and graphical analysis, and an in-house modified version of NIH-Image was used for the generation of the gridded maps.

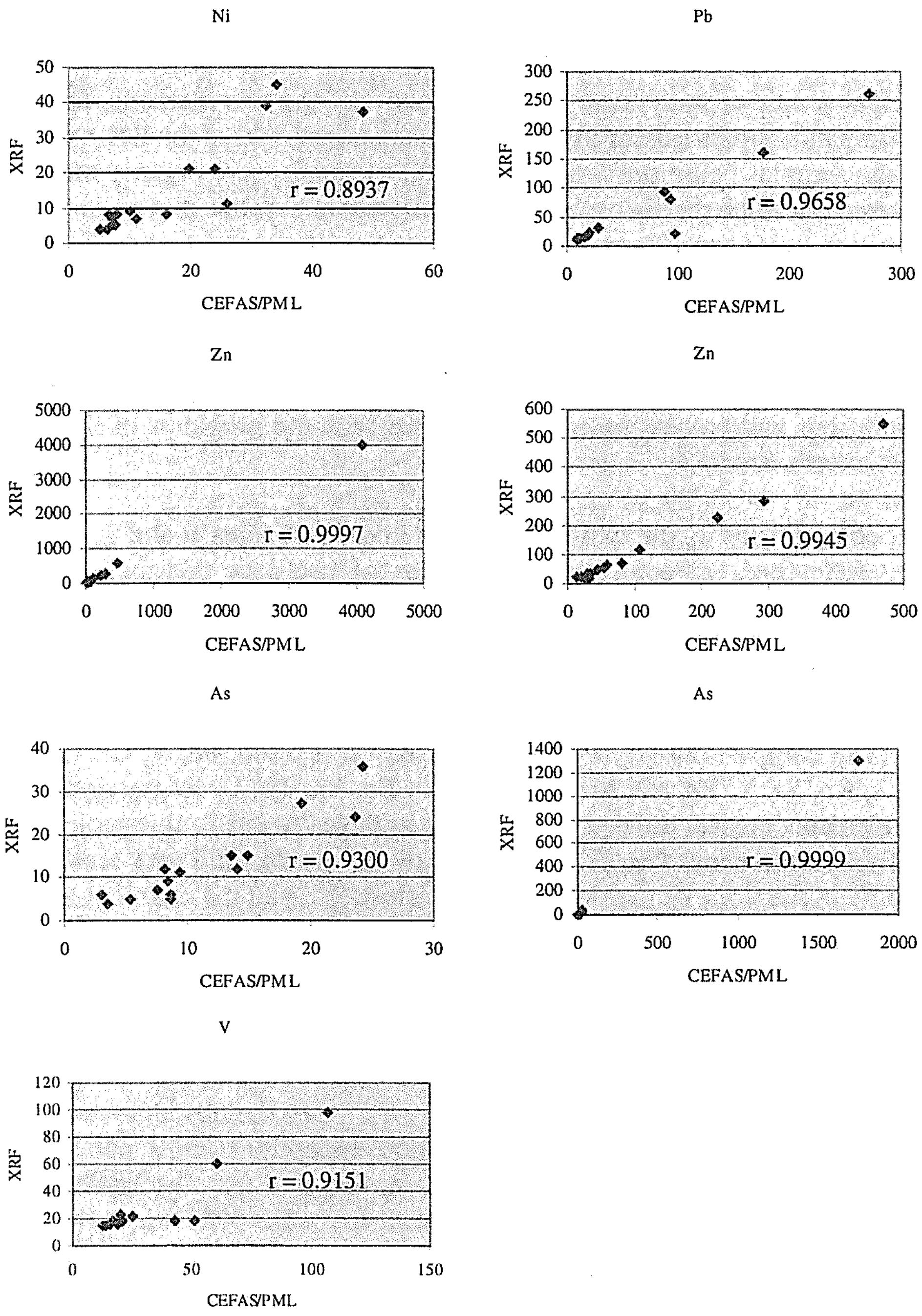

Figure 7. Continued.

The DR-OES and WD-XRF analytical methods are described elsewhere (BGS, 1997; Ingham and Vrebos, 1994) and need not be described in detail here. Both methods generate data for a wide range of major, minor and trace elements with varying degrees of sensitivity and precision. Most elements previously determined by DR-OES can be determined by WD-XRF, often at better levels of accuracy, but XRF cannot determine the light elements such as Li, Be and B. Consequently, the set of 29 selected elements examined and compared was:

Majors and Minors: CaO, Fe_2O_3, K_2O, MgO, MnO, P_2O_5, and TiO_2
Traces: Ag, Ba, Bi, Cd, Co, Cr, Cu, Ga, La, Mo, Nb, Ni, Pb, Rb, Sn, Sr, V, Y, Zn, Zr.

The principal source of systematic difference between the two methods, for soils and stream sediment samples (rather than rocks or standards), is that the DR-OES method relies on the samples being pre-ignited at 450°C to destroy any organic matter which would cause failure of the firing of the graphite sample pellet during analysis. The loss on ignition value was not routinely determined, so no compensation is applied for organic matter content. The XRF method does not use pre-ignited material and takes the organic matter content into account. Consequently, DR-OES values tend generally to be higher than XRF values for organic-rich samples, all other factors being equal. Other factors involved are the greater degree of automatic compensation within the XRF calibrations and processing software to deal with the problems of inter-element and matrix interferences.

Statistical comparisons of the two methods are given in Tables 6 and 7, showing, in particular, differences at equivalent percentiles of the data distribution, whilst a summary of the regression equations and correlation coefficients are given in Table 8.

For the comparison between WD and ED-XRF data, 470 samples were analysed by both methods. The elements determined differ slightly from those used in the WD-XRF/DR-OES comparison: Na, Mg, Al, Si, P, K, Ca, Ti, Mn, Fe, V, Cr, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Y, Zr, Nb, Mo, Ag, Cd, Sn, Ba, La, Th, U. Regression equations for those elements present at levels considered suitable for use in this project are also given in Table 8 and show that, in general, the two methods yield very similar data; r^2 values are high, the slope of the regression line close to 1 and the intercept small.

3.4.1.2 Discussion

For most elements, and for both the soils and stream sediments, WD-XRF and DR-OES data are strongly correlated and can be inter-converted with confidence using the simple regression equations shown in Table 8, even when the absolute values may be markedly different. There are unfortunately some exceptions, most notably Ag and Mo. The closeness of WD and ED-XRF data suggests that the same regression equations could be used to convert DR-OES data to an ED-XRF equivalent, but the use of both sets of regression equations to effect the conversion is preferred. Some relatively poor correlations between the WD and ED-XRF data are apparent with Co (not shown in Table 8), Mo, La and U being prominent.

3.4.1.3 Conclusions

Within the areas chosen for the comparison study, and by extrapolation those data produced in other areas using similar calibrations, XRF (from both WD and ED methods) and DR-OES data are comparable for most analytes and can be inter-converted with confidence using simple regression equations. Some analytes, e.g. Ag, Co, La, Mo and U cannot be readily converted and compared with the same degree of confidence.

Table 6. Comparison of DR-OES and WD-XRF data for 3301 stream sediment samples from North Wales. See text for further information.

Element	1%	2%	3%	4%	5%	10%	20%	30%	40%	50%	60%	70%	80%	90%	95%	96%	97%	98%	99%
Silver Ag																			
XRF	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	1	1	2	2	3	3	4	4	4	5	6
DR-OES	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.4	0.6	0.9	1	1.3	1.8	3.65
Cadmium Cd																			
XRF	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	1	1	1	2	2	3	5	6	7	10	14.5
DR-OES	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.7	0.9	1.4	2.1	3.9	5.7	6.6	7.8	9.8	12.8
Tin Sn																			
XRF	1	1	2	2	2	2	3	3	4	4	5	6	8	13	19.5	22	25.5	34	51
DR-OES	2	2	2	2	2	2	2	2	3	3	4	4	7	13	24	29	34	43	66.5
Lanthanum La																			
XRF	18	20	22	23	24	28	32	36	40	43	46	49	52	59	68	72	76	85	106.5
DR-OES	0	1	3	6	7	14	22	28	34	39	44	51	57	68	76	80	84	90	101.5
Nickel Ni																			
XRF	7	9	10	11	12	16	22	26	30	33	36	40	45	54	67	70	76	88.5	115.5
DR-OES	7	9	13	15	16	22	30	35	40	46	50	55	62	77	95	99	112.5	132	176.5
Copper Cu																			
XRF	5	7	8	8.5	9	11	13	15	18	20	22	26	32	47	78.5	91	115.5	184	368.5
DR-OES	6	7	8	9	9	12	15	18	20	23	26	31	40.5	60.5	100	119.5	151.5	231.5	502.5
Zinc Zn																			
XRF	33	42	48	51	54.5	67	87	100	116	130	148	174	223	331.8	525.4	583.9	737.8	1002	1584
DR-OES	46	58	65	72	76	92.5	129	151	174	204	240	288.5	374	583	953.5	1096	1365	1802	2989
Gallium Ga																			
XRF	5	5	6	6	6	7	10	12	14	16	18	19	20	22	24	25	26	26	28
DR-OES	3	4	5	5	6	8	11	14	18	20	22	24	26	28	30	31	32	33	34
Rubidium Rb																			
XRF	33	42	45	49	51	57	65	73	81	88	97	106	116	126	133	135	137	141	148
DR-OES	37	43.5	47	50	52	60	74	86	97	110	123	136	150	168	182	185	189.5	198	212
Strontium Sr																			
XRF	23	32	36	39	41	47	55	60	65	70	75	80	87	99	110	115	121.5	128.5	154.5
DR-OES	31.5	42.5	48.5	52	54	62	72	80	87	93	100	107	115	128	144	152	160	173	199
Yttrium Y																			
XRF	14	15	16	17	18	20	23	25	26	27	29	31	34	40	49	54	60	68.5	84.5
DR-OES	13	15	17	18	18.5	22	24	27	29	32	33	36	40	47	58	64	70	82	102
Zirconium Zr																			
XRF	124	138	150	159.5	167	192	217	240	272	318	387	504	684	1020	1442	1607	1809	2188	2936
DR-OES	111.5	153.5	179	194	214	268	343	403	468	552	679	950	1396	2277	3292	3702	4240	5086	6153
Niobium Nb																			
XRF	6.7	7.7	8.1	8.5	8.8	10	11	12	13	14	15	15.6	16.5	18.3	21	22	23.2	25.6	29
DR-OES	0	0	0	0	2	7	13	16	18	20	21	23	25	28	30.5	31	32	33	35
Molybdenum Mo																			
XRF	1	1	1	1.7	2	2	2.7	3	3.3	3.7	4	4.4	5	6.1	8.1	8.8	9.8	11	14.1
DR-OES	0	0	0	0	0	0	0	0	0	0	1	1	1	2	2	2	3	3	5
Lead Pb																			
XRF	15	17	18	20	20.5	24	30	34	39	45	52	65	87	151	287	397.5	533.9	772.1	1600
DR-OES	19	21	23	24	25	30	35	41	47	54	62	77	102.5	193	413.5	548.5	841	1293	3174
Bismuth Bi																			
XRF	0	0	0	0	0	0	0	0	0.1	0.3	0.5	0.7	1	1	1.4	1.6	2	2	2.9
DR-OES	0	0	0	0	0	0	0	0	0	0	0	1	1	2	2	2	2	3	4
Magnesium MgO																			
XRF	0.45	0.5	0.6	0.6	0.7	0.8	1	1.2	1.3	1.4	1.6	1.8	2.1	2.5	3.2	3.5	3.9	4.8	6.4
DR-OES	0.3	0.38	0.44	0.5	0.56	0.75	1.08	1.31	1.49	1.65	1.83	2.05	2.31	2.72	3.33	3.55	3.81	5.47	7.48
Phosphorus P2O5																			
XRF	0.06	0.07	0.08	0.09	0.09	0.11	0.14	0.16	0.18	0.21	0.24	0.27	0.32	0.42	0.54	0.58	0.63	0.68	0.79
DR-OES	0	0.01	0.01	0.01	0.02	0.03	0.05	0.07	0.09	0.11	0.14	0.16	0.19	0.24	0.3	0.31	0.34	0.38	0.45
Potassium K2O																			
XRF	0.98	1.19	1.28	1.39	1.43	1.64	1.87	2.06	2.23	2.38	2.56	2.76	2.94	3.18	3.34	3.39	3.44	3.51	3.67
DR-OES	0.82	1	1.08	1.15	1.21	1.4	1.64	1.85	2.04	2.23	2.4	2.58	2.8	3.09	3.35	3.47	3.63	3.82	4.03
Calcium CaO																			
XRF	0.06	0.08	0.1	0.12	0.13	0.18	0.26	0.35	0.43	0.55	0.68	0.86	1.15	1.81	2.88	3.25	3.94	5.13	7.74
DR-OES	0.06	0.1	0.12	0.13	0.14	0.18	0.24	0.3	0.36	0.42	0.58	0.85	1.28	2.45	4.18	4.87	5.87	7.2	11
Titanium TiO2																			
XRF	0.382	0.441	0.473	0.496	0.518	0.587	0.68	0.753	0.826	0.882	0.922	0.96	1.011	1.103	1.253	1.3	1.394	1.615	2.181
DR-OES	0.55	0.575	0.6	0.62	0.64	0.69	0.75	0.8	0.84	0.87	0.9	0.94	0.98	1.044	1.15	1.19	1.275	1.45	2.05
Manganese MnO																			
XRF	0.023	0.03	0.036	0.04	0.045	0.057	0.085	0.114	0.15	0.203	0.296	0.438	0.706	1.506	2.568	2.976	3.376	4.973	7.867
DR-OES	0.027	0.033	0.037	0.042	0.046	0.058	0.085	0.119	0.164	0.209	0.278	0.401	0.625	1.266	2.212	2.946	3.547	4.684	7.574
Iron Fe2O3																			
XRF	1.59	1.923	2.144	2.28	2.41	3.078	4.161	5.11	6.08	6.79	7.73	8.08	9.14	11.23	13.44	14.11	15.21	16.91	19.29
DR-OES	1.235	1.6	1.791	2	2.261	3.26	4.66	5.87	6.66	7.7	8.631	9.65	10.98	13.69	16.1	16.93	18.29	20.14	23.33
Vanadium V																			
XRF	26	30	33	36	38	47	62	78	91	101	109	115	122	136	149	154	162	182	235
DR-OES	32	37	40	42	44	52	63	72	82	90	96	103	110	121	133	138	143	156	175
Chromium Cr																			
XRF	27.5	37.5	43	46	49	60	72	78	84	88	92	97	102	115	134	140	148	163	200
DR-OES	32	41.5	50	53.5	57	65	78	84	90	95	101	109	120	153	192	208	226	256	331
Cobalt Co																			
XRF	5	6	7	8	8	11	15	19	22	26	30	37	50	82	125	143	177	232	364
DR-OES	4	5	6	7	7	9	12	15	18	21	25	34	49	89	143	172	210	293	454
Barium Ba																			
XRF	174	228	259	281	297	353	414	452	486	516	547	583	643	777	1023	1155	1365	1957	4536
DR-OES	211	259	283	304	320	374	443	492	533	573	613	659	722	865	1147	1262	1503	2004	3647

Table 7. Comparison of DR-OES and WD-XRF data for 854 soil samples from North Wales. See text for further information.

Element	Mean	Min.	Max.	Std. Deviation	10%	25%	50%	75%	90%	95%	99%
Silver Ag											
XRF	1.18	0.95	29	1.526	0.95	0.95	0.95	0.95	0.95	2	4
DR-OES	0.674	0.35	53.9	2.665	0.35	0.35	0.35	0.35	0.7	1.2	4.5
Cadmium Cd											
XRF	0.783	0.5	25	1.476	0.5	0.5	0.5	0.5	1	2	4
DR-OES	0.859	0.3	16	1.425	0.3	0.3	0.3	0.8	1.9	3.2	6.2
Tin Sn											
XRF	13.028	1	1094	48.087	2	3	5	11	22	33	89
DR-OES	13.463	2.5	834	47.245	2.5	2.5	2.5	9	27	45	140
Lanthanum La											
XRF	36.395	11	102	10.046	26	31	35	40	50	55	65
DR-OES	33.888	0	162	19.354	13	20	32	45	56	65	90
Nickel Ni											
XRF	34.093	4	288	20.491	17	23	30	40	52	62	106
DR-OES	45.398	1	536	35.354	19	29	39	54	72	90	175
Copper Cu											
XRF	45.756	1	1132	75.458	10	18	28	46	85	128	380
DR-OES	60.979	3	1384	112.023	12	20	33	60	112	171	599
Zinc Zn											
XRF	149.772	9	2852	205.515	39	57	89	180	296	400	901
DR-OES	241.314	13	4362	352.377	60	86	139	264	494	688	1584
Gallium Ga											
XRF	13.611	3	47	4.324	8	11	13	16	19	21	26
DR-OES	15.347	1.6	34.7	5.58	8.1	11.8	15	18.6	23	25	29.7
Rubidium Rb											
XRF	82.112	12	143	17.671	61	71	82	93	103	112	131
DR-OES	99.722	39	202	27.574	67	81	98	115	136	151	177
Strontium Sr											
XRF	84.409	35	257	22.122	66	72	80	90	105	121	171
DR-OES	105.231	52	360	34.157	79	87	98	112	130	167	257
Yttrium Y											
XRF	25.285	7	76	5.919	19	22	25	28	32	34	41
DR-OES	26.696	4	93	9.195	17	20	26	31	37	42	55
Zirconium Zr											
XRF	484.823	51	7906	462.278	242	298	369	510	807	1082	1982
DR-OES	923.632	7	9123	862.546	381	493	661	977	1762	2456	4355
Niobium Nb											
XRF	11.218	2	25	2.327	8	10	11	13	14	15	16
DR-OES	14.602	0	36	8.573	0	9	15	21	25	28	32
Molybdenum Mo											
XRF	3.424	0.5	32	2.913	1	2	3	4	6	8	15
DR-OES	2.569	2.5	14.9	0.695	2.5	2.5	2.5	2.5	2.5	2.5	5.4
Lead Pb											
XRF	113.684	8	4252	243.124	25	36	58	113	227	301	735
DR-OES	152.344	13	7412	417.194	28	40	64	127	262	424	1480
Bismuth Bi											
XRF	0.772	0.5	24	1.052	0.5	0.5	0.5	1	1	1	2
DR-OES	2.582	2.5	38	1.499	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Magnesium MgO											
XRF	2.084	0.3	8.8	1.069	1	1.4	1.9	2.6	3.3	3.9	5.7
DR-OES	1.721	0.13	10.99	1.057	0.79	1.11	1.52	2.04	2.72	3.35	6.2
Aluminium Al2O3											
XRF	13.502	4.9	25.8	3.275	9.4	11.6	13.4	15.2	18	19.4	22.7
DR-OES	15.893	4.4	41.4	6.657	8.7	11.3	14.5	18.9	24.5	29.4	37.7
Silica SiO2											
XRF	59.559	11.4	80	7.083	51.5	55.7	60.3	63.7	67.2	69.4	76.2
DR-OES	80.964	36.8	90	8.657	68.9	74.8	82.3	90	90	90	90
Phosphorus P2O5											
XRF	0.309	0.04	1.49	0.225	0.1	0.15	0.25	0.4	0.6	0.75	1.19
DR-OES	0.269	0	3.229	0.287	0.05	0.09	0.18	0.34	0.55	0.73	1.37
Potassium K2O											
XRF	2.33	0.36	4.13	0.433	1.83	2.06	2.32	2.56	2.85	3.07	3.57
DR-OES	1.957	0.8	4.58	0.454	1.47	1.64	1.89	2.2	2.53	2.7	3.38
Calcium CaO											
XRF	1.202	0.03	11.52	1.28	0.29	0.5	0.75	1.42	2.53	3.61	6.8
DR-OES	1.343	0	21.57	1.99	0.21	0.35	0.56	1.54	3.15	5.07	9.91
Titanium TiO2											
XRF	0.714	0.21	1.547	0.141	0.531	0.639	0.724	0.795	0.876	0.926	1.023
DR-OES	0.801	0.44	2.23	0.133	0.67	0.73	0.8	0.86	0.93	0.98	1.1
Manganese MnO											
XRF	0.124	0.004	5.009	0.224	0.027	0.044	0.073	0.125	0.268	0.386	0.761
DR-OES	0.16	0.012	8.253	0.329	0.04	0.061	0.092	0.167	0.338	0.46	0.879
Iron Fe2O3											
XRF	5.205	0.47	21.99	2.399	2.59	3.8	4.83	6.2	7.9	9.65	12.42
DR-OES	5.999	0.31	28.15	3.245	2.58	3.95	5.55	7.39	9.76	11.38	16.23
Vanadium V											
XRF	87.351	20	310	26.422	57	74	87	100	117	125	154
DR-OES	78.999	11	295	23.624	54	64	77	90	105	114	152
Chromium Cr											
XRF	99.657	28	499	38.473	69	82	94	109	128	151	241
DR-OES	131.046	27	1147	76.449	82	95	114	144	183	217	416

Table 8. Regression equations and correlation coefficients linking: DR-OES and WD-XRF data; and WD-XRF and ED-XRF data. See text for further explanation.

Element	Regression equation (x = DR-OES, y = WD-XRF)	Correlation coefl
Ag	$y = 5.701x - 0.732$	0.788
Cd	$y = 0.796x + 0.258$	0.978
Sn	$y = 0.790x + 1.455$	0.979
La	$y = 0.609x + 19.143$	0.992
Ni	$y = 0.694x + 1.221$	0.999
Cu	$y = 0.752x + 2.133$	0.999
Zn	$y = 0.533x + 19.611$	0.999
Ga	$y = 0.737x + 1.39$	0.995
Rb	$y = 0.639x + 18.279$	0.999
Sr	$y = 0.771x - 1.141$	0.999
Y	$y = 0.786x + 2.996$	0.996
Zr	$y = 0.413x + 86.205$	0.999
Nb	$y = 0.401x + 6.876$	0.936
Mo	$y = 2.167x + 2.556$	0.782
Pb	$y = 0.687x + 8.216$	0.996
MgO	$y = 0.921x + 0.023$	0.982
P2O5	$y = 1.546x + 0.049$	0.987
K2O	$y = 0.902x + 0.376$	0.998
CaO	$y = 0.667x + 0.171$	0.988
TiO2	$y = 1.508 + 0.444$	0.992
MnO	$y = 1.1179 - 0.023$	0.999
Fe2O3	$y = 0.790x + 0.59$	0.999
V	$y = 1.217x - 13.551$	0.991
Cr	$y = 0.594x + 25.668$	0.948
Co	$y = 0.846x + 5.95$	0.996
Ba	$y = 0.870x + 21.145$	0.999

Element	Regression equation (x = WD-XRF, y = ED-XRF)	Correlation coefl
MgO	$y = 1.1295x - 0.0235$	0.9872
P2O5	$y = 0.9354x - 0.0329$	0.7842
K2O	$y = 1.0013x + 0.0095$	0.9873
CaO	$y = 0.9786x + 0.0293$	0.9819
TiO2	$y = 0.9876x - 0.0311$	0.8837
MnO	$y = 0.8878x - 0.0019$	0.9989
Fe2O3	$y = 0.8525x + 0.2831$	0.9768
V	$y = 0.918x - 2.4717$	0.8712
Cr	$y = 0.8673x + 3.63$	0.9776
Ni	$y = 1.0958x - 0.7432$	0.9634
Cu	$y = 1.1337x - 2.4164$	0.9619
Zn	$y = 1.1425x + 2.2644$	0.9996
Ga	$y = 1.0341x - 0.4378$	0.8982
As	$y = 0.9887x - 1.1898$	0.9988
Rb	$y = 1.0814x - 1.1952$	0.9944
Sr	$y = 1.1009x + 0.5929$	0.9961
Y	$y = 1.0805x - 2.9329$	0.9387
Zr	$y = 1.0112x + 4.6991$	0.9983
Nb	$y = 0.9271x + 1.5092$	0.8476
Mo	$y = 0.3774x + 0.5712$	0.1847
Sn	$y = 0.966x - 0.8121$	0.9316
Ba	$y = 0.8088x + 43.452$	0.9699
La	$y = 0.4803x + 14.745$	0.2619
Pb	$y = 0.9953x + 3.2363$	0.999
U	$y = 1.0559x + 0.1856$	0.6111

3.5 Summary

It was clear from the review of existing data that a programme of new sampling and analysis was the only way to fulfil the project objectives. Within the analytical programme, new analyses derived by XRF methods can be compared with the DR-OES derived onshore database values if the appropriate regression equations are applied.

4. PART A MULTI-ELEMENT GEOCHEMISTRY

4.1 Sampling Programme

The general methodology, based on earlier work in the Humber region (Rees *et al.*, 1998), uses bedload stream and river sediments to allow new samples to be compared with the extensive database of stream sediment chemistry (GBase) assembled by BGS for Scotland, northern England and Wales.

Four estuaries (Solway, Wyre, Ribble and Mersey) and associated drainage basins were selected for study (Fig. 8). The technique was tested in catchments from headwater regions to the lower reaches of rivers and the results applied to whole drainage basins. The Solway Firth is regarded as an estuary with minimal industrial anthropogenic contamination. The drainage systems of the Nith, Esk, Waver, Eden and Ellen all flow into the Solway. The first three contain only a few small sources of contamination, whilst the Eden and Ellen catchments contain mineralisation and hosted historical mining activity. The Ribble, Wyre and Mersey estuaries are contaminated to varying degrees, largely from urban and industrial development. The sampling programme was designed with two objectives:

1. To assess the relationship between the geochemistry of sediment samples from uncontaminated major rivers and the average geochemical signature of samples from 1-2 km^2 drainage basins making up the catchment area; and

2. To compare the geochemistry of sediment samples from major rivers and estuaries downstream of contaminant sources with that of the uncontaminated catchment upstream.

Details of sampling sites are given in Appendix 2 and general locations shown in Figure 8. Sites were selected in rivers upstream and downstream of contaminant sources, in the estuaries and offshore. Onshore sampling started in the Ribble in May, 1999 and finished in the Mersey in November, 1999. Offshore sampling took place as part of the **BIOAVAILABILITY** programme, described below.

Whole sediment or, where coarse sediment was present, material sieved to < 2 mm (using nylon sieve cloth in a wooden frame) was collected. In general, more than 2 kg of sediment were collected at each site in plastic bottles or bags. Samples were made up of material collected from several different places at each site, a method which experience has shown to produce representative and reproducible data (e.g. Ridgway and Midobatu, 1991). At some sites this encompassed the whole width of the river,

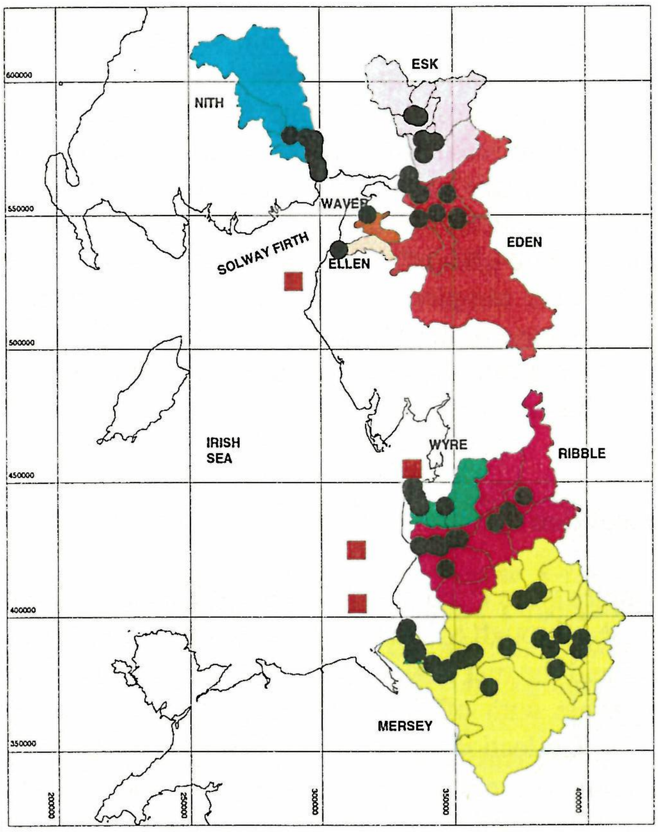

Figure 8. Location of the study catchments, river sample sites (black circles) and offshore sample sites (red squares).

Figure 9. Sampling in the River Goyt near Stockport showing wooden sieve with nylon mesh (lower centre) and < 2mm sieved material in a wooden collecting bowl (lower left).

whilst at others both left and right banks were sampled separately. At upstream sites the rivers commonly had gravel beds and suitable sediment was difficult to collect. Mid-stream sites were either too deep to allow access (even in waders) or fast-flowing, making it difficult to preserve the fine fraction, which tended to be swept away by the current. Sites selected from maps frequently had to be changed in the field and recourse was often made to sampling lag gravel bars near the inside of bends or the downstream ends of islands. In the lower reaches of major rivers, where the sediment was sufficiently fine-grained, a Van Veen grab sampler was deployed from bridges. Estuarine sites were sampled by walking out on sandbanks and mudflats at low tide, by boat or, in the case of the Mersey, by hovercraft. Short cores, collected by driving polycarbonate tubing into the estuarine muds and muddy sands by hand, were taken at several sites in the Mersey Estuary.

4.2. Sample Preparation

In the laboratory, samples were dried at 40°C, disaggregated using a pestle and mortar and, if necessary, passed through a 2 mm mesh nylon sieve. A portion of the < 2 mm material was retained and the rest sieved to < 150 µm. These two fraction were taken in order to be compatible with offshore sediments and the BGS onshore database sediments respectively. Collection of sediment offshore commonly results in there being too little material to yield a suitable weight of the < 150 µm fraction for analysis and the < 2 mm fraction has to be used instead. Following sieving, the samples were prepared for XRF analysis by grinding 12.00 g sample with 3.00 g binder in an agate planetary ball mill for 3 minutes then pressing at 25 tons load into 40 mm diameter pellets. The binder used for the pressed powder pellets was a mixture of 9 parts EMU120FD styrene co-polymer (BASF plc) and 1 part Ceridust 3620 micronised polyethylene wax (Hoechst).

4.3 Analysis

Analyses were carried out in the BGS laboratories at Keyworth which are UKAS accredited. BGS also participates in several other analytical quality control programmes: ISE (International Soil Exchange); Quasimeme (Marine AQC); GeoPT; Aquacheck (water chemistry) and Contest (contaminated land assessment); thus ensuring that analytical quality assurance and control meet the specifications of the contract.

The samples were analysed by energy dispersive (polarised) x-ray fluorescence spectrometry (ED(P)XRFS) using a Spectro X-LAB 2000 spectrometer fitted with a 400 W/54 kV palladium anode x-ray tube and controlled by Spectro XLABPro software. Determination of Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5, SO_3, Cl, K_2O, CaO, Sc, TiO_2, V, Cr, MnO, Fe_2O_3, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Ag, Cd, In, Sn, Sb, Te, I, Cs, Ba, La, Ce, Pr, Nd, Hf, Ta, W, Hg, Tl, Pb, Bi, Th, and U is carried out simultaneously.

Pellets were placed into 14 position sample plates together with an instrumental quality control (QC) sample. The configuration of the instrument is given in Table 9.

Table 9. Configuration of the Spectro X-LAB 2000 ED(P)XRF Spectrometer.

Model:	X-LAB 2000
Serial No:	9902/98A
Tube:	Palladium End Window Tube
Tube rating:	400 W Max. 54 kV Max. 15 mA
Detector:	Liquid nitrogen cooled lithium drifted silicon solid state
Secondary target (and beam filter):	Molybdenum (Niobium) Cobalt (Iron)
Polarisation target (and beam filter):	Aluminium oxide (Tantalum) Boron carbide (Palladium) Highly oriented pyrolytic graphite (None)

The sample is irradiated by x-rays, which in turn cause x-ray fluorescence of the atoms within the sample. In ED(P)XRFS, the primary x-radiation is scattered off a secondary/polarisation target, which is used to optimise the power of the exciting x-radiation and to minimise the spectral background. Five different secondary/polarisation targets are used to give optimal coverage of 52 elements from Na to U; all elements are measured to improve the accuracy of the corrections on the analytes of interest.

The whole of the emitted x-ray spectrum is detected simultaneously using a Si(Li) detector. The acquired spectrum is deconvoluted, then evaluated using a calibration prepared by the instrument manufacturer. Corrections are made within the calibration for matrix effects and spectral interferences. Inherent mineralogical and particle size effects will, however, contribute to the overall analytical error. The calibrations are validated by analysis of 200 Reference Materials. Instrumental drift is corrected for weekly and analysis is carried out under quality assurance procedures to BS EN ISO 9000.

For each element, data from the QC sample are plotted on Shewhart charts. No QC data failed the QC criteria, but had they done so, analysis of the entire sample plate of 13 samples and one QC sample would have been repeated for all elements.

Quality control was also exercised through the analysis of replicate samples. Correlation coefficients for 11 replicate pairs of samples indicated that data for only 30 elements were likely to be of value in this study (Table 10). The number of elements actually considered in the interpretation was reduced to 23 because of a lack of comparable DR-OES data or poor correlation with the DR-OES data. Thus Hf, Ce, La, I, Cl, Si and Al have not been used.

The ED-XRF data are presented in Appendix 3.

Table 10. Correlation coefficients for 11 replicate pairs of samples by ED XRF

Correlation Coefficients

Pb	0.99358	Y	0.96845	SiO_2	0.82303
Hf	0.99381	Sr	0.99820	Al_2O_3	0.97484
Ce	0.94500	Rb	0.99480	Fe_2O_3	0.99644
La	0.88637	Br	0.99927	Na_2O	0.89868
I	0.95456	As	0.95569	K_2O	0.99186
Ba	0.97969	Zn	0.99866	CaO	0.99689
Sn	0.90553	Cu	0.96032	MgO	0.94531
Cl	0.98083	Ni	0.95210	MnO	0.98702
Nb	0.94959	V	0.90199	TiO_2	0.97902
Zr	0.98641	Cr	0.97784	P_2O_5	0.86446

4.4 Interpretation

A MapInfo GIS database was assembled, incorporating information on the BGS GBase database of stream sediment chemistry, mine and mineral deposit types and locations, urban areas, geology, coastline, major river sample locations, the drainage network and catchment boundaries. Interpretation of the data relied heavily on the use of normalised multi-element diagrams (spidergrams) to compare the geochemical signatures of each catchment basin with the major river sample at the catchment mouth. In spidergrams, element concentrations are normalised to a suitable average value, in this case the upper crustal average of Wedepohl (1995), and plotted on a logarithmic (Y-axis) scale against element position on the X-axis. This allows elements with widely different concentrations in sediments to be plotted easily on the same diagram. Average catchment geochemistry was computed using a point in polygon method based on catchment boundaries.

Because average catchment geochemistry was based on DR-OES data, the regression equations relating DR-OES to WD-XRF and WD-XRF to ED-XRF were applied to each signature to facilitate comparison.

An additional normalisation was applied to compensate for grain-size differences between major river and catchment stream sediment samples. The rivers of north-western England and southern Scotland, particularly the more northerly ones, are largely fast flowing with boulder beds. Fine-grained sediment is winnowed out by the strong currents and there is a strong probability that the grain-size distribution in the < 150 μm fraction of the major river samples is different to that of the same fraction in the GBase stream sediments from 1-2 km^2 drainage basins, being depleted in the finer-grained material. To compensate for this, in all the signatures, elements which are known to have strong associations with the fine, particularly clay mineral, fraction in sediments have been normalised to Ga as a proxy for grain size. Aluminium is the most commonly used grain size proxy (Loring and Rantala, 1992), but Al data are not reliable in the DR-OES dataset. Gallium, however, is reliable in both DR-OES and XRF datasets and correlates strongly ($r^2 = 0.797567$; $n = 470$) with Al in the ED-XRF stream sediment data.

The typical effects of normalising the elements Ti, Fe, Mn, V, Cr, Ni, Cu, Zn, Rb and Pb on signatures from a relatively uncontaminated catchment are shown in Figure 10. The trace of the major river sample (Irthing 1) corresponds more closely with the trace of the catchment signature (Irthing) after normalisation. The shift from the original trace is greater for the river sample signature, normalisation having little effect on the catchment signature, thus demonstrating the validity of the hypothesis set out in the preceding paragraph.

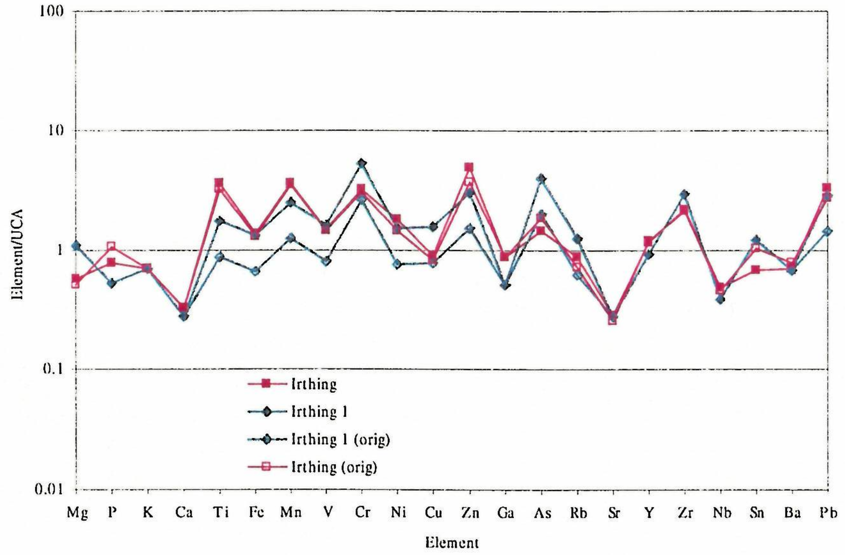

Figure 10. Comparison of normalised and non-normalised (orig) geochemical signatures for a typical catchment basin (Irthing) and its representative river sample (Irthing 1). See text for further explanation.

The generally close tie between geology and stream sediment chemistry has been used as the basis for the development of model geochemical signatures, which allow natural background levels to be estimated even where catchments have extensive mining and industrial contamination. Drift cover of glacial or other origin appears to have relatively little influence on the relationship of stream sediment geochemistry to geology, as illustrated by the match between geochemical patterns and underlying lithology in the Lake District region (BGS, 1992). Model geochemical signatures were calculated by computing the percentages of different geological lithologies within the catchment (Table 11) and combining typical geochemical signatures from pristine areas of similar lithologies on a weighted basis. Data are given in Appendix 4.

4.5 Results

In the following discussions, frequent reference will be made to:

Catchment signature:-	spidergram of the average of all GBase samples in the catchment upstream of the major river site sampled for this project
Model catchment signature:-	spidergram calculated from the percentages of geological lithologies underlying the catchment and

Table 11. Physical and geological make-up of the study catchments and the number of GBase samples used to generate the model catchment signatures.

Catchment	Key River Site	Catchment Make Up Parentheses indicate multiple catchments	Area sq km	GBase Samps.	Geological Make Up
NITH					
Upper Nith	Nith 3	Unitary	856	779	60% Lower Palaeozoic seds, 20% Westphalian, 15% Permian sst, 5% Permian volcanics
Old Water	Cluden Water 3	Unitary	35	17	100% Lower Palaeozoics seds.
Cluden	Cluden Water 1, 2	Cluden + Old Water	241	168	90% Lower Palaeozoic seds, 10% Permian sst.
Middle Nith	Nith 5	Upper Nith + (Cluden)	1124	974	85% Lower Palaeozoic seds, 4% Carb lst (sst), 7% Permian sst, 4% Permian volcanics
Cargen Pow	Nith 6, 7	(Middle Nith) +Cargen Pow	1218	985	85% Lower Palaeozoic seds, 5% Carb lst (sst), 5% Permian sst, 5% Permian volcanics
ESK					
Upper Esk	Esk 1, 2	Unitary	282	286	99% Lower Palaeozoic seds.
Ewes Water	Ewes Water 1	Unitary	75	111	90% Lower Palaeozoic seds, 10% Carb ssts and volcanics
Liddell	Liddell 1, 2	Unitary	300	357	75% Carb lst (sst), 20% Lower Palaeozoic seds, 5% Carb volcanics
Middle Esk	Esk 3	Ewes Water + Middle Esk	477	525	80% Lower Palaeozoic seds, 15% Carb lst (sst), 5% Carb volcanics,
Lower Liddell	Esk 4, 5	(Middle Esk) + Liddell + Lower Liddell	822	916	70% Lower Palaeozoic seds, 15% Carb lst (sst), 5% Carb volcanics,5% Westphalian,5% Sherwood sst.
Lower Esk	Esk 6	(Lower Liddell) + Lower Esk	1154	1135	40% Lower Palaeozoic seds, 40% Carb lst (sst), 10% Sherwood sst, 5% Westphalian, 5% Carb volcanics
WAVER					
Waver	Waver 1	Unitary	95	52	25% Mercia mdst, 25% Sherwood sst, 25% Westphalian, 15% Namurian, 5% Carb lst, 5% Permian sst
ELLEN					
Ellen	Ellen 1	Unitary	97	36	up to 25% each Volcanics, Slates, Carb lst, Namurian, Westphalian.
EDEN					
Upper Eden	Eden 3, 4	Unitary	1345	706	35% Permian, 30% Carb lst, 30% Volcanics, 5% others
Irthing	Irthing 1	Unitary	315	234	70% Carb lst, 20% Sherwood sst, 10% Namurian
Petteril	Petteril 1	Unitary	128	42	40% Namurian, 20% Carb lst, 20% Westphalian, 20% Permian
Caldew	Caldew 1	Unitary	224	123	up to 20% each Volcanics, Slates, Carb lst, Namurian, Westphalian, Permian
Middle Eden	Eden 1, 2	Upper Eden + Irthing + Petteril + Caldew+ Middle Eden	2256	1108	25% Carb lst, 20% Namurian, 25% Sherwood sst, 20% Borrowdale volcs, 5% Skid slates, 5% Mercia mdst.
Lower Eden	Eden 5, 6	(Middle Eden) + Lower Eden	2309	1135	20% Carb lst, 20% Namurian, 30% Sherwood sst, 15% Borrowdale volcs, 5% Skid slates, 10% Mercia mdst.
WYRE					
Upper Wyre	Wyre 6	Unitary	270	234	50% Namurian, 25% Carb Lst, 25% Sherwood sst
Middle Wyre	Wyre 1-5	Upper Wyre + Middle Wyre	348	267	25% Carb lst, 25% Namurian, 25% Sherwood sst, 25% Mercia mdst.
Lower Wyre	Wyre 7 etc.	(Middle Wyre) + Lower Wyre	410	336	20% Carb lst, 25% Namurian, 25% Sherwood sst, 30% Mercia mdst.
RIBBLE					
Top Ribble	Ribble 1	Unitary	356	221	60% Carb Lst, 30% Namurian, 10% Palaeozoic slates
Hodder	Hodder 1	Unitary	264	267	50% Namurian, 50% Carb Lst (basinal)
Calder	Calder 1, 2	Unitary	316	193	60% Westphalian, 40% Namurian
Upper Ribble	Ribble 2	Top Ribble + Hodder + Calder + Upper Ribble	1068	800	35% Carb lst, 30% Namurian, 35% Westphalian
Middle Ribble	Ribble 7, 8	(Upper Ribble) + Middle Ribble	1289	923	30% Carb lst, 30% Namurian, 30% Westphalian, 10% Sherwood sst.
Upper Douglas	Douglas 2	Unitary	227	76	70% Westphalian, 20% Permo-Trias (mostly Sherwood sst), 10% Namurian
Lower Douglas	Douglas 1	Upper Douglas + Lower Douglas	424	145	40% Westphalian, 20% Sherwood sst, 20% Mercia Mudst, 20% Namurian
Lower Ribble	Ribble 3-6	(Middle Ribble) + (Lower Douglas) + Lower Ribble	1817	1068	25% Carb lst, 25% Namurian, 25% Westphalian, 20% Sherwood sst, 5% Mercia Mudst.
MERSEY					
Croal	Croal 1	Unitary	143	59	60% Westphalian, 40% Namurian
Irwell	Irwell 2	Unitary	168	61	50% Westphalian, 50% Namurian
Roch	Roch 1	Unitary	167	73	75% Westphalian, 25% Namurian
Tame	Tame 1	Unitary	144	61	60% Namurian, 30% Westphalian, 10% Permian
Etherow	Etherow 1	Unitary	145	122	90% Namurian, 10% Westphalian
Goyt	Goyt 1	Unitary	165	101	50% Namurian, 50% Westphalian
Upper Bollin	Bollin 2	Unitary	53	17	45% Namurian, 45% Sherwood sst, 5% Permian, 5% Mercia mdst
Bollin-Dean	Bollin 1	Upper Bollin + Bollin-Dean	272	86	40% Mercia mdst, 40% Sherwood sst, 10% Namurian, 10% Westphalian.
Weaver	Weaver 1	Unitary	1237	494	70% Mercia mdst, 10% Namurian, 10% Westphalian, 5% Sherwood sst, 5% Lias clay
Micker Brook	Micker Brook 1	Unitary	55	11	45% Westphalian, 45% Sherwood sst, 10% Permian
Lower Irwell	Irwell 1	Roch + Irwell + Lower Irwell	368	141	55% Westphalian, 40% Namurian, 5% Permian sst.
Mid Mersey	Mersey 1	Tame + Etherow + Goyt + Micker Brook + Mid Mersey	1231	314	35% Westphalian, 35% Namurian, 25% Sherwood sst, 5% Mercia mdst.
Main Mersey	Richmond Bank	Croal + (L. Irwell) + (Mid Mersey) + (Bollin-Dean) + Main Mersey	2866	739	35% Westphalian, 25% Namurian, 25% Sherwood sst, 10% Mercia Mudst., 5% Permian sst.
Lower Mersey	New Brighton 1	(Main Mersey) + Weaver + Lower Mersey	4102	1233	25% Westphalian, 20% Namurian, 25% Sherwood sst, 25% Mercia Mudst., 3% Permian sst, 2% Lias clay

	typical GBase samples from pristine areas of those lithologies
River signature:-	spidergram of the geochemistry of a major river sample collected in this project

Catchment sizes and the number of GBase samples in the catchment are given in Table 11.

4.5.1 Comparison of Catchment and Model Catchment Signatures

4.5.1.1 'Pristine' Basins

In catchments with little or no mineralisation, mining or industrialisation, Catchment and Model Catchment signatures show very close compatibility.

For the Nith (Solway) catchment there is a consistent tendency for the model signature to overestimate P, Ca, Mn and Sn and underestimate Zn, but the discrepancies are relatively small. The reasons for the variations are not clear, but probably relate to natural geochemical variation in the lithologies and the choice of samples used in the model (Table 11). Overall the match between Catchment and Model Catchment signatures is very good (Fig. 11).

Compatibility is also good for the Esk (Solway) system (Fig. 12), only the Upper and Middle Esk signatures showing a strong tendency for the model to overestimate values for several elements. The catchments of the Hodder and the topmost Ribble contain only minor Pb mineralisation and their catchment and model signatures also show good compatibility (Fig. 12), although Zn values (and to a lesser extent Pb) are relatively high in both catchment traces. This may be a function of chemically highly mobile Zn associated with the Pb mineralisation.

In the Eden (Solway) system, the Irthing and Petteril catchments contain only minor mineralisation and this is shown in the close comparison between the model and catchment traces (Fig. 13). Similarly, the Waver basin lacks mineralisation and the two signatures are very close (Fig. 13). Minor variations between the catchments reflect their different geological make up.

The Upper Wyre and Middle Wyre catchments are unaffected by mineralisation or major industry and the comparability of the model and catchment signatures reflects this, although the model signatures overestimate several elements, most notably Ca, Mn and Sn (Fig. 13) for reasons which are not clear. In the Lower Wyre region, development is concentrated around the estuary and the catchment itself is relatively free from industry. This is reflected in the close match between the signatures, only Ca in the model being significantly at variance (Fig. 13).

4.5.1.2 Mineralised Basins

The basins of the Eden, Caldew and Ellen demonstrate the effects of mineralisation and mining on catchment signatures. Each of these basins has an abundance mineral occurrences and historical small mines. For elements not associated with the mineralisation the match between catchment and model signatures is generally very good, but for Pb, Zn, As, and Ba in particular accompanied by Cu in the Ellen and Caldew, clear discrepancies are seen (Fig. 14) reflecting the type of mineralisation present.

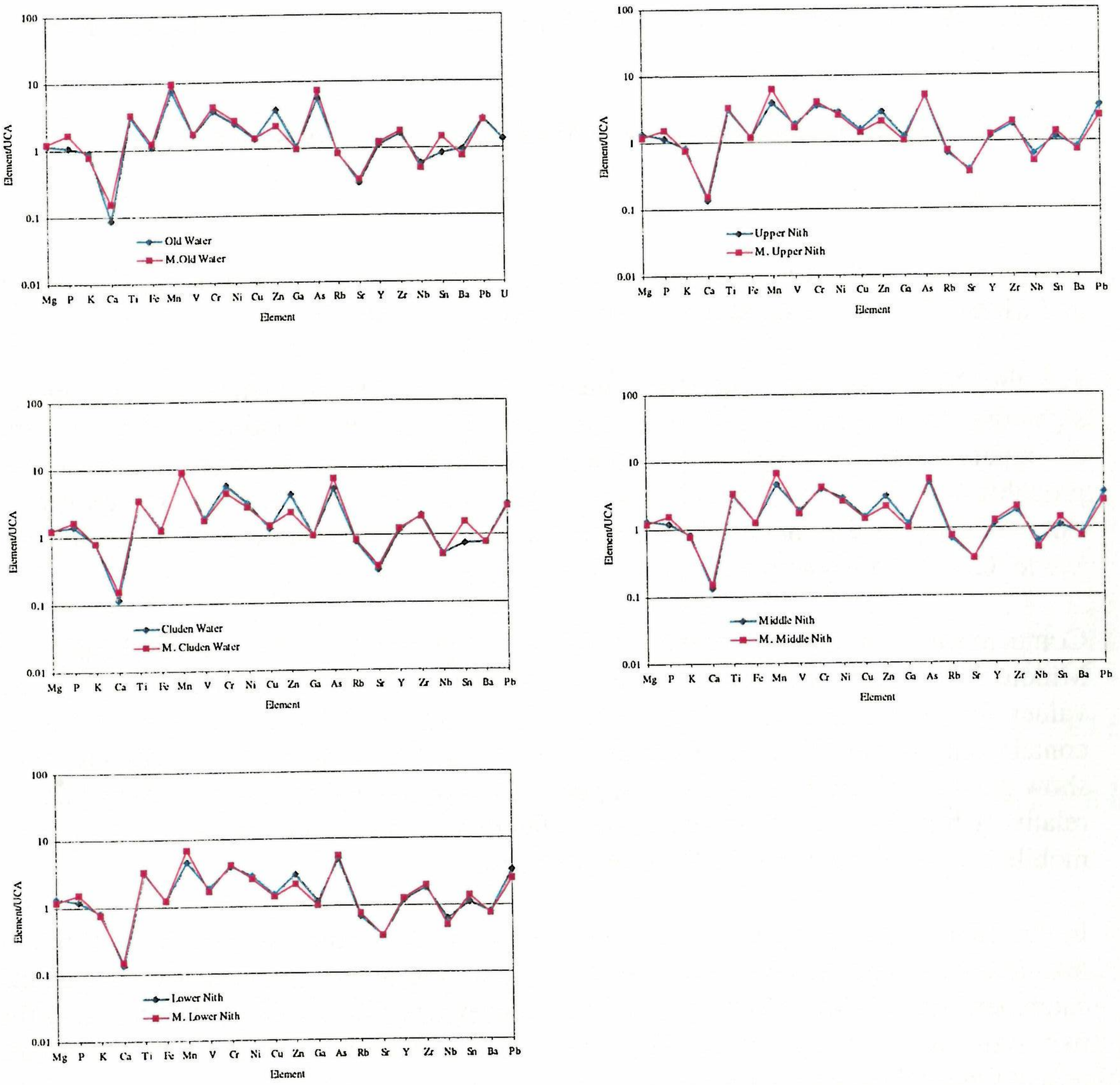

Figure 11. **Comparison of Ga normalised catchment and model catchment signatures for the 'pristine' Nith drainage basin. See text for further explanation.**

The use of model signatures thus has the potential to allow the effects of historical mining on a catchment to be assessed. Careful choice of model areas to include mineralised but un-mined catchments should provide a means to distinguish between natural metal levels from un-worked mineralisation and metals released into the environment as a result of mining activity.

4.5.1.3 Urbanised and Industrialised Basins

Parts of the Ribble and almost all of the Mersey catchment are affected by urbanisation and industrial development to some degree.

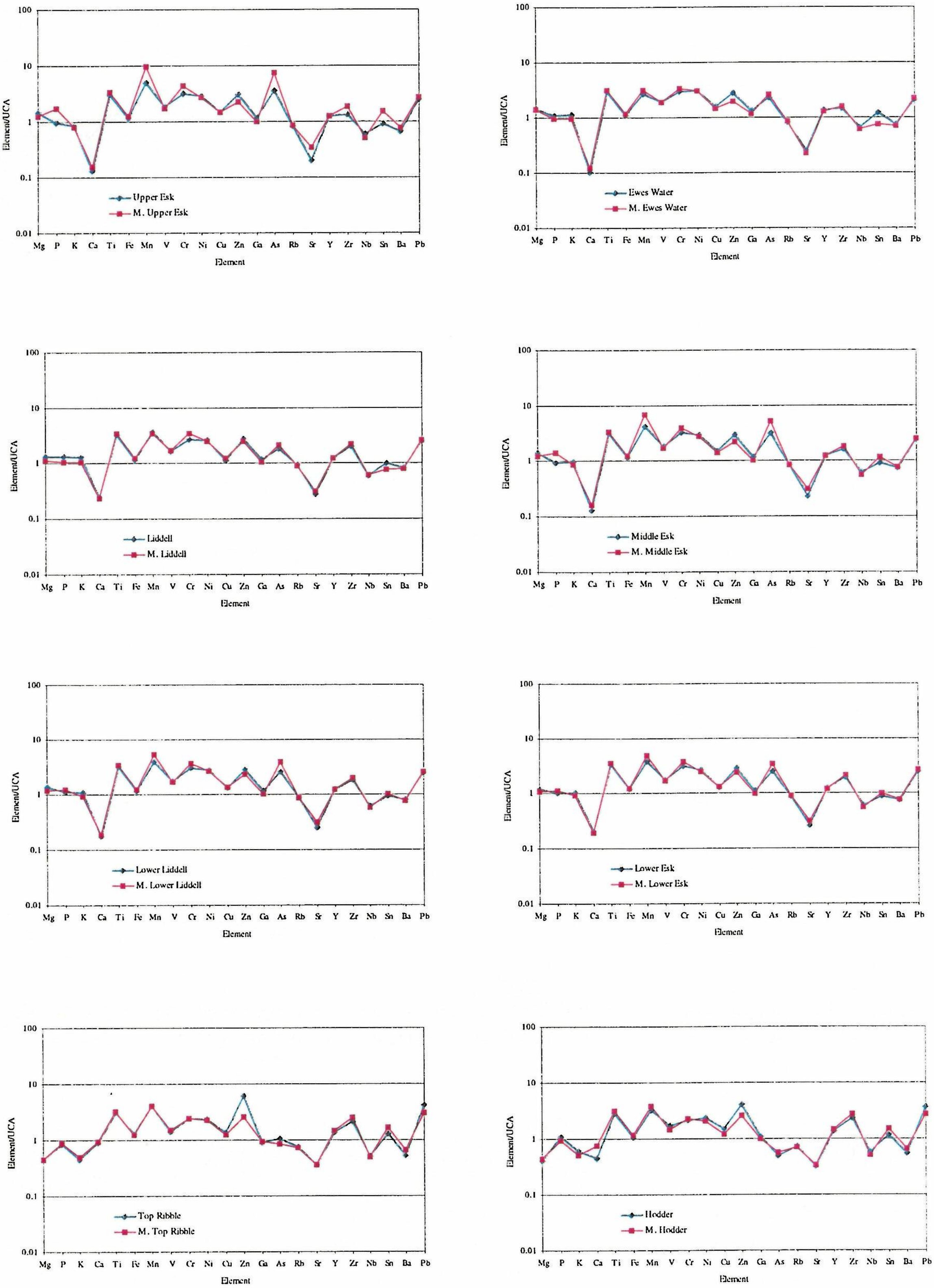

Figure 12. Comparison of Ga normalised catchment and model catchment signatures for the 'pristine' Esk, topmost Ribble and Hodder drainage basins. See text for further explanation.

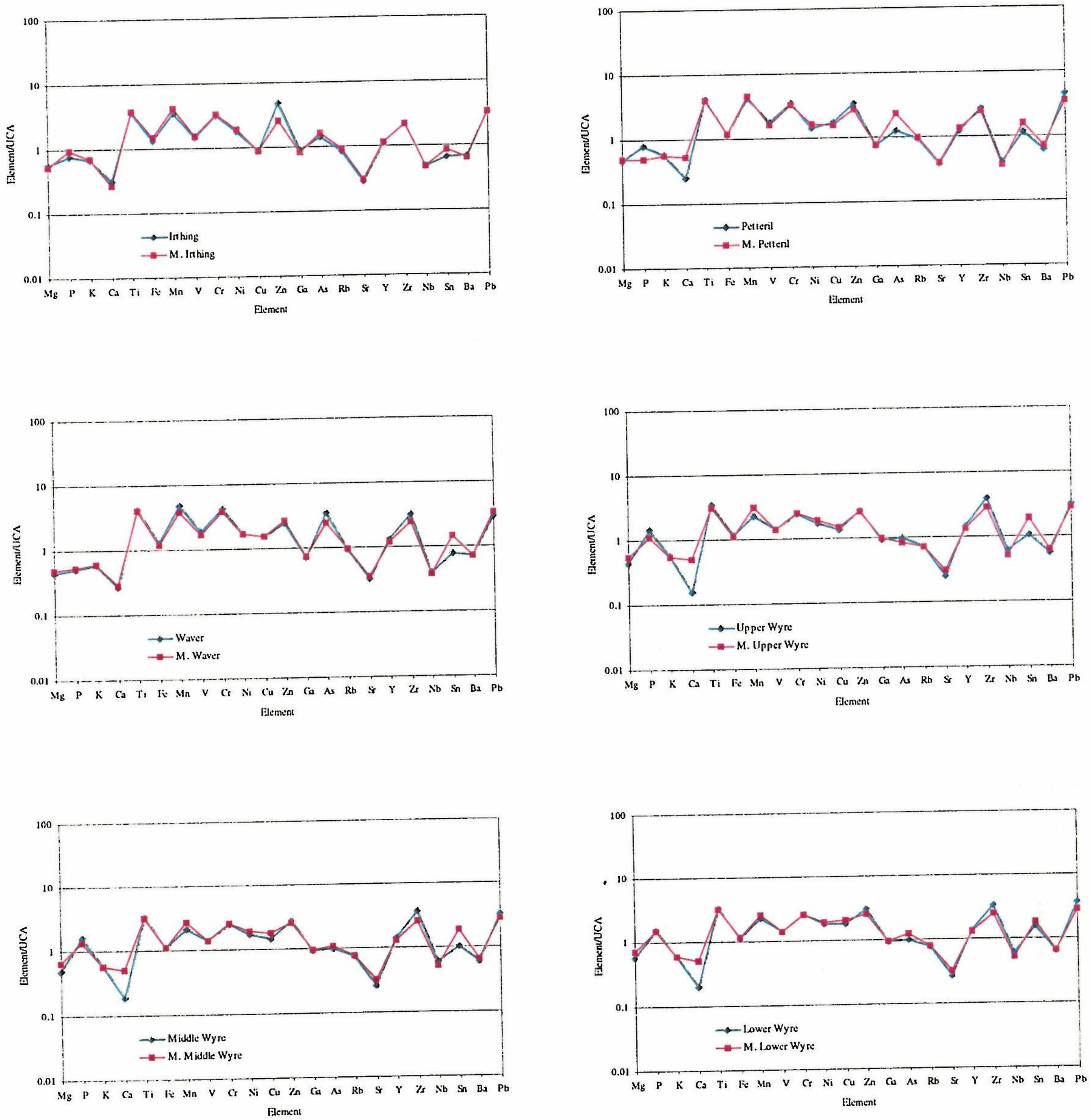

Figure 13. Comparison of Ga normalised catchment and model catchment signatures for the 'pristine' Ithing, Petteril, Waver and Wyre drainage basins. See text for further explanation.

In the Ribble basin, the River Calder drains the towns of Accrington, Burnley, Nelson and Colne with their associated industries. Comparison of model and catchment signatures for the Calder shows enhanced levels of Zn, Sn and possibly Ba in the latter, reflecting relatively low levels of urban and industrial contamination. The higher values for Cu and As in the model signature are puzzling, but can be taken to illustrate the natural geochemical-geological variation in the major lithological units which complicates the development of accurate model signatures in some areas (Fig. 15). This pattern is seen in all the Ribble catchments. The Upper Ribble catchment includes the Hodder and Calder as well as the higher reaches of the Ribble and its signature shows higher Zn and Pb in comparison with the model. Contamination from the Calder appears to have been diluted, but the relatively high Zn levels seen in the Topmost Ribble and Hodder (Fig. 12) are still in evidence (Fig. 15). The situation for the Middle Ribble catchment, which included Preston, is much the same (Fig. 15). The Douglas, which drains Wigan, shows evidence of catchment contamination in Zn, Sn and Pb (Fig. 15). The Lower Ribble, encompassing the whole of the Ribble system shows continuing Zn contamination, but lower levels of Pb and Sn (Fig. 15).

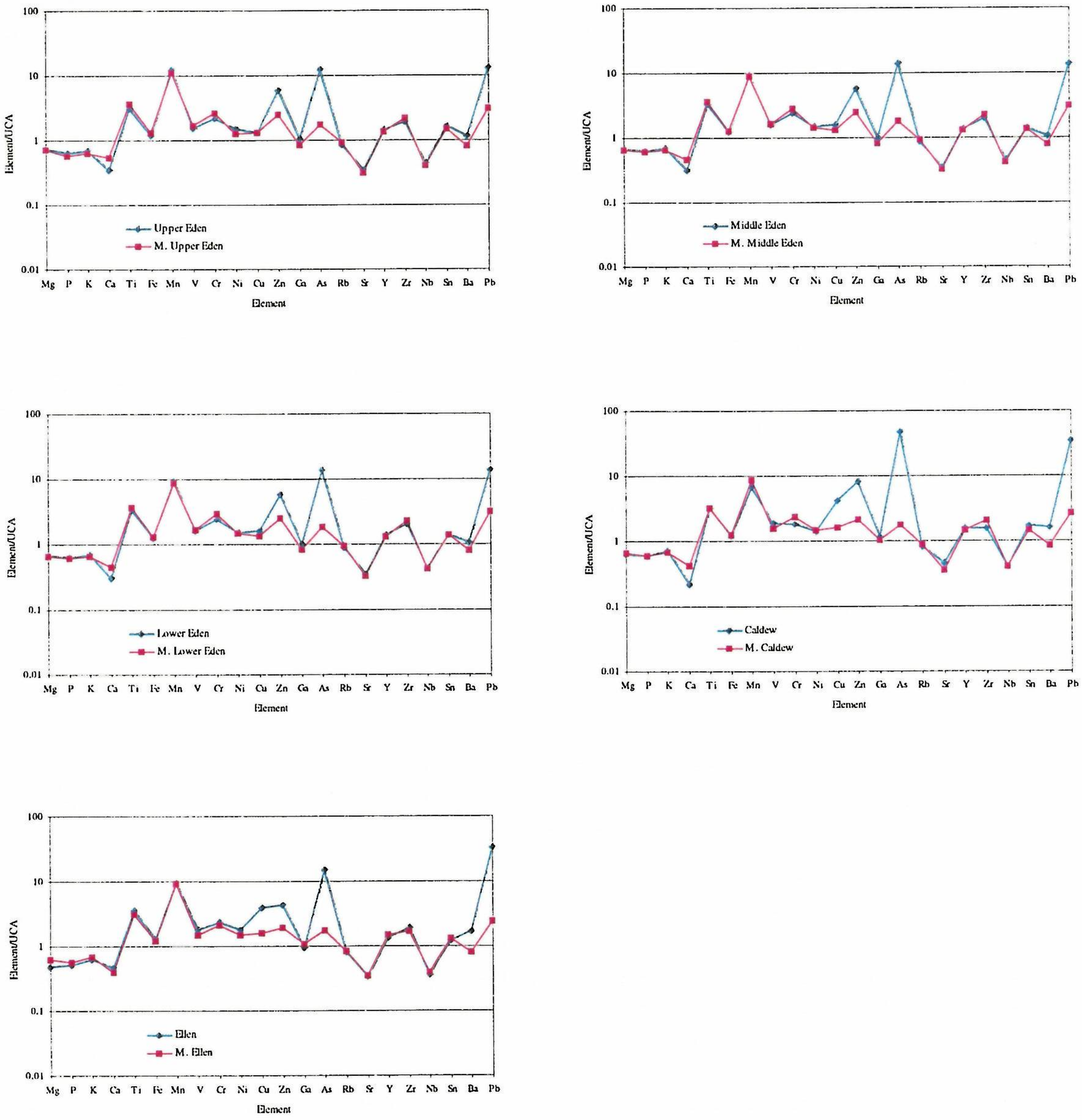

Figure 14. Comparison of Ga normalised catchment and model catchment signatures for the mineralised Upper, Middle and Lower Eden, Caldew and Ellen drainage basins. See text for further explanation.

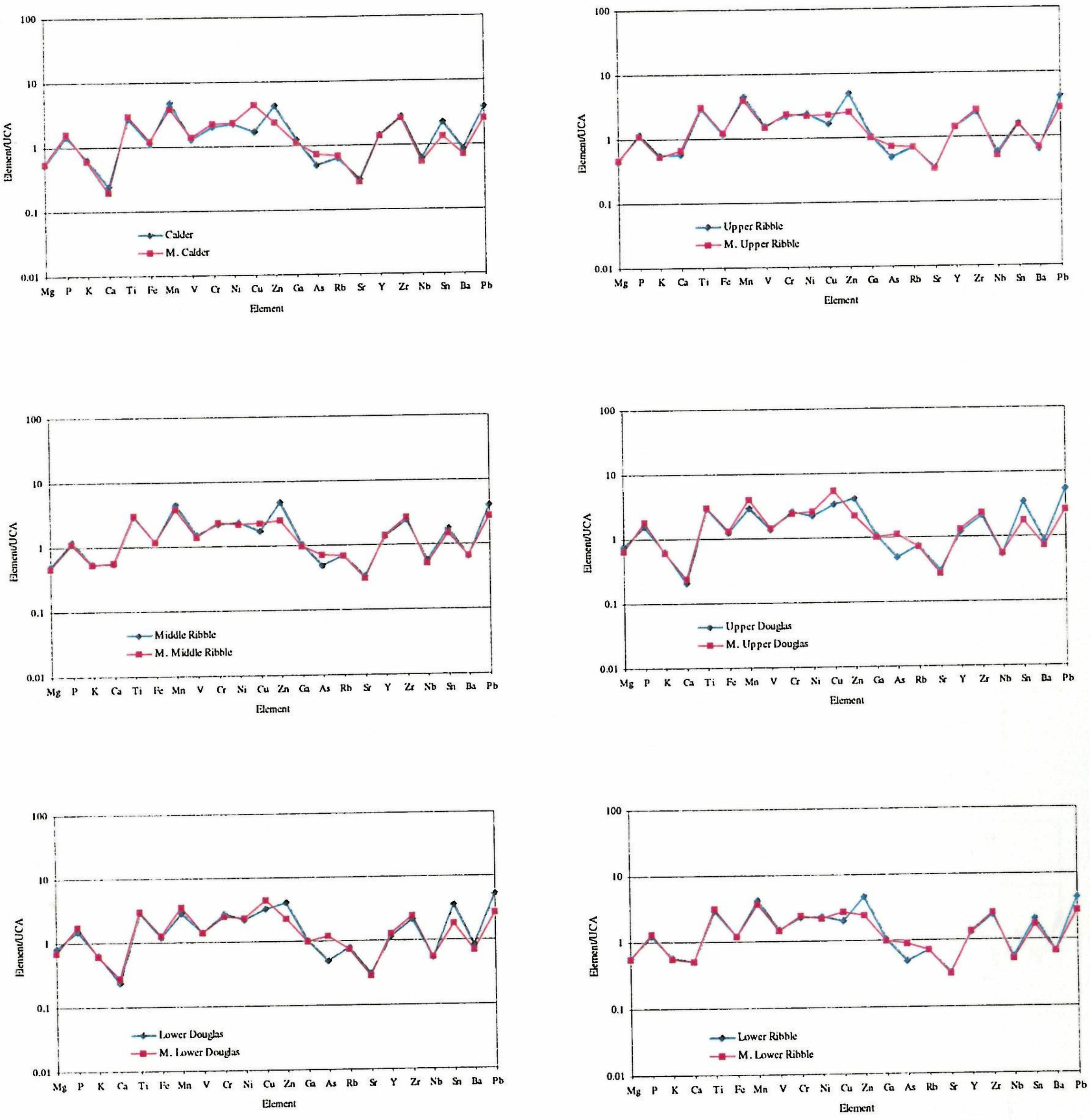

Figure 15. Comparison of Ga normalised catchment and model catchment signatures for the industrialised Calder, Douglas and Ribble drainage basins. See text for further explanation.

On the north side of Manchester, model and catchment signatures for the Croal, Roch and Irwell are very similar with Cu, As and Zr consistently higher in the models and evidence of catchment contamination in Zn, Sn and Pb (Fig. 16). To the south-east of Manchester, the Tame, Etherow and Goyt catchment and model traces are also similar to each other with the model consistently relatively high in Mn, Ni and Cu. In the Tame and Etherow Zn is also high in the model. There is some evidence of As and Pb contamination in all three catchments and of Sn in the Tame only (Fig. 16). Micker Brook, also to the south-east of Manchester shows evidence of catchment contamination in Mn, As and Sn with Cu again high in the model accompanied by Ba (Fig. 16).

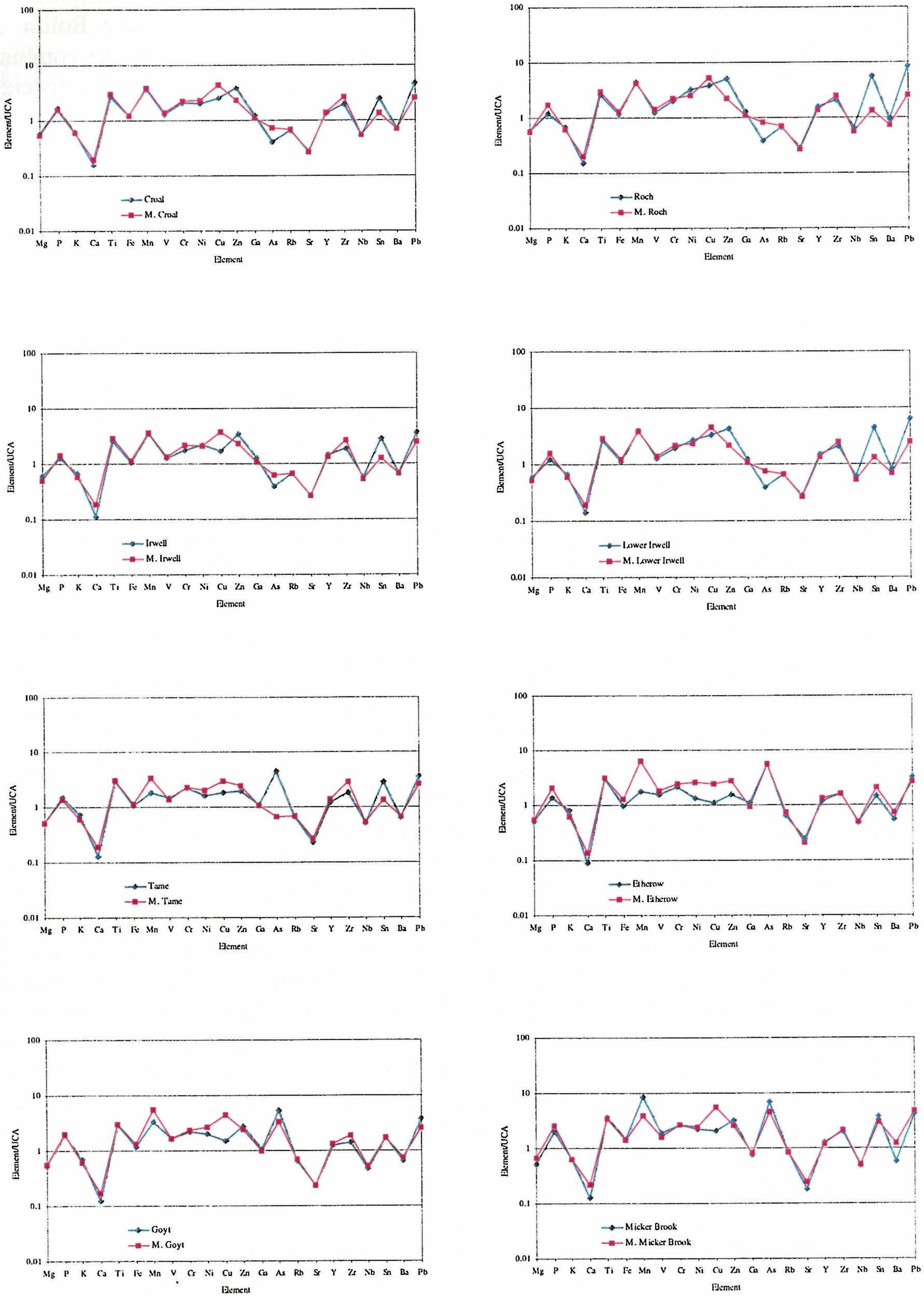

Figure 16. Comparison of Ga normalised catchment and model catchment signatures for the industrialised Croal, Roch, Irwell, Lower Irwell, Tame, Etherow, Goyt and Micker Brook drainage basins. See text for further explanation.

The Bollin and combined Bollin and Dean catchments on the south side of Manchester, largely draining urbanised, but non-industrial, Cheshire, display little sign of contamination. Catchment and model traces for the Upper Bollin are extremely close, very similar to those from 'pristine' catchments. For the combined catchment the model tends to be higher with Ti, Fe, V, Cr, Ni, Cu and Zn especially prominent (Fig. 17).

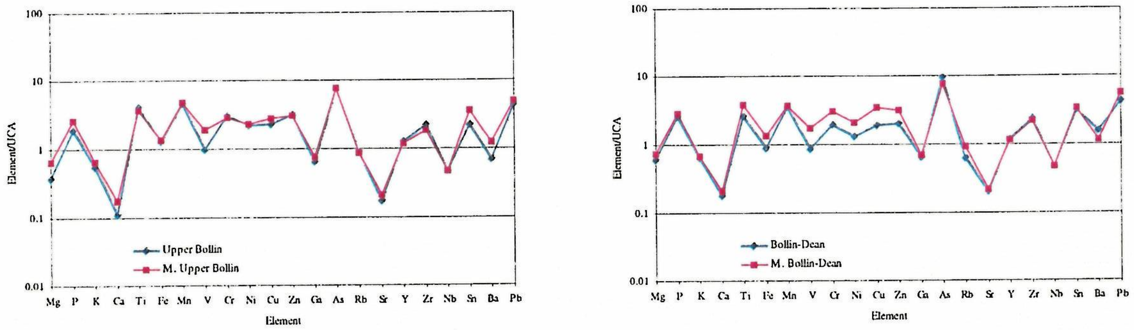

Figure 17. Comparison of Ga normalised catchment and model catchment signatures for the urbanised, but non-industrial, Bollin and Bollin-Dean drainage basins. See text for further explanation.

The Tame, Etherow, Goyt and Micker Brook combine to form the Mersey which, as the Middle Mersey catchment, shows a very similar relationship to its model signature: Mn, Ni, Cu and Zr, are higher in the model and As, Sn and Pb appear as contaminants (Fig. 18). The Main Mersey catchment incorporates the whole of the Manchester conurbation and also takes in Warrington. All of the river catchments in the Manchester area discussed above are included. The catchment signature shows evidence of contamination in Zn, As, Sn and Pb, whilst the model trace again is notably higher in Cu and Zr (Fig. 18). The River Weaver enters into the Mersey Estuary immediately south of Runcorn and drains a mainly rural region with small market towns, but which includes the industrial town of Crewe. The catchment signature indicates contamination in P, Mn, As, Sn, Ba and Pb in comparison with the model, which shows high Cr (Fig. 18). When the whole of the Mersey catchment, including streams draining directly into the estuary, is considered, there is surprisingly little evidence of large scale contamination in the catchment signature. Phosphorous, Zn, As, Sn and Pb are all higher in the catchment trace, whilst the model signature is slightly enhanced in Cr, Cu and Zr (Fig. 18).

4.5.1.4 Summary

Comparison of catchment and model signatures potentially provides a useful method for assessing the contribution of contamination in small streams to overall catchment geochemistry so that even in areas of known contamination major river sediment chemistry can be compared with a natural background. The modelled signatures were produced taking into account the characteristic lithology of the dominant geological units in the catchments as far as possible. Thus the Lower Carboniferous in the Esk catchment is predominantly sandstone, while in the Top Ribble it is mainly limestone,

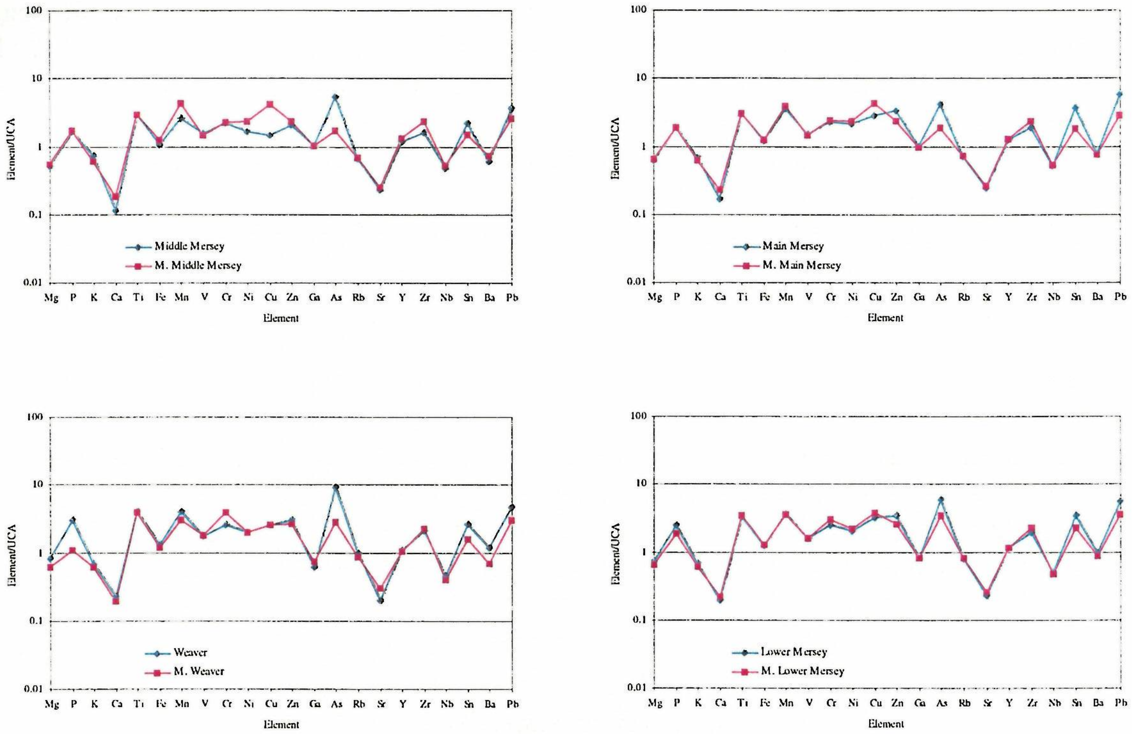

Figure 18. Comparison of Ga normalised catchment and model catchment signatures for the largely industrialised catchments of the lower parts of the Mersey drainage basin. See text for further explanation.

and in the Hodder the sequence is dominated by deep-water mudstones and black shales. At the catchment level this style of modelling usually works well, but there is always the possibility that rock units with a distinct geochemical character, though comprising only a small part of the total outcrop area, may have a strong local influence on the catchment signature.

The methodology clearly works well in pristine basins where the selection of samples for inclusion in the model presents no problems. In mined, urban and industrial areas the choice of samples for the model can be more difficult: in particular, samples from uncontaminated sites might be few in number and the selection of a representative suite for different lithologies can be a problem. For example, finding an uncontaminated catchment on which to base the modelled signature of the Coal Measures (Westphalian) is especially difficult since they are almost all heavily urbanised and industrialised to a greater or lesser degree, with resultant contamination problems. Thus for some drainage basins model signatures have higher element concentrations than the catchment signature, throwing doubt on the validity of the whole of the model signature. However, it should be possible to overcome these difficulties through a more rigorous and extensive exercise to establish the representative geochemistry of the major geological units than was possible within this project. Such an exercise could also establish background levels for mineralised, but un-mined, areas to allow the impact of historical mining to be calculated and distinguished from industrial contamination.

Overall, the most striking differences between model and catchment signatures are in mineralised, non-industrialised drainage basins where the effects of small scale mining in the upper reaches of drainage systems are clearly seen (Fig. 14). In industrialised basins the situation is more complex and to be confident of not overestimating natural background levels it can be argued that the lower of the model or catchment values should be used as the representative background concentration.

4.5.2 Comparison of Catchment and River Sediment Signatures

4.5.2.1 Solway Firth

Nith

The Nith drains into the Solway Firth on the north side, south of the town of Dumfries. Several small Pb mines occur in the headwaters region, but apart from these and Dumfries itself there are few sources of contamination. Figure 19 shows the drainage basins, geology, GBase and river sample sites, town and mine locations.

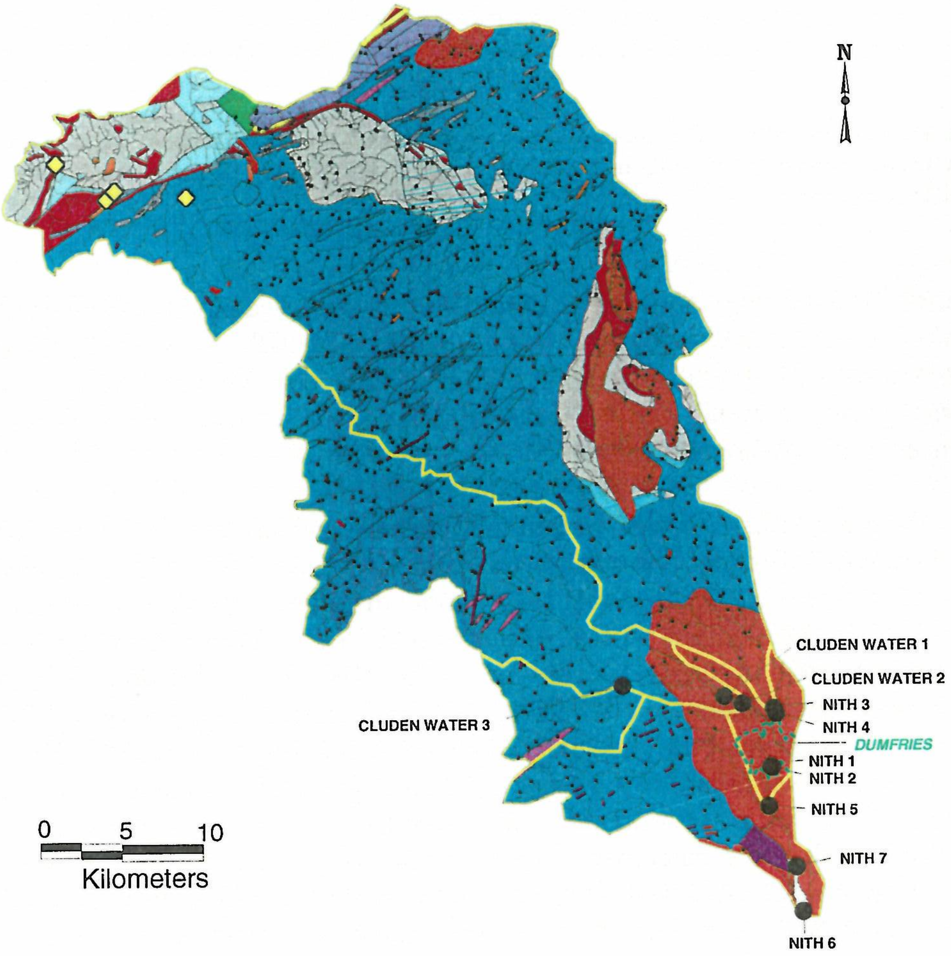

Figure 19. Geology, drainage basins, sample sites, urban areas, mines and mineralisation for the Nith basin. For key see Figure 20. See text for further explanation.

KEY

●	MAJOR RIVER SAMPLE SITE
◇	MINE OR MINERAL LOCATION
·	G-BASE SAMPLE SITE
—	BOUNDARY OF GEOLOGICAL UNIT
☐	CATCHMENT BOUNDARY
⬚	URBAN AREA WITH *NAME*
🟨	JURASSIC (Lias)
▨	TRIASSIC (Mercia Mudstone)
🟧	TRIASSIC (Sherwood Sandstone)
🟥	PERMIAN (Sandstone and Marls)
⬜	WESTPHALIAN (Coal Measures)
🟦	NAMURIAN (Millstone Grit)
🟦	DINANTIAN (Carboniferous Limestone)
🟩	CARBONIFEROUS (Undifferentiated)
🟥	ORDOVICIAN AND CARBONIFEROUS VOLCANICS
🟩	LOWER PALAEOZOIC SKIDDAW SLATES
⬛	LOWER PALAEOZOIC SLATES (Undifferentiated)
🟪	SCOT. LOWER PALAEOZOIC 2 (including small areas of Devonian)
🟦	SCOT. LOWER PALAEOZOIC 1 (including small areas of Devonian)

Simplified key for rock units used in this study

Figure 20. General key for study drainage basin maps.

River sample Cluden Water 3 was taken just above the confluence of Old Water with Cluden Water (Fig. 19). The catchment is the smallest of the Nith basins (35 km^2) and expected to be the least contaminated. As noted above, catchment and model signatures are closely matched, although P, Ca, Mn, Zn and Sn show some deviation in detail (Fig. 11). Catchment and river signatures also are close over most of their length (Fig. 21). Slightly elevated concentrations of As, Ba and Pb in the catchment signature may be related to low level mineralisation. Higher values of Ti and Mn in the catchment signature and elevated Cr and Sn in the river sample probably reflect the winnowing out of fine-grained micas and concentration of a heavy mineral fraction in the river sediment.

Cluden Water 1 and Cluden Water 2 were taken above the confluence of Cluden Water with the Nith and represent the whole of the Cluden Water catchment (206 km^2), including Old Water. Catchment and model signatures show a slightly better match than described above for Old Water (Fig. 11). Cluden Water 1, collected slightly upstream of an old ford presents a fine example of local contamination. Small pieces of copper wire were noticeable in the sediment and the ford must have been a site of illegal rubbish dumping. High levels of contamination, particularly Cu, but also Pb, Cr, Zn, Sn and Ni are evident in the river signature (Fig. 21). Cluden Water 2 from upstream of Cluden Water 1, has slightly elevated Cu which can be attributed to contamination, but the high Cr and Sn may have the same explanation as advanced above for a similar pattern of variation between river and catchment signatures at Cluden Water 3 (Fig. 21).

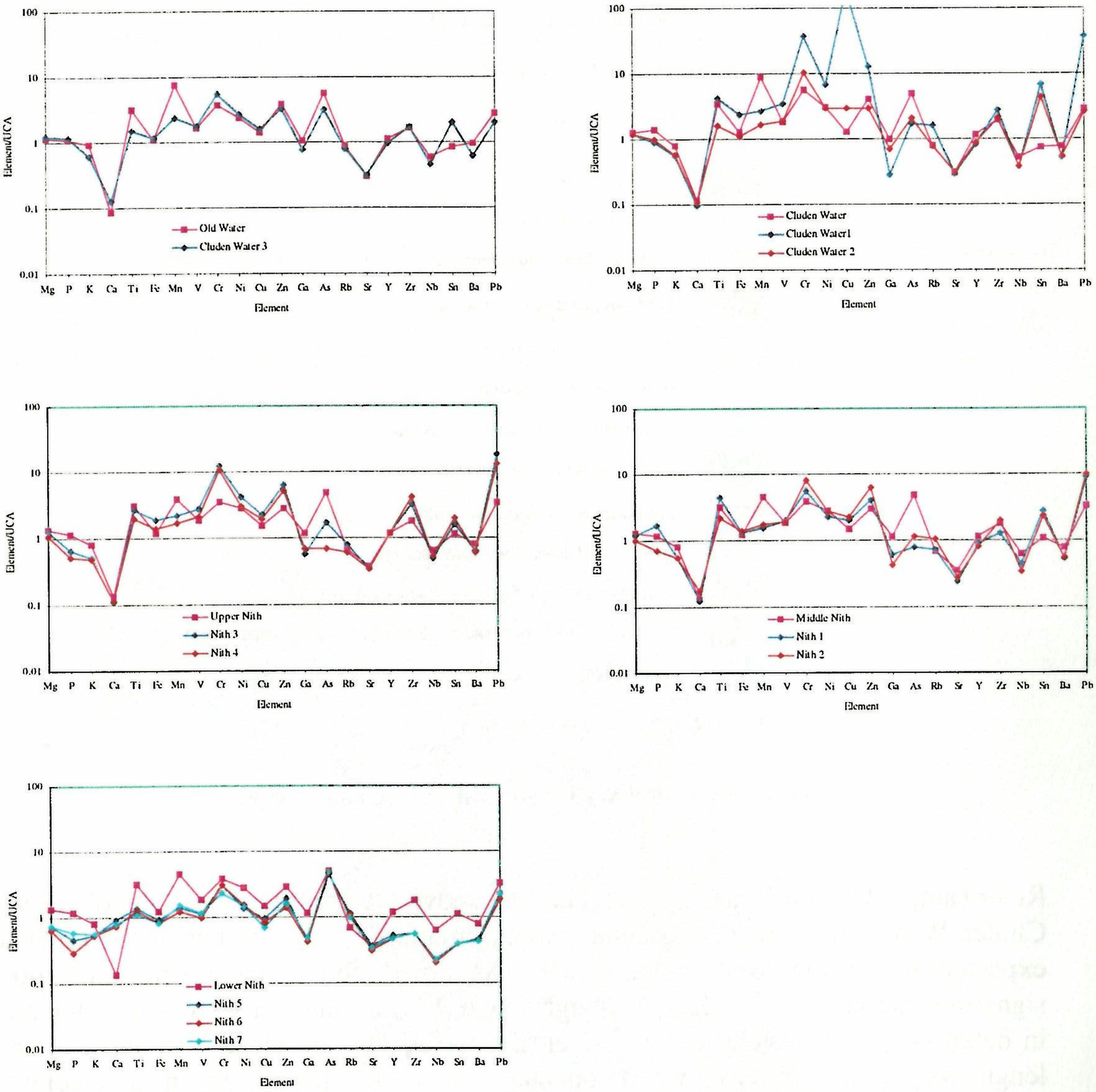

Figure 21. Comparison of Ga normalised catchment and representative river sediment sample signatures for the Nith drainage basin. See text for further explanation.

Nith 3 and 4 represent the Upper Nith basin (856 km^2), whose catchment and model signatures are closely aligned (Fig. 11). The river signatures, however, show significant variation from that of the catchment. Enhanced levels of Cr, Zr and Sn in the river chemistry could be related to heavy mineral accumulations but the higher levels of Pb and Zn are most likely linked to the location of two small Pb mines in the headwaters region of the catchment (Fig. 19 and Fig. 21).

Just downstream of Dumfries model and catchment signatures for the Middle Nith, which incorporates the Upper Nith and the whole Cluden Water basin (1124 km^2)

show a close relationship (Fig. 11). The river signatures of Nith 1 and 2 display variations akin to those seen in Nith 3 and 4, but the differences are generally smaller with Zr ceasing to be anomalous (Fig. 21). The similarity of the overall pattern of variation to that seen for Nith 3 and 4 suggests that the high Pb and Zn are still related to mining inputs and that contamination from Dumfries itself is minimal.

Some 3 km further downstream in the tidal estuary, the model and catchment signatures for the whole of the Nith system (1218 km^2) , including the tributary of Cargen Pow are again closely matched (Fig. 11). In contrast, the signatures for the estuarine sediments of Nith 5-7 are generally much lower, with only Ca being higher than in the catchment signature (Fig. 21). The Ca enrichment may be due to a higher shell content in the estuarine material whilst dilution of the Nith catchment sediment by clean and well winnowed marine sands moving up estuary is the most probable explanation for the lower values of other elements.

The Nith catchment thus shows some evidence of mining related Pb and Zn moving into the estuary, but in the estuary itself dilution by marine sands has removed all sign of this contamination.

Esk

The features of the Esk drainage basin are depicted in Figure 22.

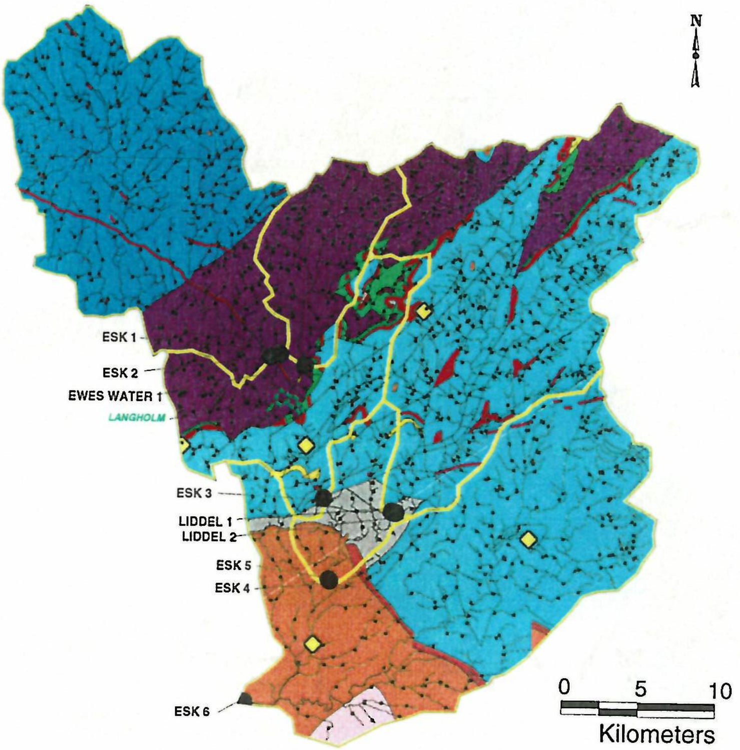

Figure 22: Geology, drainage basins, sample sites, urban areas, mines and mineralisation for the Esk basin. See Figure 20 for key.

The three headwater catchments in the Esk system: the Upper Esk (279 km^2), Ewes Water (75 km^2) and Liddell Water (300 km^2); have similar relationships between catchment and river signatures (Figs. 22 and 23). Catchment traces have relatively high levels of K, Ti and Fe, whilst river samples are typically enhanced in Cr and Sn. In the Ewes and Liddell Water samples, Zr is also high. Model signatures, especially for the Ewes Water and Liddell Water catchments are very similar to the catchment traces (Fig. 12). Again, the differences between river sediment and catchment signatures can be ascribed to winnowing of fine grained material from, and accumulation of heavy minerals in, the river sediment. The relatively large differences between Liddell Water 1 and 2 in Cr and Sn and Esk 1 and 2 in Sn supports this view, the slightly different sediment collection sites having accumulated heavy minerals to different degrees. The low Ga and As values in Liddell Water 1 and 2 might also be considered to back this explanation.

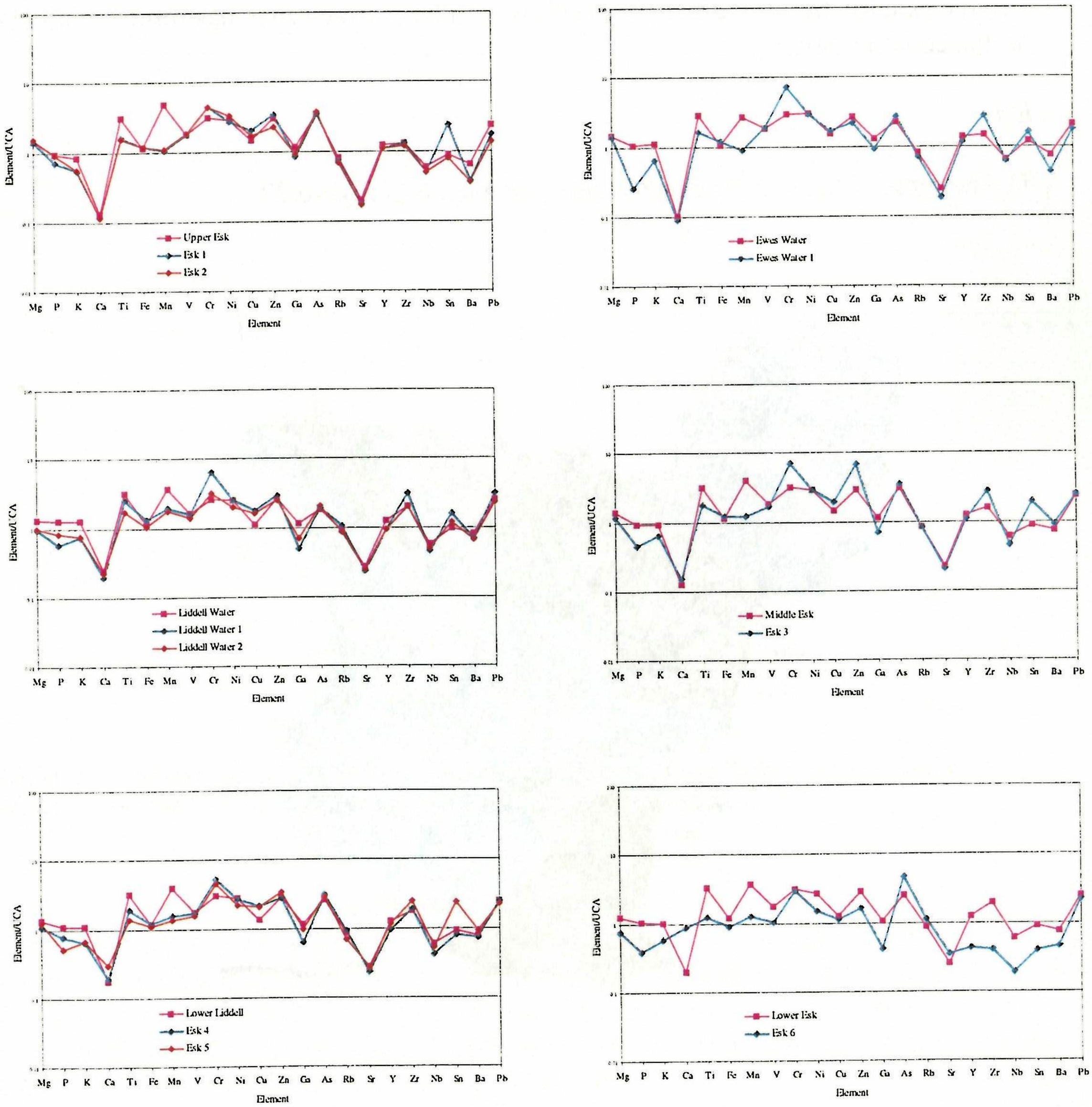

Figure 23. Comparison of Ga normalised catchment and representative river sediment sample signatures for the Esk drainage basin. See text for further explanation.

Sample Esk 3 and the Middle Esk catchment (477 km^2), which includes the Upper Esk and Ewes Water, display similar patterns of variation to those described in the preceding paragraph, but Esk 3 is also enriched in Zn relative to the catchment (Fig 23). The Zn could derive from the town of Langholm, which lies between Esk 1 and 2/Ewes Water 1 and Esk 3 or perhaps from mineralisation (mainly Pb) to the south of Langholm (Fig 22).

Esk 4 and 5 lie at the mouth of Lower Liddell basin (822 km^2), which includes all the Esk rivers described above and patterns of variation between river sediment and catchment signatures are very similar to those detailed above (Fig. 23)

Sample Esk 6, from the esturial Esk, is representative of the whole Esk catchment (Lower Esk, 1154 km^2) and shows the same relationship to the catchment signature (Fig. 23) as discussed above for the Nith estuary samples. Again the influx of marine sands into the estuary is indicated.

Eden

The distribution of catchments in the Eden basin and their geology is shown in Figure 24.

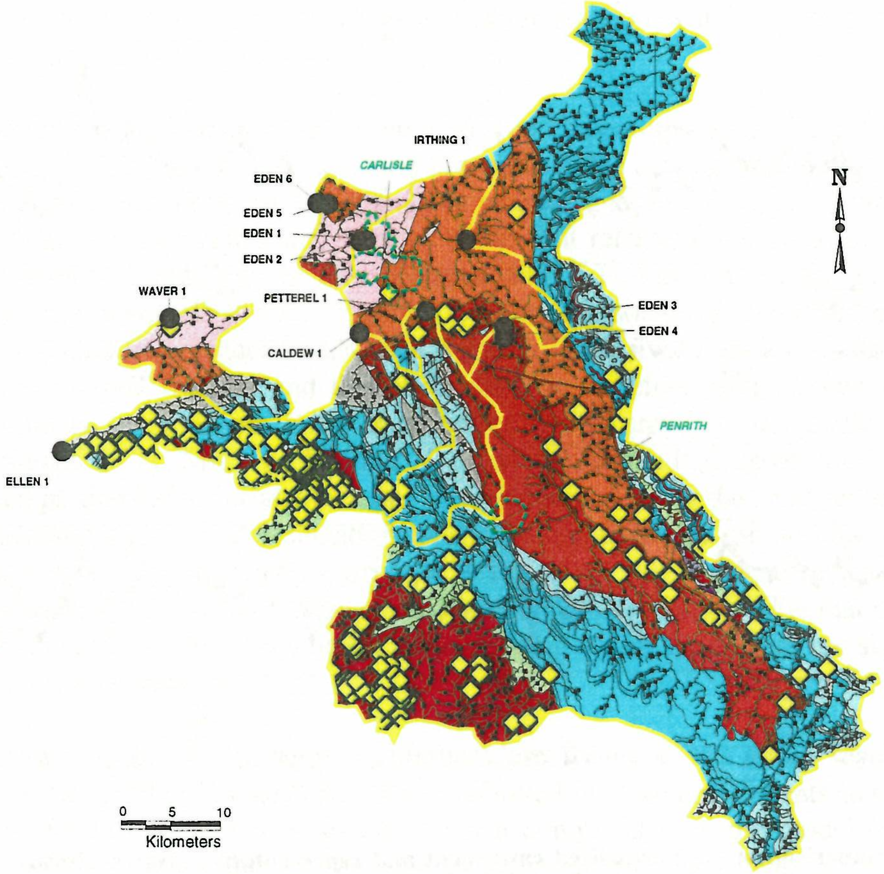

Figure 24: Geology, drainage basins, sample sites, urban areas, mines and mineralisation for the Eden, Ellen and Waver basins. See Figure 20 for key.

The traces of river sediment sample Irthing 1 and the Irthing catchment (315 km^2) show the same relationship that has been considered above to relate to the winnowing of fines and accumulation of heavy minerals in the river sediment. This is borne out by the closeness of the model and catchment signatures (Fig. 13) which show that Ti and Mn in the catchment are compatible with the levels expected from the model. Zinc, however, is higher in the catchment trace than in the model and could be related to agricultural activity. In addition, Irthing 1 is enriched in Cu, As, Rb and Mg, a feature which probably relates to agricultural practices in the catchment (Fig. 25 and 24).

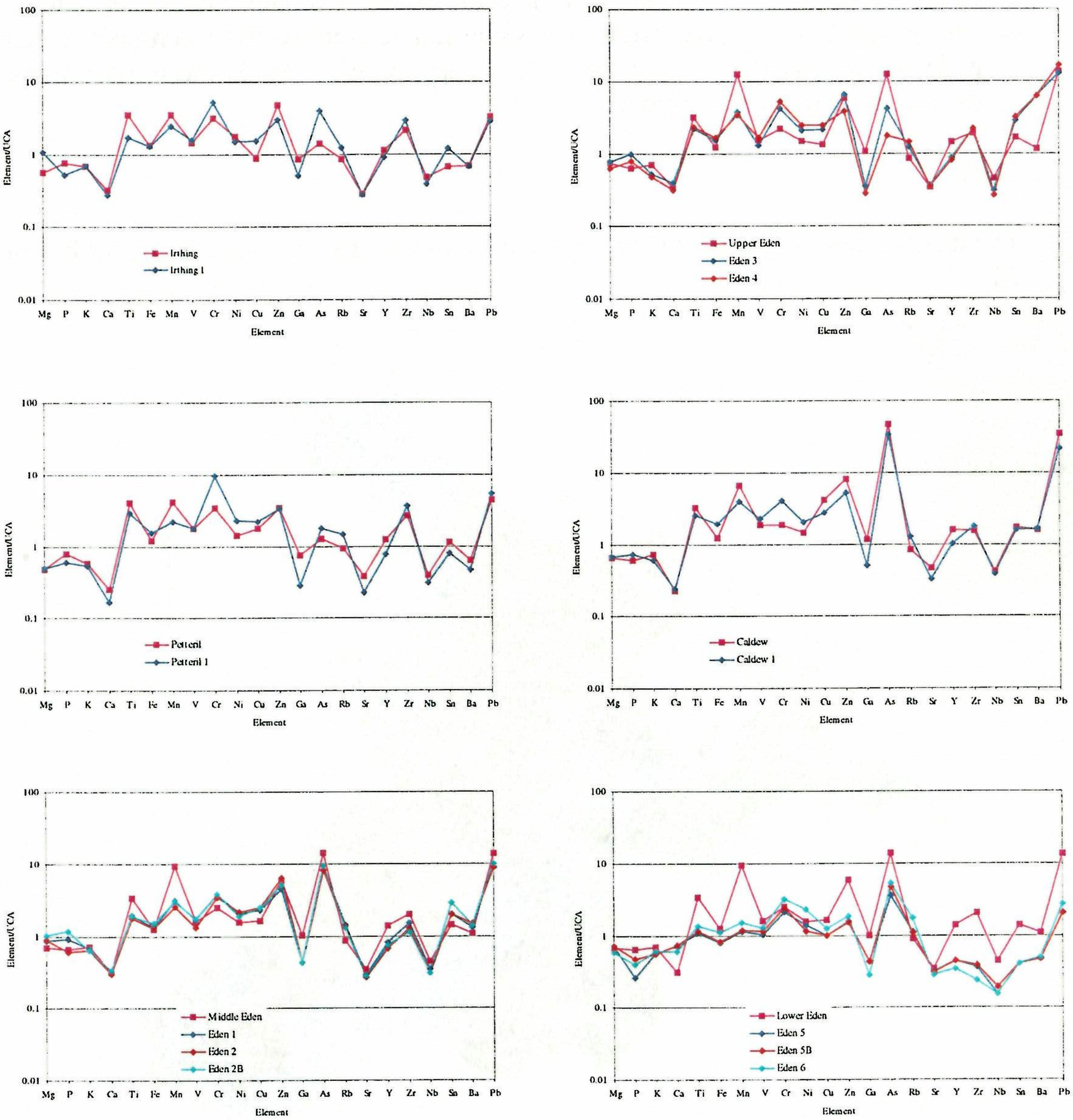

Figure 25. Comparison of Ga normalised catchment and representative river sediment sample signatures for the Eden drainage basin. See text for further explanation.

The catchment of the Upper Eden (1345 km^2) is the largest headwater basin studied and contains abundant mineralisation and small scale mine workings (Fig. 24). The relationships between model, catchment and river sediment (Eden 3 and 4) signatures are complex (Fig. 14 and 25) and are considered to reflect the mineralogical form of the elements released into streams and rivers from mineral workings. Manganese, is considerably higher in both the catchment and model traces than in the river sediment and thus may be present as a 'natural' oxy-hydroxide coating on clay minerals which have been winnowed out of the river sediment. This contention is supported by other elements which are often associated with fine-grained micas and clays (Ga, Fe, K, Y) also being relatively high in both model and catchment signatures with respect to river sediment. Arsenic is high in the catchment trace in comparison with both model and river signatures, implying that As has been released into streams from mining activity and quickly scavenged by Fe-Mn oxy-hydroxides onto clay particles, subsequently being winnowed from the sediments in the larger, fast flowing water courses. Chromium, Ni, Cu, are all enriched in the river sediment when compared with both the catchment and model. These elements are thus presumed to be either derived from mining activity in catchments larger than those sampled for the GBase programme, and/or concentrated in the heavy mineral fraction of the major river sediments. Tin and Ba are slightly enriched in the catchment signature with respect to the model, but highly enriched in river sediment in comparison with the catchment. They must be associated with mining, but also concentrated in the heavy mineral fraction of the river sediment. Zinc and Pb, however, both higher in the catchment than in the model signature and therefore related to mine working, are compatible in catchment and river sediment. They must occur in a mineral fraction which is not preferentially concentrated in the larger rivers.

The Petteril is a tributary of the Eden with a catchment upstream of the sampled site of 128 km^2. Only minor mineralisation is present in the catchment and this is reflected in the close match between model and catchment signatures (Fig. 13). Comparison of catchment and river signatures shows a significant relative enrichment of Cr, Ni, Rb and possibly Cu and Zr in the river sediment and of Ti, Mn, Ga, As, Sr, Y, Sn and Ba in the catchment (Fig. 25). Possible reasons for some of these differences are relatively easy to advance: the Cr, Ni, Cu and Zr in the river sediment could be held in a heavy mineral fraction and this explanation is therefore strengthened for similar enrichments in the Upper Eden as described in the previous paragraph; catchment enrichment in Ti, Mn, As, Ga and Y could be ascribed to association with fine-grained particulate material which has been winnowed out of the river sediment, again as discussed above. The explanation for differences in Rb, Sr, Sn and Ba, and also in P and Ca is more difficult to arrive at. Despite the use of regression equations to compensate for the use of different analytical techniques it is possible that some of the variation is purely due to analytical error. Judging which differences are significant is thus somewhat subjective.

Numerous mines and mineral occurrences are found in the upper reaches of the Caldew catchment (224 km^2) and this is reflected in large enrichments in Cu, Zn, As, Ba and Pb in the catchment signature when compared with the model (Fig 14). In general these enrichments are maintained, although at a lower level, when catchment is compared with river sediment (Fig. 25). The possible effects of heavy mineral accumulation in the river sediment are seen in Cr and Ni enhancements (see above) and also in the elimination of a Ba difference between catchment and river traces. Evidence of winnowing is seen in the relatively high levels of Mn, Ga and Y in the catchment signature and this mechanism might also have contributed to the maintenance of the Cu, Zn, As, and Pb enrichment (Fig. 25).

The Middle Eden catchment of 2256 km^2 includes the Irthing, Upper Eden, Petteril and Caldew basins. The influence of mining in the various catchments is seen in the high catchment to model ratios of Zn, As, Ba and Pb (Fig. 14). Samples Eden 1, 2 and Eden 2B, at the mouth of the catchment, were collected downstream of Carlisle and show similar relationships between river and catchment signatures as have been described above for other systems. Relatively high Ti, Mn, Ga, As and Y in the catchment trace probably represent the effects of winnowing on the river sediment, whilst higher Cr, Ni, Cu, Sn and Ba in the river sediment could be related to heavy mineral accumulation (Fig. 25). Given that this latter group of elements is also high in the Upper Eden river signature (Fig. 25), it would seem that little contamination is contributed to the Eden by industrial and urban development in Carlisle.

Both model and catchment signatures for the Lower Eden (2309 km^2) are virtually identical to those of the Middle Eden (Fig. 8:6 b and c, Fig. 8:17 e and f) and nothing can be added about their relationship to what has been said above. Samples Eden 5, 5B and 6 are all from the Eden estuary, Eden 6 being collected from approximately 1 km further seaward than Eden 5 and 5B. With the exception of Ca, and Cr, Ni and Rb in Eden 6 only, the signatures of the estuary samples are depleted in most of the elements considered. This taken to indicate that relatively clean marine sediments have moved into the estuary from further out in the Solway Firth, diluting the mining related anthropogenic contamination seen in the river sediments immediately below Carlisle.

Waver

The river Waver has a small catchment of 95m km^2 that is free of mineralisation (Fig. 24). This is reflected in the very close match between catchment and model signatures (Fig. 13). However, catchment and river signatures are relatively poorly matched (Fig. 26) with discrepancies which are not easily explained. High P in the river sediment could be agricultural contamination and but the high Sn is more difficult to account for since there is little urbanisation or other source of contamination in the catchment. Some of the catchment enrichments may relate to winnowing effects as described above for other catchments, but higher levels of Zr and Ba, in particular, are not normally amenable to such an explanation, being elements which commonly are associated with the heavy mineral fraction. Combined mineralogical and chemical examination of the sediments, would help solve the problem.

Ellen

The catchment of the Ellen (97 km^2) is almost the same size as that of the Waver but contains both mineral occurrences and old mine workings (Fig. 24). The effects of this are clearly shown in the differences between the model and catchment signatures with the latter displaying high values of Cu, Zn, As, Ba and Pb (Fig. 14). The differences between catchment and river signatures (Fig. 26) again present some problems because some elements appear to be associated with sediment fractions they would not normally be found in. The river sediment is high in P which, as with the Waver, could be related to agricultural contamination. Higher Mn, As, Y, Sr, Y, Zr, Ba and Pb in the catchment signature, accompanied by higher Ga, strongly suggests that these elements are all carried in the fine grained fraction, subject to winnowing from the river sediment. This explanation might thus apply also to the Zr and Ba in Waver basin. Higher Cr and Ni in the river sediment are presumed to be carried in a heavy mineral phase. Copper and Zn are at the same level in catchment and river traces and can be assumed to be in neither heavy mineral nor fine fractions.

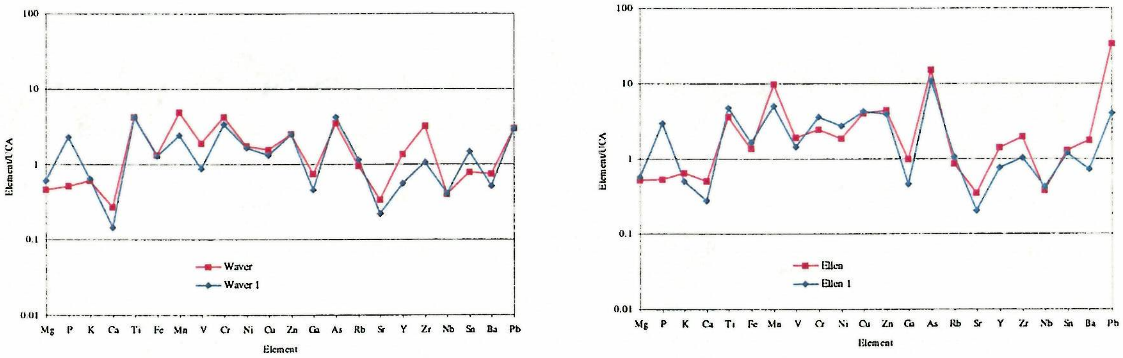

Figure 26. Comparison of Ga normalised catchment and representative river sediment sample signatures for the Waver and Ellen drainage basins. See text for further explanation.

4.5.2.2 Wyre

The Wyre catchment, shown in Figure 27, is unmineralised and the only significant industrial development is near the mouth.

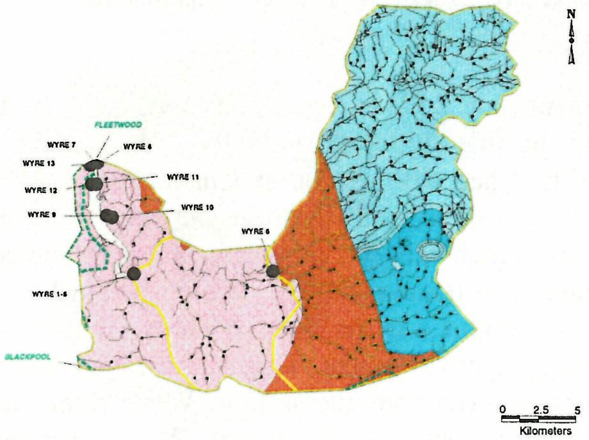

Figure 27: Geology, drainage basins, sample sites, urban areas, mines and mineralisation for the Wyre basin. See Figure 20 for key.

The model and catchment signatures for the Upper Wyre (270 km^2) are generally well matched (Fig. 13), although Ca, Mn and Sn are all enhanced in the model trace (As data are missing from the Wyre catchment dataset and have been set to 1 for plotting purposes). Despite the lack of mineralisation and development, the catchment and river signatures (Fig. 28) for the Upper Wyre are very different. Sample Wyre 6 was collected from just above a weir and it therefore seems likely that the mismatch is attributable to contamination associated with the building of the weir, most elements, with the notable exception of P, being higher in the river sediment.

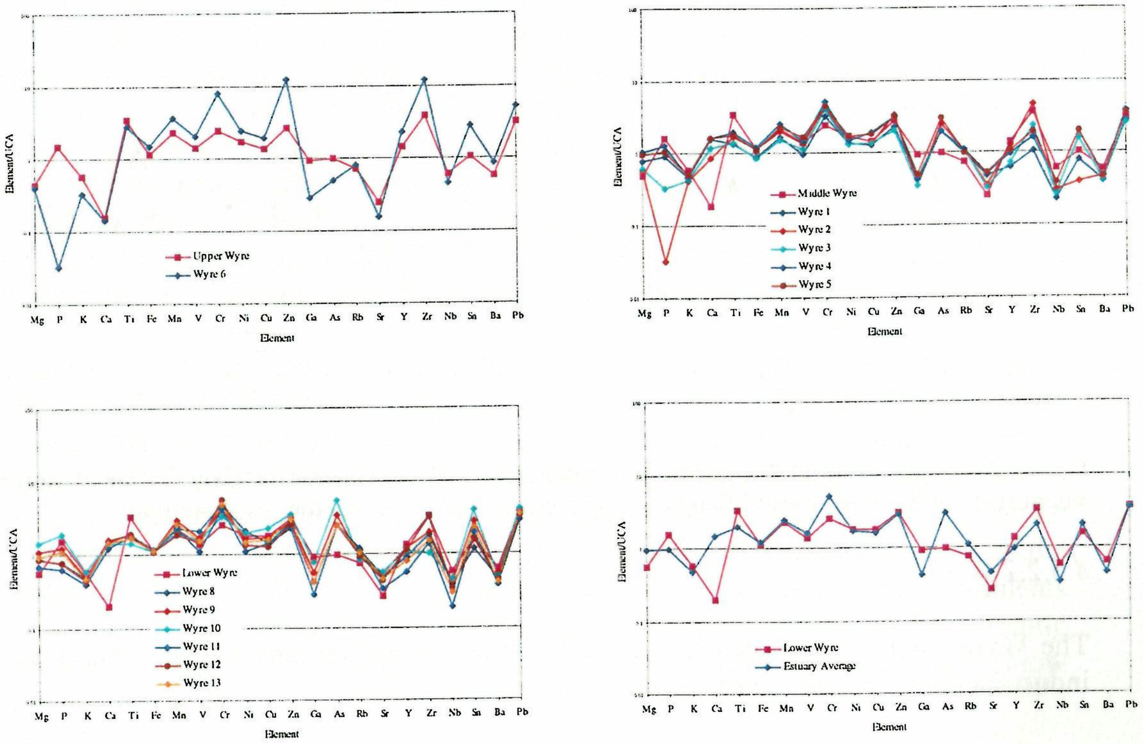

Figure 28. Comparison of Ga normalised catchment and representative river sediment sample signatures for the Wyre drainage basin. See text for further explanation.

The Middle Wyre catchment (348 km^2) is represented by 5 samples taken across the width of the river below the tidal limit. As with the Upper Wyre, catchment and model signatures are well matched with similar enhancements in the model (Fig 13). The 5 river samples show some significant variations between them, particularly in P, Zr, Sn and U, but overall the match between river and catchment looks good (Fig. 28). High Ti and Ga in the catchment trace again can perhaps be attributed to winnowing of the river sediment and the high Ca in the river probably represents shelly material present because of the estuarine environment. The catchment signatures of the Upper and Middle Wyre are very similar, but the middle Wyre river samples show no evidence of the contamination found in the Upper Wyre river sediment, except perhaps for higher Cr levels than in the catchment.

The Lower Wyre catchment (410 km^2) and model traces (Fig. 13) are closer than the comparable pairings for the higher reaches of the system whilst the catchment signatures of all three parts of the basin are very similar. Six estuarine samples (Fig. 27) represent the Lower Wyre sediments (Fig. 28) and as with the Middle Wyre a considerable spread in values for P, Zr and Sn is seen. The average trace for the estuary sediment (Fig. 28) shows high levels of Ca and Cr. The former most probably represents an increase in shelly material in the estuarine environment, whilst the latter could be contamination or due to a natural heavy mineral concentration. It is difficult to decide which is the most likely explanation: there are no known sources of Cr rich heavy minerals in the Wyre catchment, but neither are there any obvious sources of Cr contamination. Although Cr was present as a contaminant in the Upper Wyre river sediment other contaminants present in the Upper Wyre do not appear in the estuary. A contaminant source on the banks of the estuary is a possibility with tidal currents carrying the contamination upstream to the Middle Wyre sampling sites.

4.5.2.3 Ribble

Figure 29 shows the main features of the Ribble basin, with extensive urban and industrial development on the south eastern margin.

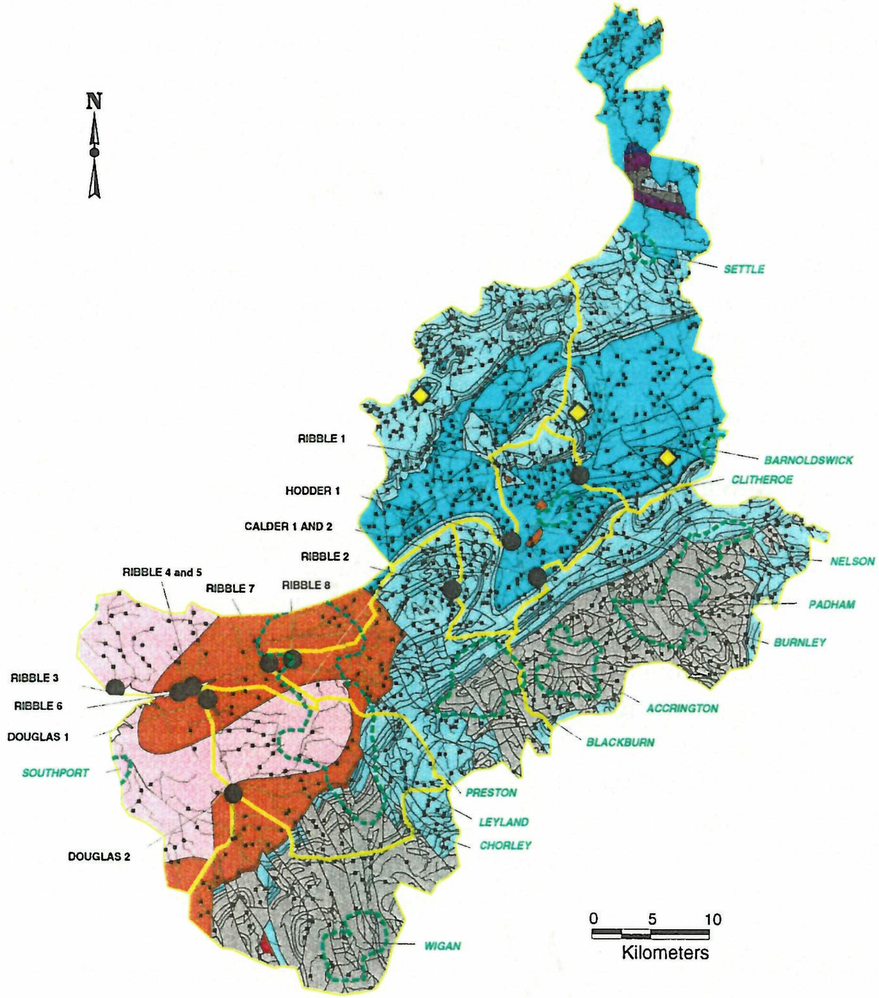

Figure 29. Geology, drainage basins, sample sites, urban areas, mines and mineralisation for the Ribble basin. See Figure 20 for key.

The uppermost part of the Ribble system, the Top Ribble basin, has an area of some 356 km^2 and contains little in the way of industry, mining or major urban development (Fig. 29). There are two small Pb mineral occurrences in the catchment and part of the town of Barnoldswick, with some industrial works, lies on the eastern watershed. Model and catchment signatures are closely matched, with the exception of Zn, which is higher in the catchment (Fig. 12) and could be related to the mineral occurrences, Zn being a mobile metal often associated with Pb mineralisation. It is thus surprising to find that the catchment and river signatures are very different, with the river sediment of Ribble 1 showing signs of significant contamination in Fe, Cr, Ni, Cu, Zn, As, Zr, Sn, Ba and Pb (Fig. 30). Major road and railway lines run close to the river over much of its course upstream of Ribble 1 and there are also several weirs above the site. A weir was considered to have been responsible for contamination in the Upper Wyre river sample and it is possible that building operations associated with the weirs and road and railway development have contributed to the high metal levels at Ribble 1. Resampling along a stretch of the river would help solve the problem.

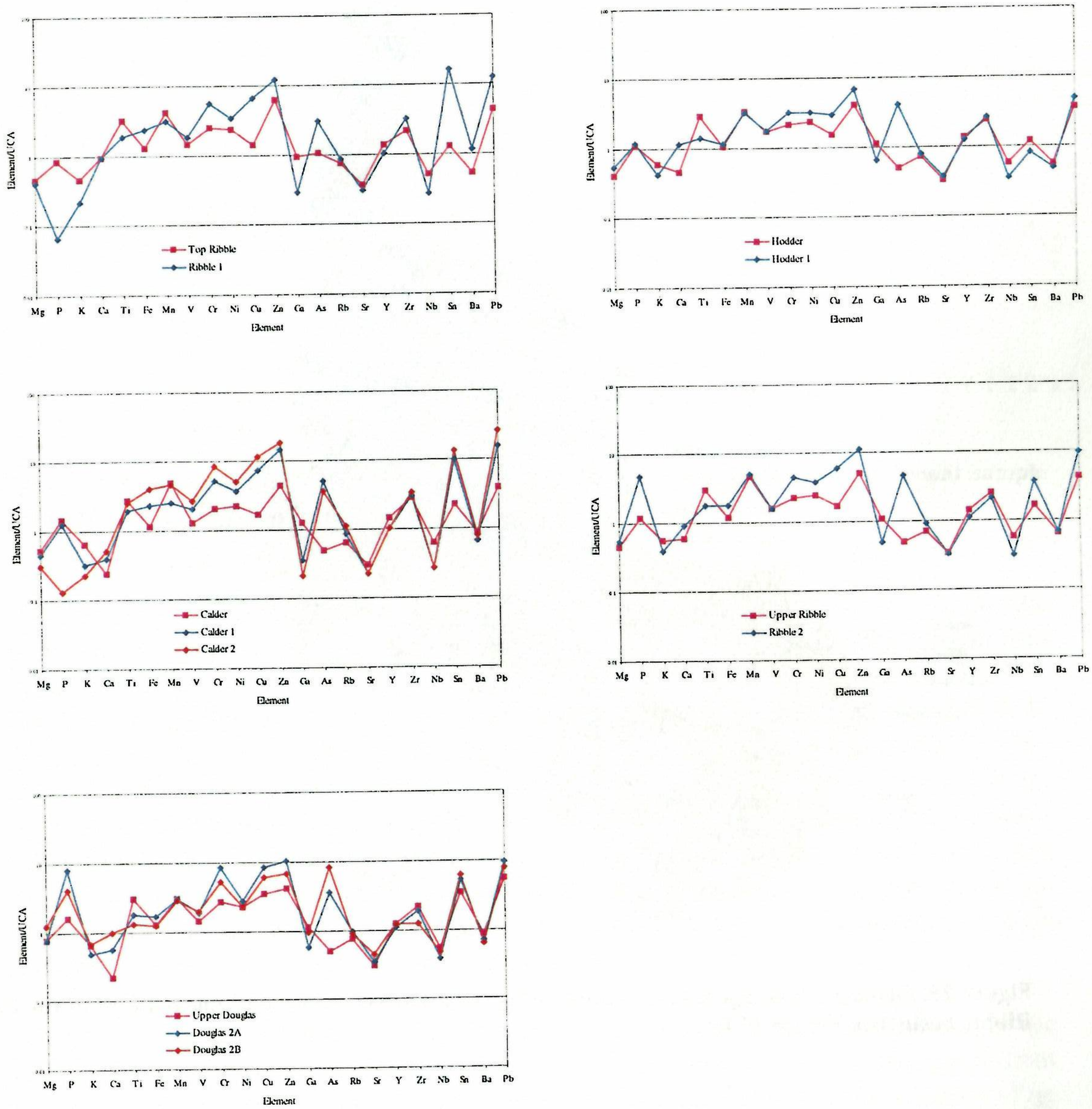

Figure 30. Comparison of Ga normalised catchment and representative river sediment sample signatures for the non-tidal parts of the Ribble drainage basin. See text for further explanation.

The River Hodder drains into the Ribble below Clitheroe and has a catchment of 264 km^2 (Fig. 29). There is no urban or industrial development in the catchment and only one Cu-Pb mineral occurrence. Model and catchment signatures are very similar with the slight elevation of Cu, Zn and Pb in the catchment trace probably reflecting the mineral occurrences (Fig. 12). There is unexpected evidence of Ca, Cr, Ni, Cu, Zn and As contamination in river sediment sample Hodder 1 (Fig. 30). All these elements have a possible association with agricultural activity, fertilisers and sewage sludge in particular (Reimann & Caritat, 1998), and in this predominantly rural area this is the most likely cause of their enrichment in the river sediment.

The River Calder also drains into the Ribble below Clitheroe, with a catchment area upstream of the sampling site of 316 km^2. The industrial towns of Nelson, Burnley, Padiham and Accrington lie within the catchment (Fig. 29) and although model and catchment signatures are very similar, with only slight evidence of Zn, Sn and Pb contamination in the catchment (Fig. 15), the river sediments of Calder 1 and 2 are heavily contaminated with Fe, V, Cr, Ni, Cu, Zn, As, Sn and Pb with an indication that Ca and Rb might also be contaminants (Fig. 30). Industry must be responsible for the bulk of this contamination.

Sample Ribble 2 is at the mouth of the Upper Ribble (1068 km^2) which includes all the above parts of the Ribble system plus the stretch of river between Clitheroe and Ribchester (Fig. 29). Model and catchment signatures are very closely matched, but with some evidence of catchment contamination in Zn and Pb (Fig. 15). The river sediment at Ribchester however (Ribble 2, Fig. 30), shows enrichment in P, Ca, Fe, Cr, Ni, Cu, Zn, As, Rb, Sn and Pb with respect to the catchment. Agricultural activity would seem the most likely reason for the high P levels, whilst V has been diluted to catchment levels. Other metals show the continued influence of industry, coupled with the agricultural and building inputs discussed above.

The River Douglas enters the tidal Ribble on the south bank approximately 10 km below Preston. The Upper Douglas basin (227 km^2) includes industrial Wigan, but also drains much agricultural land (Fig. 29). The catchment signature shows evidence of Zn, Sn and Pb contamination when compared with the model (Fig. 15), but the river sediment signatures of Douglas 2A and 2B indicate more severe contamination in P, Ca, V, Cr, Cu, Zn, As, Sn and Pb with respect to the catchment (Fig. 30). Douglas 2A is, in addition, enriched in Fe and Ni and both samples are relatively high in Sr. Contamination is of the same nature as that in the Calder and Upper Ribble and most probably stems from similar industrial, agricultural and building related sources.

The Middle Ribble catchment (1289 km^2) includes the Upper Ribble and also takes in the towns of Blackburn and Preston (Fig. 29). Model and catchment signatures are almost identical to those of the Upper Ribble (Fig. 15). Samples Ribble 7 and 8 were collected from the tidal river just below Preston and much of the contamination seen in the Upper Ribble has now disappeared (Fig. 31), only Ca, Cr, As and Rb remaining significantly higher in the river signature in comparison with the catchment and most elements showing signs of depletion. The reasons for this are not entirely clear. Whilst it is possible that Preston and Blackburn produce little contamination and that the Upper Ribble signature has been diluted by clean sediment entering the river, it is more likely that the action of strong tidal currents in this narrow part of the estuary has removed contaminants held in the finer-grained fractions.

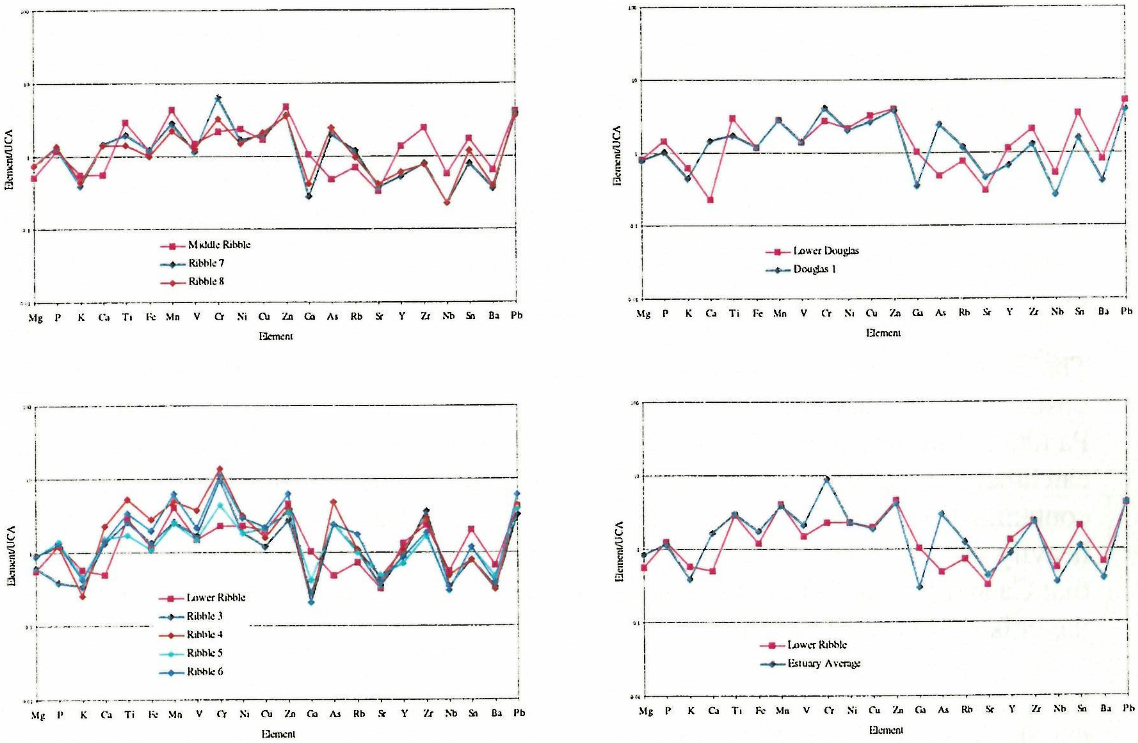

Figure 31. Comparison of Ga normalised catchment and representative river sediment sample signatures for the tidal parts of the Ribble drainage basin. See text for further explanation.

Sample Douglas 1 from the tidal Lower Douglas, representing the whole Douglas catchment of 424 km^2 (Fig. 31), exhibits a similar relationship to the Upper Douglas as Ribble 7 and 8 do to the Upper Ribble. Again model and catchment signatures are almost identical to those from the higher catchment (Fig. 15), but contamination in the river sediment is restricted to Ca, Cr, As and Rb, only this time accompanied by Sr (Fig. 31). A similar explanation for the differences seems most probable.

When the whole Ribble catchment (Lower Ribble, 1817 km^2) is considered, model and catchment signatures (Fig. 15) are very similar to those from the Middle Ribble showing catchment contamination in Zn and Pb (and possibly Sn). Samples from the tidal Ribble (Ribble 3-6, Fig. 29) display considerable variation although the overall shape of their signatures is very similar (Fig. 31). An estuary average signature (Fig. 31) indicates contamination in Mg, Ca, Fe, V, Cr, As, Rb and Sr and depletion in K, Ga, Y, Nb, Sn and Ba with respect to the catchment average. The major industrial contamination seen in samples from higher in the catchment (Fig. 30) has largely disappeared, presumably being carried out to sea in a relatively fine-grained sediment fraction.

4.5.2.4 Mersey

The Mersey catchment (4102 km^2) contains much of the major industrial conurbation of western Lancashire as well as smaller centres in Cheshire and Merseyside, including Manchester, Bolton, Bury, Rochdale, Oldham, Stockport, Warrington, Widnes, Runcorn, St Helens, Ellesmere Port, Crewe, Tranmere and Liverpool (Fig.

32). As discussed above, the spread of urban development has made the generation of reliable model signatures for parts of the Mersey catchment difficult. The problem becomes less acute as the catchments grow in size and more GBase samples are available for inclusion in the model. However, less mention will be made of model signatures for the Mersey than was the case in the above discussions of the Solway, Wyre and Ribble systems.

Figure 32. Geology, drainage basins, sample sites, urban areas, mines and mineralisation for the Mersey basin. See Figure 20 for key.

The Croal (143 km^2), Roch (167 km^2), Irwell (168 km^2) and Lower Irwell (368 km^2, including Roch and Upper Irwell), drain the northern part of the headwater region of the Mersey (Fig. 32) and all show similar patterns of river sediment contamination in P, Ca, Fe, V, Cr, Ni, Cu, Zn, As, Rb, Zr, Sn and Pb (Figs. 33). The Tame (144 km^2), Etherow (145 km^2), Goyt (165 km^2) and Micker Brook (55 km^2) drain the eastern headwater region and show slightly different contamination patterns to the northern region. The Tame drains the most heavily urbanised area and is the most contaminated with P, Ca, Fe, Mn, V, Cr, Ni, Cu, Zn, Rb, Y, Zr, Sn, Ba and Pb all showing enrichment in the river sample with respect to the catchment average. The Etherow river sample is similar but P, V, Rb and Ba are not contaminants, whilst in the Goyt P, Mn and V are not enriched. In Micker Brook the river sediment shows evidence of contamination in Ca, Cr, Ni, Cu, Zn, Rb, Zr, Sn and Pb. In general the eastern headwaters region shows less P, V and As but more Y and Zr enrichment than in the north (Figs. 33).

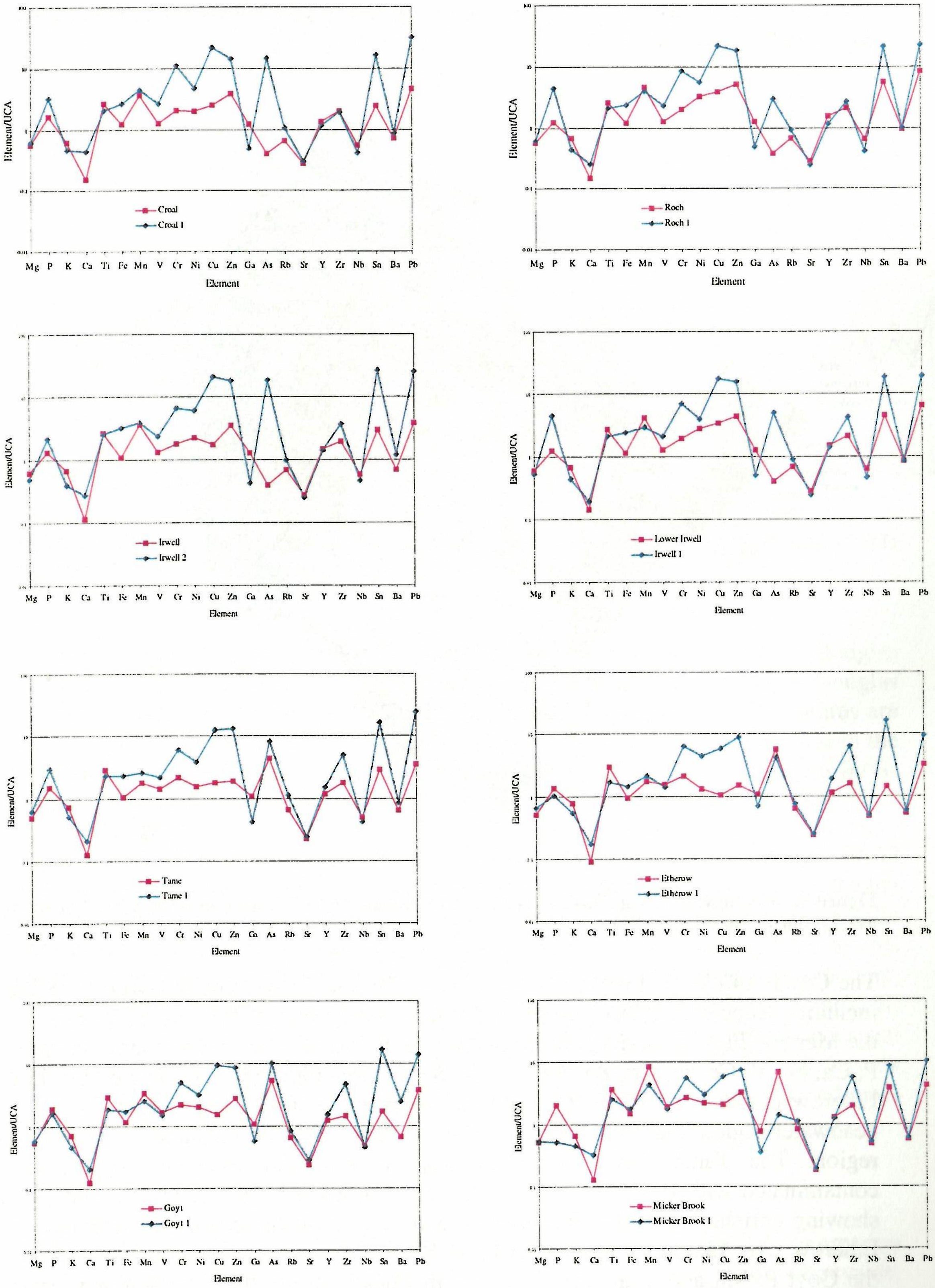

Figure 33. Comparison of Ga normalised catchment and representative river sediment sample signatures for the headwater regions of the Mersey drainage basin. See text for further explanation.

The Mid-Mersey catchment takes in the Mersey basin upstream of Chorlton Water Park to the east of Sale and includes the Tame, Etherow, Goyt and Micker Brook catchments giving a total catchment area of 1231 km^2 (Fig. 32). River sample Mersey 1 shows contamination in P, Ca, Ti, Fe, V, Cr, Ni, Cu, Zn, Rb, Sr (possibly), Y, Zr, Nb, Sn, Ba and Pb in comparison with the catchment signature The type of contamination seen in the eastern headwater catchments has been enhanced in the passage of the river through the southern outskirts of Manchester (Fig 33 and 34).

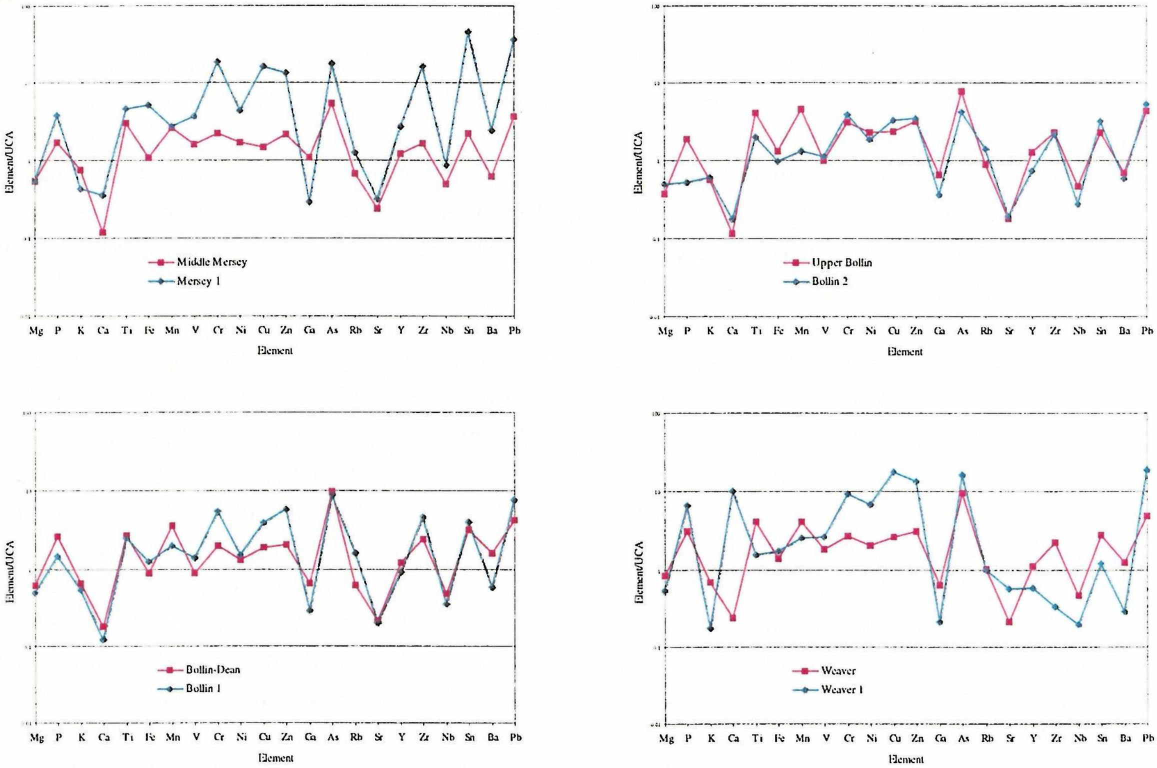

Figure 34. Comparison of Ga normalised catchment and representative river sediment sample signatures for the southern headwater and middle regions of the Mersey drainage basin. See text for further explanation.

On the south side of Manchester the River Bollin and its tributary, the Dean, drain more suburban areas and this is reflected in lower levels of contamination in the river sediments. Bollin 2 at the mouth of the Upper Bollin basin (53 km^2) shows only slight enrichment in Ca, Cr, Cu, Rb, Sn and possibly Pb in comparison with the catchment, despite draining the town of Macclesfield (Fig. 32). Bollin 1 representing the whole of the Bollin and Dean catchment area (272 km^2) is enriched in Cr, Cu, Zn, Rb, Zr, Sn and possibly Pb, but the levels of enrichment are much lower than in the urban and industrial catchments of northern and eastern Manchester (Figs. 33 and 34).

The River Weaver drains a mostly rural area to the south of Manchester, but includes the towns of Crewe, Nantwich, Northwich and the north western (non-industrial) edge of Stoke-on-Trent in the 1237 km^2 catchment (Fig. 32). Model and catchment signatures match reasonably well with the catchment showing evidence of contamination in P, As, Sn, Ba and Pb (Fig. 18). The river sediment of Weaver 1, however, shows strong enrichment in P, Ca, V, Cr, Ni, Cu, Zn, Sr and Pb with respect to the catchment average whilst other elements are depleted (Fig. 34). Some of these changes in the signatures may relate to winnowing and concentration effects, as described previously, but others probably reflect the influence of agricultural activity and urban contamination from the nearby town of Northwich.

The Main Mersey basin includes all of the above catchments, with the exception of the Weaver, and extends downstream to Richmond Bank in the tidal Mersey, some 5 km downstream of the tidal limit at Howley Weir in Warrington and 1.5 km upstream of Fiddler's Ferry, giving a total catchment area of 2866 km^2 (Fig. 32). The model and catchment signatures show a generally good match, with the catchment trace indicating Zn, As, Sn and Pb contamination (Fig. 18). Comparison of the catchment trace with those from surface sediment at Richmond Bank (Richmond Bank 2) and the top 5 cm of a shallow core from the same site (Richmond Bank 1 0-5 cm) shows significant enhancement in the river sediments of Ca, Cr, Cu, Zn, As and Sr, and a lesser degree of enrichment in Mg, P, Rb and Pb (Fig. 35). The Ca and Sr here are probably held in shelly material and the depletion in some elements in the sediment signatures can be ascribed to the effects of tidal currents winnowing out size fractions in which particular elements are bound.

The Lower Mersey catchment (4102 km^2) incorporates the whole of the Mersey drainage system, including the Weaver and the estuarine area. Model and catchment traces for the Lower Mersey are very similar and suggest that any contamination in the catchment is only slight and restricted to P, Zn, Sn and Pb (Fig. 18). Within the estuary samples have been collected from sites over a length of the channel stretching from near the mouth at New Brighton and Seaforth Docks to opposite Fiddler's Ferry power station, some 37 km inland (Fig 32). There is considerable variation in the signatures of these estuarine samples (Fig. 35) which could have several different causes, the most significant of which is probably the grain-size distribution in the individual samples. All the samples are enriched in Ca and Sr relative to the catchment, most likely because these elements are held in the shells of estuarine benthic organisms. All samples also contain more Cr and Zn than the catchment average and this must be contamination. Depletion in Ga and Ba is common to all samples but for other elements there is a spread about the catchment concentration. If an average for the estuarine samples is examined it can be seen that the only significant contaminants with respect to the catchment average are Cr, Zn, As, Rb and Zr (Fig 35). However, in comparison with the model signature for the catchment, Sn and Pb are also contaminants (Fig. 35).

Contaminant levels in the estuary thus are considerably lower than in the rivers higher in the catchment. Figure 35 compares the model signature for the whole (Lower) Mersey catchment with the river sediment signatures for Irwell 2 and Mersey 1, feeder catchment samples from the industrialised areas of northern and eastern Manchester, Richmond Bank 2 and the estuary average (13 samples). Richmond Bank, in the upper tidal reaches of the estuary, has some of the lowest levels of contaminants in comparison with Irwell 2 and Mersey 1, the estuary average, although itself relatively low, being notably higher in Cr, Y and Zr. It appears that considerable quantities of Fe, V, Cr, Ni, Cu, Y, Zr, Sn, Ba and Pb are either being: stored in the Main Mersey basin above Richmond Bank, perhaps trapped in the Manchester Ship Canal which forms part of the drainage system in the Manchester area; diluted by relatively clean sediment entering the system below Irwell 2 and Mersey 1 or coming into the estuary from offshore; or carried out of the estuary in suspension. Further work would be needed to clarify this matter.

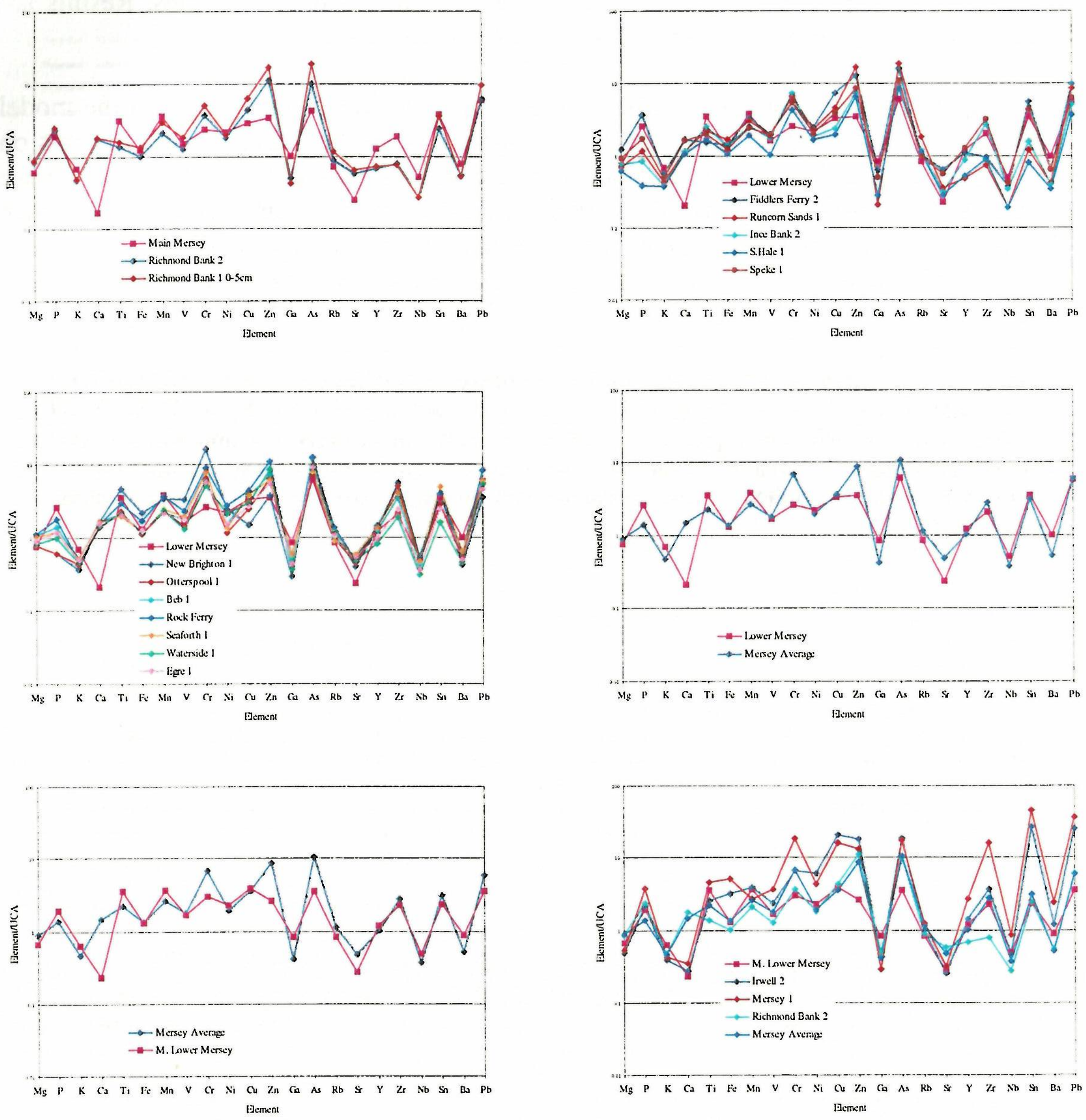

Figure 35. Comparison of Ga normalised catchment and representative river/estuarine sediment sample signatures for the tidal parts of the Mersey drainage basin. See text for further explanation.

4.5.3 Anthropogenic Inputs to the Irish Sea

On the basis of the above, it is possible to estimate natural background levels and anthropogenic inputs of selected metals to the Irish Sea for each of the major drainage basins studied. Using the upper crustal average and Ga normalised data on which the spidergrams are based, the method involves the establishment of a background value for each element for each estuary drainage basin, determination of the average input of each element to the estuary, calculation of the difference expressed as a percentage and the application of this percentage difference to calculate the percentage of the original concentration which can be attributed to anthropogenic activity. It is necessary to use normalised data in order to minimise the effects of different grain size distributions in river sediment and GBase stream sediment samples. Results are expressed as a proportion of the < 150μm sediment fraction.

Background values for each drainage basin ideally would be derived from the model signature which theoretically should minimise the possible anthropogenic impacts on GBase scale drainage basins. In practice, actual catchment signatures based on GBase data are sometimes lower than the model and the background has therefore been taken to be the lower of the two so that there is little likelihood of anthropogenic influences being underestimated. The results are presented in Table 12 and summarised in Table 13.

Table 12. Estimated natural background and anthropogenic inputs to the Irish Sea from the study catchments for the < 150μm sediment fraction. Background is the lower of the model and GBase values. Catchment input is the difference between background and estuary average. %catchment input is catchment input as a percentage of the estuary average. Actual input is the %catchment input applied to the actual estuary average. See text for further explanation. Continued......

Catchment			MgO	P2O5	K2O	CaO	TiO2	Fe2O3	Mn	V	Cr	Ni	Cu	Zn	Ga	As	Rb	Sr	Y	Zr	Nb	Sn	Ba	Pb
			%	%	%	%	%	%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
	Nomalised	Model Lower Nith	1.21	1.57	0.79	0.15	3.41	1.24	6.99	1.73	4.19	2.65	1.43	2.14	1.04	5.57	0.78	0.36	1.28	2.04	0.51	1.42	0.76	2.54
	Nomalised	GBase Lower Nith	1.36	1.21	0.82	0.14	3.23	1.24	4.65	1.90	3.95	2.88	1.51	3.01	1.16	5.06	0.70	0.36	1.20	1.86	0.63	1.12	0.80	3.36
	Nomalised	Background	1.21	1.21	0.79	0.14	3.23	1.24	4.65	1.73	3.95	2.65	1.43	2.14	1.04	5.06	0.70	0.36	1.20	1.86	0.51	1.12	0.76	2.54
NITH	Nomalised	Nith Estuary Average	1.12	1.23	0.57	0.15	3.40	1.38	1.67	2.02	6.94	2.54	2.14	5.28	0.53	0.98	0.90	0.26	0.86	1.66	0.40	2.60	0.56	9.53
	Nomalised	Cachment input	-0.09	0.02	-0.22	0.02	0.18	0.14	-2.98	0.28	2.99	-0.11	0.72	3.14	-0.51	-4.07	0.20	-0.10	-0.33	-0.20	-0.12	1.48	-0.20	6.99
	Nomalised	% Catchment Input	-8.44	1.57	-38.34	10.33	5.14	10.44	-178.21	13.93	43.05	-4.41	33.44	59.41	-97.05	-414.55	22.24	-37.69	-38.67	-12.14	-29.34	56.81	-35.92	73.35
	Actual	Nith Estuary Average	2.50	0.19	1.96	0.62	0.99	3.20	459.64	56.49	123.15	24.45	15.96	138.57	7.38	1.00	50.30	81.87	17.86	392.63	10.34	6.49	375.07	84.58
	Actual	Nith Input	-0.21	0.00	-0.75	0.06	0.05	0.33	-819.15	7.87	53.02	-1.08	5.34	82.33	-7.16	-4.15	11.19	-30.85	-6.91	-47.65	-3.03	3.69	-134.71	62.04
	Nomalised	Model Lower Esk	1.09	1.15	0.94	0.20	3.56	1.25	4.89	1.72	3.77	2.55	1.32	2.46	0.99	3.49	0.91	0.32	1.22	2.14	0.57	1.00	0.78	2.70
	Nomalised	GBase Lower Esk	1.23	1.04	1.03	0.20	3.36	1.20	3.81	1.75	3.18	2.70	1.28	2.92	1.09	2.56	0.89	0.26	1.23	1.96	0.60	0.89	0.75	2.53
	Nomalised	Background	1.09	1.04	0.94	0.20	3.36	1.20	3.81	1.72	3.18	2.55	1.28	2.46	0.99	2.56	0.89	0.26	1.22	1.96	0.57	0.89	0.75	2.53
ESK	Nomalised	Esk Estuary Average	1.18	0.66	0.67	0.25	1.65	1.16	1.46	1.64	4.91	2.48	2.14	3.11	0.82	3.06	0.82	0.26	1.06	2.21	0.48	1.60	0.83	2.38
	Nomalised	Cachment Input	0.10	-0.39	-0.27	0.05	-1.71	-0.04	-2.34	-0.08	1.72	-0.07	0.85	0.65	-0.17	0.50	-0.07	0.00	-0.16	0.25	-0.08	0.71	0.08	-0.15
	Nomalised	% Catchment Input	8.19	-59.03	-40.54	19.21	-103.51	-3.26	-160.29	-4.76	35.12	-2.75	39.88	20.86	-20.19	16.36	-8.71	-1.11	-14.99	11.28	-17.65	44.30	10.13	-6.12
	Actual	Esk Estuary Average	2.65	0.10	2.32	1.01	0.68	4.16	624.03	71.00	139.00	37.00	25.00	135.50	11.50	5.00	71.50	82.00	22.00	524.50	12.50	4.00	557.50	33.00
	Actual	Esk Input	0.22	-0.06	-0.94	0.19	-0.70	-0.14	-1000.26	-3.38	48.82	-1.02	9.97	28.27	-2.32	0.82	-6.22	-0.91	-3.30	59.17	-2.21	1.77	56.46	-2.02
	Nomalised	Model Lower Eden	0.65	0.63	0.65	0.45	3.76	1.31	8.90	1.68	2.95	1.47	1.32	2.50	0.83	1.84	0.94	0.33	1.31	2.27	0.42	1.39	0.79	3.21
	Nomalised	GBase Lower Eden	0.68	0.64	0.70	0.31	3.34	1.24	9.43	1.59	2.49	1.53	1.61	5.79	0.99	13.92	0.87	0.35	1.37	2.01	0.44	1.39	1.06	13.56
	Nomalised	Background	0.65	0.63	0.65	0.31	3.34	1.24	8.90	1.59	2.49	1.47	1.32	2.50	0.83	1.84	0.87	0.33	1.31	2.01	0.42	1.39	0.79	3.21
EDEN	Nomalised	Eden Estuary Average	0.92	0.90	0.64	0.31	1.85	1.35	2.89	1.57	3.64	2.01	2.39	5.25	0.43	8.94	1.35	0.28	0.74	1.31	0.32	2.27	1.40	9.61
	Nomalised	Cachment Input	0.27	0.27	-0.01	0.00	-1.49	0.11	-6.00	-0.02	1.16	0.54	1.07	2.75	-0.40	7.10	0.48	-0.05	-0.57	-0.70	-0.10	0.87	0.61	6.40
	Nomalised	% Catchment Input	29.03	30.16	-1.64	0.17	-80.10	8.17	-207.35	-1.58	31.75	26.86	44.83	52.43	-94.21	79.39	35.54	-18.30	-76.54	-53.49	-31.24	38.57	43.44	66.60
	Actual	Eden Estuary Average	2.07	0.14	2.22	1.28	0.41	2.55	653.75	35.67	54.67	16.00	14.67	117.00	6.00	7.67	63.67	87.00	15.33	310.00	8.33	5.67	933.33	70.00
	Actual	Eden Input	0.60	0.04	-0.04	0.00	-0.33	0.21	-1355.57	-0.56	17.36	4.30	6.57	61.35	-5.65	6.09	22.63	-15.92	-11.74	-165.82	-2.60	2.19	405.44	46.62
	Nomalised	Model Waver	0.50	0.54	0.62	0.29	4.03	1.20	3.80	1.73	3.80	1.73	1.57	2.68	0.74	2.41	0.96	0.35	1.19	2.45	0.38	1.45	0.73	3.41
	Nomalised	GBase Waver	0.46	0.51	0.60	0.27	4.24	1.29	4.79	1.89	4.16	1.72	1.56	2.49	0.73	3.44	0.94	0.33	1.33	3.20	0.39	0.78	0.72	2.91
	Nomalised	Background	0.46	0.51	0.60	0.27	4.03	1.20	3.80	1.73	3.80	1.72	1.56	2.49	0.73	2.41	0.94	0.33	1.19	2.45	0.38	0.78	0.72	2.91
WAVER	Nomalised	Waver Estuary Average	0.60	2.27	0.64	0.14	4.14	1.25	2.40	0.87	3.39	1.61	1.32	2.50	0.45	4.15	1.14	0.22	0.55	1.03	0.40	1.46	0.50	2.91
	Nomalised	Cachment Input	0.15	1.76	0.04	-0.13	0.11	0.06	-1.40	-0.86	-0.41	-0.12	-0.24	0.01	-0.28	1.73	0.19	-0.11	-0.65	-1.42	0.03	0.68	-0.22	0.00
	Nomalised	% Catchment Input	24.61	77.67	6.05	-89.08	2.67	4.40	-58.32	-99.26	-12.12	-7.26	-18.40	0.40	-60.78	41.80	16.97	-52.00	-118.02	-138.12	6.29	46.69	-44.53	-0.14
	Actual	Waver Estuary Average	1.35	0.35	2.20	0.59	0.97	2.50	572.86	20.84	53.71	13.52	8.53	58.77	6.33	3.75	56.58	68.94	11.34	244.30	10.49	3.65	334.13	22.35
	Actual	Waver Input	0.33	0.27	0.13	-0.52	0.03	0.11	-334.11	-20.69	-6.51	-0.98	-1.57	0.24	-3.85	1.57	9.60	-35.85	-13.39	-337.42	0.66	1.70	-148.80	-0.03

Table 12. Continued.

Catchment			MgO	P2O5	K2O	CaO	TiO2	Fe2O3	Mn	V	Cr	Ni	Cu	Zn	Ga	As	Rb	Sr	Y	Zr	Nb	Sn	Ba	Pb
			%	%	%	%	%	%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
	Normalised	Model Ellen	0.64	0.59	0.70	0.40	3.13	1.24	9.35	1.54	2.13	1.50	1.62	1.97	1.08	1.78	0.85	0.36	1.51	1.74	0.41	1.34	0.84	2.48
	Normalised	GBase Ellen	0.50	0.52	0.63	0.49	3.57	1.34	9.63	1.85	2.38	1.83	3.94	4.32	0.97	15.27	0.84	0.35	1.39	1.93	0.37	1.25	1.71	34.15
	Normalised	Background	0.50	0.52	0.63	0.40	3.13	1.24	9.35	1.54	2.13	1.50	1.62	1.97	0.97	1.78	0.84	0.35	1.39	1.74	0.37	1.25	0.84	2.48
ELLEN	Normalised	Ellen Estuary Average	0.56	2.93	0.49	0.27	4.71	1.64	4.89	1.43	3.52	2.69	4.22	3.87	0.45	10.70	1.04	0.20	0.75	1.01	0.42	1.15	0.71	3.97
	Normalised	Catchment Input	0.06	2.41	-0.14	-0.13	1.57	0.40	-4.46	-0.11	1.39	1.19	2.60	1.90	-0.52	8.93	0.20	-0.14	-0.63	-0.73	0.04	-0.10	-0.12	1.49
	Normalised	% Catchment Input	10.58	82.18	-28.54	-48.74	33.44	24.38	-91.34	-7.65	39.51	44.30	61.57	49.21	-113.93	83.40	19.60	-71.42	-83.98	-72.93	10.75	-8.82	-17.23	37.56
	Actual	Ellen Estuary Average	1.25	0.45	1.69	1.12	1.11	3.27	1165.27	34.25	55.77	22.65	27.28	91.05	6.33	9.69	51.74	63.85	15.59	238.46	10.86	2.88	477.61	30.56
	Actual	Ellen Input	0.13	0.37	-0.48	-0.54	0.37	0.80	-1064.39	-2.62	22.04	10.03	16.80	44.81	-7.22	8.08	10.14	-45.60	-13.09	-173.90	1.17	-0.25	-82.29	11.48
	Normalised	Model Lower Wyre	0.73	1.50	0.59	0.51	3.24	1.16	2.62	1.42	2.60	1.97	2.06	2.57	0.96	1.25	0.79	0.33	1.31	2.53	0.53	1.86	0.67	2.89
	Normalised	GBase Lower Wyre	0.57	1.57	0.60	0.20	3.36	1.15	2.33	1.42	2.59	1.83	1.83	3.07	0.95	-0.35	0.77	0.27	1.37	3.39	0.59	1.58	0.64	3.65
	Normalised	Background	0.57	1.50	0.59	0.20	3.24	1.15	2.33	1.42	2.59	1.83	1.83	2.57	0.95	-0.35	0.77	0.27	1.31	2.53	0.53	1.58	0.64	2.89
WYRE	Normalised	Wyre Estuary Average	0.97	1.00	0.48	1.49	2.02	1.21	2.49	1.62	5.26	1.75	1.64	2.94	0.44	3.00	1.11	0.46	0.97	2.05	0.35	2.05	0.45	3.59
	Normalised	Catchment Input	0.39	-0.50	-0.11	1.29	-1.22	0.06	0.16	0.20	2.67	-0.08	-0.19	0.36	-0.51	3.35	0.34	0.19	-0.35	-0.48	-0.18	0.47	-0.19	0.70
	Normalised	% Catchment Input	40.67	-49.82	-23.16	86.44	-60.53	5.04	6.41	12.52	50.74	-4.85	-11.89	12.42	-116.67	111.74	30.88	41.09	-35.99	-23.42	-53.37	23.10	-41.81	19.49
	Actual	Wyre Estuary Average	2.16	0.15	1.65	6.16	0.44	2.29	562.98	38.00	74.88	14.38	10.75	68.50	6.13	6.00	50.63	144.25	20.00	486.38	9.00	5.13	301.63	27.25
	Actual	Wyre Input	0.88	-0.08	-0.38	5.32	-0.26	0.12	36.10	4.76	37.99	-0.70	-1.28	8.51	-7.15	6.70	15.63	59.27	-7.20	-113.91	-4.80	1.18	-126.10	5.31
	Normalised	Model Lower Ribble	0.56	1.32	0.57	0.51	3.13	1.22	3.65	1.45	2.44	2.24	2.82	2.47	1.00	0.92	0.73	0.31	1.39	2.60	0.53	1.71	0.68	2.80
	Normalised	GBase Lower Ribble	0.58	1.26	0.58	0.51	2.95	1.20	4.20	1.51	2.33	2.36	2.00	4.69	1.05	0.50	0.73	0.33	1.35	2.42	0.57	2.10	0.69	4.36
	Normalised	Background	0.56	1.26	0.57	0.51	2.95	1.20	3.65	1.45	2.33	2.24	2.00	2.47	1.00	0.50	0.73	0.31	1.35	2.42	0.53	1.71	0.68	2.80
RIBBLE	Normalised	Ribble Estuary Average	0.85	1.18	0.39	1.66	3.05	1.74	3.93	2.13	9.05	2.34	1.92	4.25	0.30	3.00	1.24	0.44	0.88	2.43	0.35	1.12	0.40	4.49
	Normalised	Catchment Input	0.29	-0.08	-0.17	1.15	0.10	0.54	0.28	0.69	6.72	0.10	-0.08	1.78	-0.70	2.50	0.51	0.13	-0.47	0.02	-0.18	-0.59	-0.28	1.69
	Normalised	% Catchment Input	33.83	-7.06	-43.50	69.29	3.13	31.12	7.10	32.21	74.30	4.36	-4.29	41.94	-232.96	83.33	41.26	29.10	-53.44	0.67	-50.13	-52.83	-68.94	37.67
	Actual	Ribble Estuary Average	1.90	0.18	1.36	6.83	0.43	2.10	565.89	31.20	85.00	12.20	8.40	64.00	4.20	6.00	39.60	139.20	18.20	576.80	9.20	2.80	268.20	22.20
	Actual	Ribble Input	0.64	-0.01	-0.59	4.73	0.01	0.65	40.17	10.05	63.16	0.53	-0.36	26.84	-9.78	5.00	16.34	40.51	-9.73	3.88	-4.61	-1.48	-184.91	8.36
	Normalised	Model Lower Mersey	0.67	1.94	0.63	0.23	3.53	1.30	3.62	1.66	3.06	2.26	3.83	2.65	0.84	3.54	0.83	0.27	1.19	2.29	0.49	2.33	0.89	3.62
	Normalised	GBase Lower Mersey	0.74	2.53	0.69	0.20	3.43	1.27	3.74	1.63	2.52	2.14	3.30	3.50	0.84	6.00	0.83	0.23	1.20	2.02	0.50	3.49	0.98	5.69
	Normalised	Background	0.67	1.94	0.63	0.20	3.43	1.27	3.62	1.63	2.52	2.14	3.30	2.65	0.84	3.54	0.83	0.23	1.19	2.02	0.49	2.33	0.89	3.62
MERSEY	Normalised	Mersey Estuary Average	0.88	1.37	0.46	1.47	2.24	1.33	2.61	1.80	6.72	1.91	3.53	8.70	0.41	10.66	1.13	0.48	1.02	2.76	0.37	3.07	0.52	5.96
	Normalised	Catchment Input	0.21	-0.57	-0.17	1.27	-1.19	0.06	-1.01	0.17	4.20	-0.22	0.22	6.04	-0.43	7.12	0.31	0.24	-0.17	0.74	-0.12	0.74	-0.37	2.35
	Normalised	% Catchment Input	24.16	-41.80	-37.65	86.21	-53.36	4.61	-38.85	9.27	62.45	-11.66	6.36	69.49	-104.63	66.77	26.99	51.34	-16.76	26.89	-32.27	23.98	-71.05	39.36
	Actual	Mersey Estuary Average	1.98	0.20	1.58	6.07	0.46	2.35	560.20	39.07	93.87	14.27	21.80	180.53	5.87	8.73	48.80	150.53	21.47	675.13	9.80	7.80	347.73	42.13
	Actual	Mersey Input	0.48	-0.08	-0.60	5.23	-0.25	0.11	-217.62	3.62	58.62	-1.66	1.39	125.46	-6.14	5.83	13.17	77.29	-3.60	181.55	-3.16	1.87	-247.06	16.59

Table 13. Summary of element inputs to the estuaries (and thus to the Irish Sea) expressed as a proportion of the < 150µm sediment fraction. Negative and zero values omitted. See text for further explanation.

Catchment	MgO	P2O5	K2O	CaO	TiO2	Fe2O3	Mn	V	Cr	Ni	Cu	Zn	Ga	As	Rb	Sr	Y	Zr	Nb	Sn	Ba	Pb
	%	%	%	%	%	%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Nith				0.06	0.05	0.33		8	53		5	82			11					4		62
Esk	0.22			0.19					49		10	28		1				59		2	56	
Eden	0.60	0.04		0.00		0.21			17	4	7	61		6	23					2	405	47
Waver	0.33	0.27	0.13		0.03	0.11								2	10				1	2		
Ellen	0.13	0.37			0.37	0.80			22	10	17	45		8	10				1			11
Wyre	0.88			5.32		0.12	36	5	38			9		7	16	59				1		5
Ribble	0.64			4.73	0.01	0.65	40	10	63	1		27		5	16	41		4				8
Mersey	0.48			5.23		0.11		4	59		1	125		6	13	77		182		2		17

For the Wyre, Ribble and Mersey, the average input to the estuary has been calculated from the average of all samples collected from within the estuary itself. In the case of the Nith, Esk and Eden, the samples collected from the estuaries themselves showed strong depletion in some elements which may be related to hydraulic sorting of the sediment under the influence of tidal and fluviatile currents (see above). For these estuaries the most seaward river samples have been used instead (Nith 1 and 2; Esk 4 and 5; Eden 1 and 2). In the case of the Ellen and Waver, the catchments are each represented by a single sample.

For some elements, the net input to the estuary is negative. Some possible explanations for this have been advanced above, but examination of Table 12 brings out some further common factors. Elements which are associated with clays or oxide coatings on clay minerals (K, Mn, Ga) are often depleted in the estuary (negative input) and this can be interpreted to indicate that clay minerals are being carried out of the estuaries in suspension. Many metals are preferentially sorbed onto clay mineral surfaces or scavenged by Mn hydroxides and the proportions of metals entering the Irish Sea thus may be larger than estimated by the methodology proposed here. Depletions in Ti, Y, Zr, Nb and Ba suggest that heavy minerals are being trapped in the river basins and are not reaching the lower parts of the drainage systems and estuaries. The importance of relatively small scale mining in producing metal contaminants is shown by the Nith and Eden Pb and Zn concentrations. Chromium is a contaminant in every estuary except the Waver. Levels of contamination in the Mersey are surprisingly low and reflect the efforts to clean up the estuary over the last decade.

4.5.4 Comparison of Offshore, Estuary and Catchment Signatures

4.5.4.1 Solway

Average values for the estuarine samples from the Nith, Esk and Eden basins yield very similar signatures which are quite different to their respective catchment traces (Fig. 36). This suggests that the estuarine sediment has a common source and, as concluded earlier, that this source is marine. However, the offshore Solway sediment has a signature which, for most elements, lies between the catchment and estuary traces, this being particularly noticeable for Ti, Fe, Mn, Cu, Zn, Y, Zr and Nb. For some elements the offshore signature is actually closer to the catchment trace, e.g. Cr, As, Sn. A possible explanation for this feature is that these elements are held in a sediment size fraction which is winnowed out of the estuarine environment by the combined action of fluvial and tidal currents and carried out to sea to accumulate under quieter conditions. However, in common with the Wyre, Ribble and Mersey, the offshore signature is based on only a single sample and this interpretation must therefore be viewed with some caution.

4.5.4.2 Wyre

For the Wyre, the estuary average and offshore signatures follow a very similar pattern (Fig. 36) and although there are differences for some elements, these are no greater than have been observed between samples from the same fluvial site or within an estuary. The estuary and offshore sediment is thus considered to be essentially the same. The difference between the catchment signature and the offshore and estuary traces is not great (Fig. 36) and can be explained by winnowing of some fine-grained material from the estuarine sediments coupled with increased levels of Ca and Sr due to shell material. This effect is seen too in the Middle Wyre catchment, which is also tidal (Fig. 28). Chromium and As are enhanced in the river/estuary sediments in comparison with the catchment (As unfortunately missing from the Lower Wyre catchment data) whilst Ti, Y, Zr and Nb are depleted. Winnowing under the influence of tidal and fluvial currents in the Wyre, however, does not appear to be as strong or effective as in the Solway.

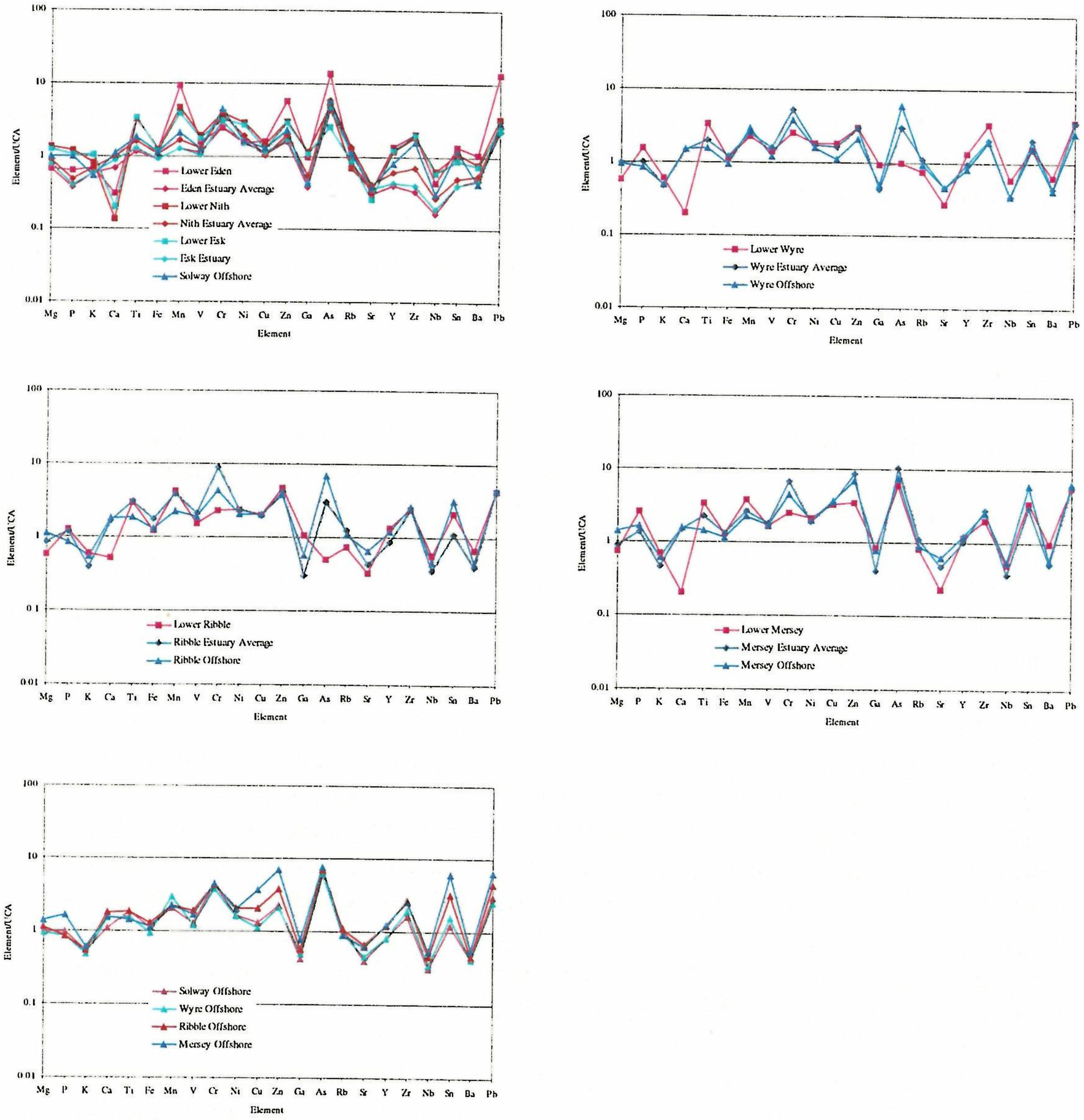

Figure 36. Comparison of offshore, estuary and catchment signatures for the major study basins. See text for further explanation.

4.5.4.3 Ribble

The situation in the Ribble is similar to that in the Wyre with estuary average and offshore sediment signatures following the same pattern (Fig. 36). Levels of Cr and As in the estuary are enhanced with respect to the catchment trace, but Ti, Y, Zr and Nb are not so noticeably depleted. However, further inland the tidal Ribble shows the same enhancements in Cr and As in the sediment as compared with the catchment, but here Ti, Mn, Y, Zr, Nb, Sn and Ba are all depleted (Fig. 31). Similar effects are seen in the tidal Douglas (Fig. 31). The situation is analogous to that in the Solway with strong tidal and fluvial currents in inner estuary areas winnowing out metal carrying sediment which is re-deposited further towards the sea.

4.5.4.4 Mersey

Here again, estuary average and offshore signatures are very similar with enhancements in Ca, Cr, Zn, As (possibly) and Sr over the Lower Mersey catchment signature. Although there are depletions in P, Ti, Mn and Ba with respect to the catchment, this effect is not seen for Y, Zr, Nb and Sn (Fig. 36). However, at Richmond Bank in the inner estuary, depletions in Y, Zr, Nb, Sn and Ba in the river sediment as compared with the Main Mersey catchment signature are observed (Fig. 35).

4.5.4.5 Summary

Estuary and respective offshore sediments for all 4 study areas show similar characteristics. The evidence for the Solway, where 3 river systems have very closely matched estuarine signatures despite differences in their catchment traces, suggests that marine sediment is moving landward into the estuaries and that metals entering the estuaries from the catchment rivers are being winnowed out. Further, an increase in metal concentrations in the offshore sediment indicates that material carried out of the estuaries is being deposited at sea.

The Ribble and the Mersey show similar features, but in both cases the loss of metals from river sediments is seen most strongly in inner estuary environments, with re-deposition taking place in the outer estuary. This re-deposition could be directly from sediment travelling downstream, or could represent shoreward movement of material previously carried out to sea. These characteristics are not so well developed in the relatively small Wyre system, but similar inner estuary depletions are seen in the Solway. The balance of evidence suggests that similar processes operate in all the estuaries; there is some transport of sediment landwards and a zone of increased winnowing in the inner estuary, close to the tidal limit.

Comparison of the signatures of the offshore sediment samples show that marine sediments off the Solway and Wyre are very similar and carry lower levels of most metals than those off the Ribble and Mersey (Fig. 36). The Mersey offshore sediments carry the highest metal loading. The results are consistent with expected findings, the industrial districts of Lancashire, Manchester and Merseyside producing the greatest contamination. Mining related metals coming from the northern and eastern lake District have little impact on the quality of the offshore sediments.

4.5.5 Comparison of depth profiles in short cores from the Mersey Estuary

Ten short cores were collected from the Mersey Estuary . The cores were collected by hammering a clear polycarbonate pipe into the sediment by hand and the length of core retrieved varied according to the type of sediment. Sandy sediments were more difficult to penetrate than muddy ones and yielded shorter cores. Each core was sub-sampled over 0-5, 5-10, 10-20 and 20-30 cm intervals and then at varying intervals depending on the length of core available. Analysis was by ED-XRF. In the following figures, selected metal concentrations are compared those in the Lower Mersey catchment as a measure of the degree of contamination in the estuary. Normalised and non-normalised concentrations are shown to demonstrate the value of normalisation in understanding the variation of contamination with depth/time. The normalised values are assumed to present the true picture of changes in levels of contamination and often show significantly different patterns of variation to the non-normalised data.

At Richmond Bank, in the Inner Estuary, the greatest contamination seen occurs in the 30-50 cm sampling interval in the normalised data, but at 5-10 cm in the non-normalised (Fig. 37). Contamination falls towards the present day surface, but is still some way above the catchment 'background' level. A similar situation is seen at Fiddler's Ferry, Hale, Ince Bank and Speke in the Inner Estuary, and also at Seaforth at the seaward end of the Estuary (Figs. 37). These are all relatively long cores of sediment with a relatively high mud content (see Fig. 32 for core locations).

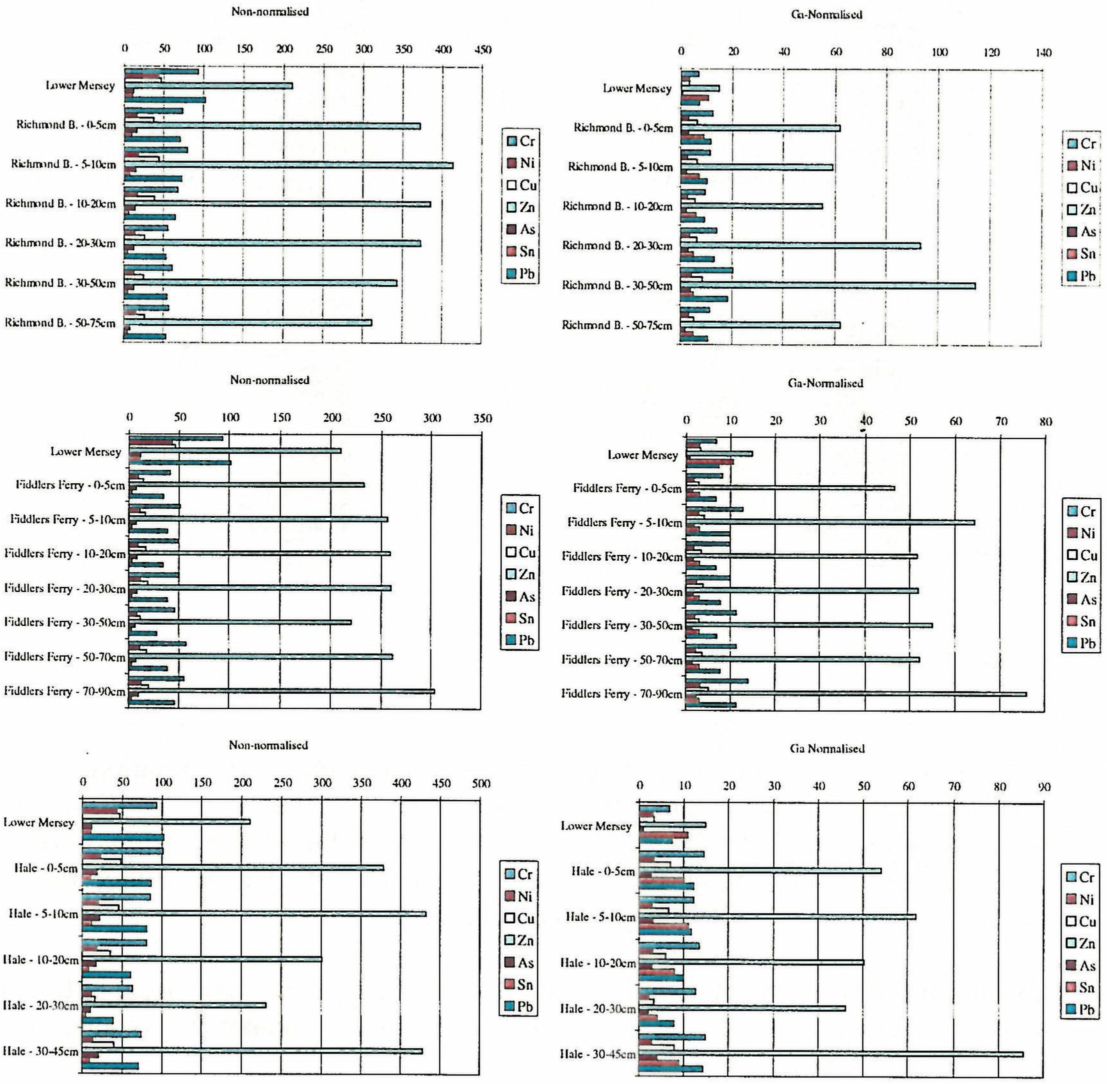

Figure 37. Non-normalised and Ga-Normalised depth profiles for selected metals in muddy short cores from the Mersey Estuary. See text for further explanation and Figure 32 for core locations. Continued……

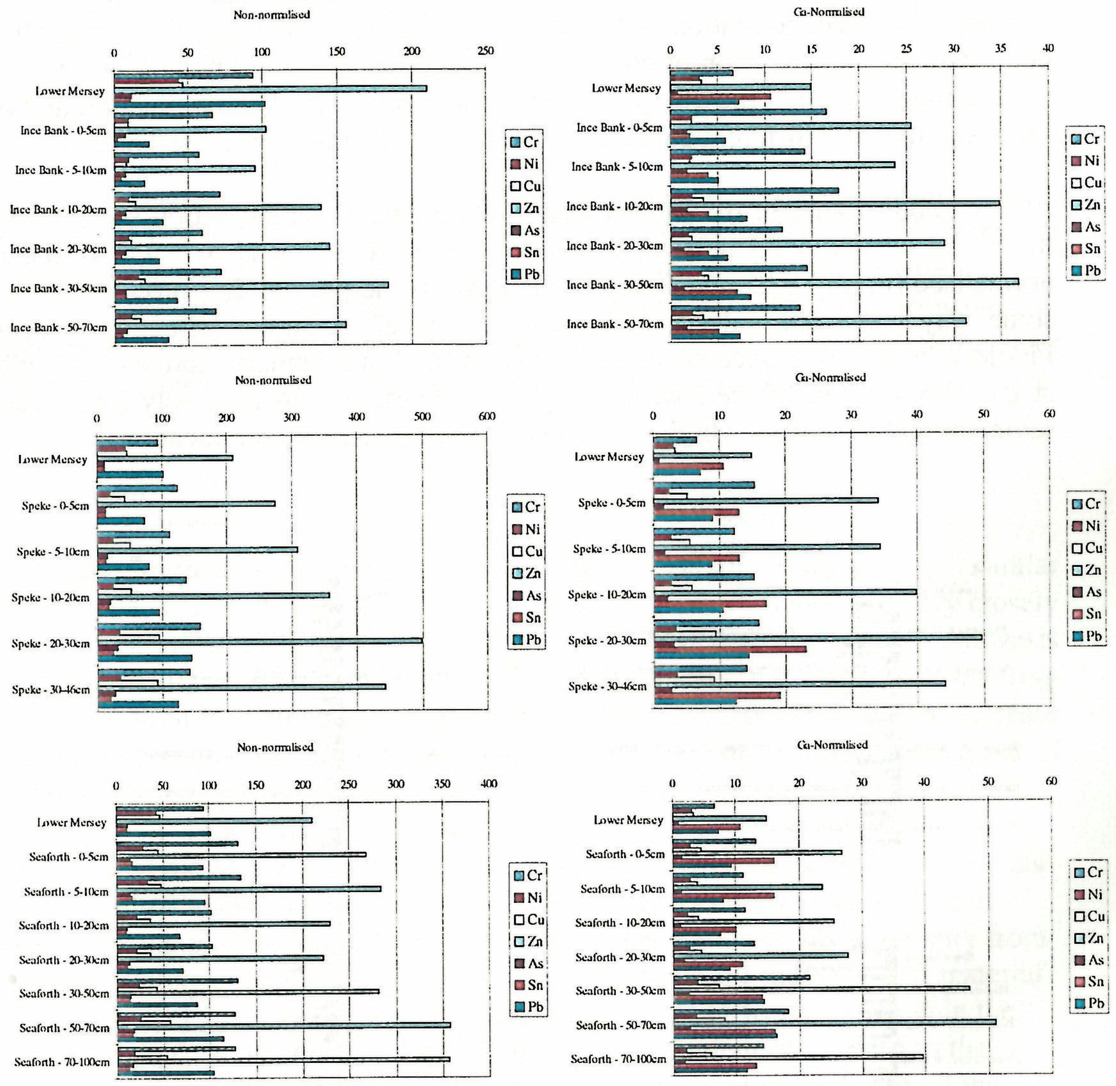

Figure 37. Continued.

The shorter, sandier cores from Bebbington, Waterside, and Egremont generally mimic the pattern of variation seen in the upper parts of the long cores (Figs. 38). In all these cores, Zn is the most prominent contaminant, but at New Brighton (Fig. 38) it falls below the level in the Mersey catchment with Cr becoming the major contaminant. Core locations are shown on Figure 32.

Overall, the cores show that contamination in the Mersey has decreased, although the time span over which the decrease has taken place cannot be judged without independent age determinations on the cores.

4.6 Summary: Multi-element Geochemistry

The methodology outlined above has been successful in addressing Objective 1: To develop a method of distinguishing between the natural and anthropogenic sources of metals entering the coastal zone through river inputs.

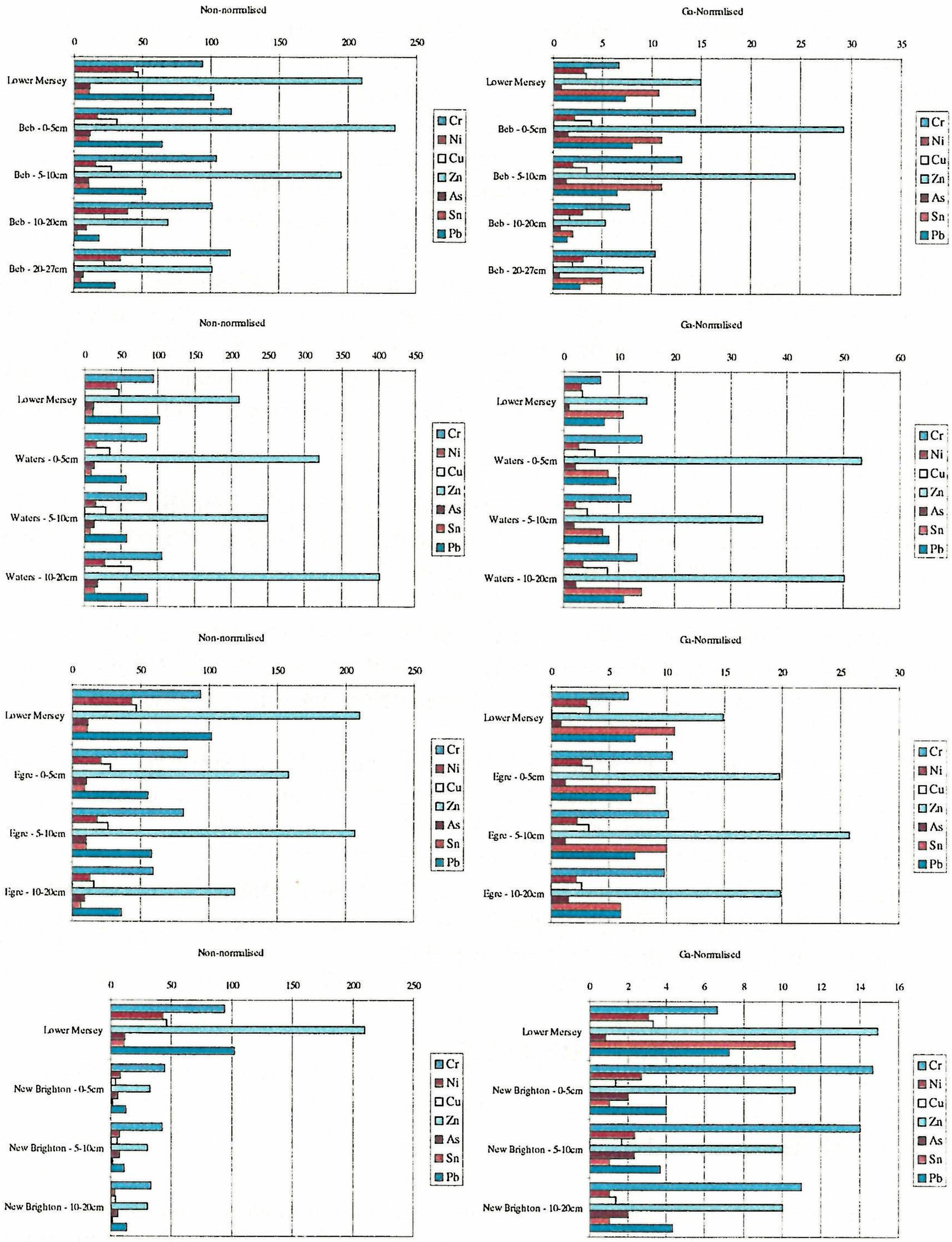

Figure 38. Non-normalised and Ga-Normalised depth profiles for selected metals in sandy short cores from the Mersey Estuary. See text for further explanation and Figure 32 for core locations.

In regions where detailed geochemistry is available (e.g. the BGS GBase data) model geochemical signatures, based on combining the signatures of different geological lithologies in proportion to their presence in the drainage basin, can be used to estimate natural background values even when mining, industry and urban development are present in the catchment. Care must be taken to distinguish between high metal values related to natural unworked mineralisation and those related to mining, but this should be relatively easy to achieve if information on the location of mines is available so that model signatures based in areas which include mineralisation, but not mining, can be generated. The methodology has also demonstrated that in 'pristine' catchments, the average catchment signature from Gbase data and the signature of the representative major river sample are almost identical. Thus where detailed geochemistry is not available, a relatively limited programme of river sampling should allow model signatures to be calculated.

Catchment signatures in mining areas can be compared with models to estimate the input of metals from mine working, but are best used in conjunction with major river samples to gauge the full impact of mining activity. Geochemical signatures of major river samples taken downstream of industrial activity, when compared with catchment and/or river samples upstream, allow industrial and mining metal inputs to be distinguished.

Where model and catchment signatures are at variance it is probably best, from an environmental point of view, to err on the side of caution and set the natural background level at the lower of the two values.

Grain size variations between drainage sediment samples from small and large catchments can make a significant difference to their metal levels. Normalisation to an element which is a good proxy for fine-grained sediment is thus essential.

In inner estuary areas, hydraulic conditions may be such that some metal values are unusually depleted. A better estimate of metal inputs can be gained from samples taken nearer the estuary mouth.

Negative inputs to the estuaries, in comparison with catchment background levels, probably reflect loss of fine-grained material to the sea in suspension and the trapping of heavy mineral concentrates in the river basins.

5 PART B: LEAD ISOTOPES

5.1 Background and rationale

Lead has been of major concern as an elemental contaminant for many years, due to its toxicity and wide spread use in both industrial and domestic environments. Riverine waters are likely to form a major means of transport of both natural and anthropogenic lead from terrestrial sources to their final sink in the Irish Sea. Although, dissolved lead levels have been recognised as relatively low, transport and deposition may also occur as fine organic or inorganic particles (Hamilton and Clifton, 1979). The mapping of lead concentrations measured in sediments using GIS systems can indicate possible sources. When the lead data is combined with other elemental data a multivariate signature may sometimes be obtained for sources. However, it is still difficult lead in an area with many potential contributing sources to apportion the amount of lead from each.

The isotope composition of lead has been use as an indicator of anthropogenic input of lead into the natural environment in numerous environmental studies over the past few decades, particularly the involvement of lead additives in petrol and their effect on human health (Graney *et al.*, 1995; Farmer *et al.*, 1996; Monna *et al.*, 1997; Whitehead *et al.*, 1997, Farmer *et al.*, 1999). Lead has four naturally occurring isotopes: ^{204}Pb (1.4%), ^{206}Pb (24.1%), ^{207}Pb (22.1%) and ^{208}Pb (52.3%). The three heavier isotopes are radiogenic decay products of ^{238}U, ^{235}U and ^{232}Th, respectively. Therefore variations in the ratios of the lead isotopes occur due to geochemical constraints and ages of lead sources. Usefully, many of the worlds major lead ore sources such as Broken Hill, Australia and Mississippi Valley Type (MVT) deposits, USA have distinct isotopic signatures (Brown, 1962). Therefore assuming anthropogenic sources of lead are not using local sources of lead ore, it should be possible to identify and apportion these from locally naturally occurring lead sources.

In the past, the wide spread use of lead isotope ratios in large scale environmental studies has been limited because the major technique for producing such data has been Thermal Ionisation Mass Spectrometry (TIMS). TIMS is a highly accurate and precise technique but relatively slow, producing typically less than 10 sample analyses per day even after extensive sample preparation (2 days). In the last few years, the use of Inductively Coupled Plasma – Quadrupole Mass Spectrometry (ICP-QMS) has allowed the rapid measurement of lead isotope ratios (40+ per day) after reduced sample preparation (1 day), but at a significant cost in terms of accuracy and precision. However most recently, the advent of Multiple Collector Inductively Coupled Plasma Mass Spectrometry (MC-ICP-MS), combining the speed advantages of ICP-QMS and accuracy and precision of TIMS promises a revolution in the use of lead isotopes in large scale environmental studies. The speed advantage of the MC-ICP-MS can been potentially improved even further by dispensing with the conventional sample preparation of dissolving the sediment, then chemically separating the lead and instead directly introducing the sediment into the mass spectrometer. This is achieved using a technique called laser ablation (LA) to remove a small amount of material from the surface of a solid and transporting it into the MC-ICP-MS.

The aim of the current study was to demonstrate the feasibility of rapidly measuring lead isotopes in sediments containing a wide range in concentrations and confirm that significant variations in those isotope ratios occurred due to natural or anthropogenic processes.

5.2 Methodology

5.2.1 Sample Selection

A series of initial samples were chosen for analysis by LA-MC-ICP-MS. These consisted of 9 samples from the Mersey covering a concentration range of 10-2500 mg.kg^{-1}. For comparison one sample was analysed from the Solway Firth (approximately 20 mg.kg^{-1}) and three control samples from PML covering the concentration range (10-300 mg.kg^{-1}) presumably collected in SW England. All the analysed samples were in the form of XRF pellets thus minimising sample preparation. Lead isotope ratios in eight of these Mersey samples were then also determined by solution MC-ICP-MS for comparison to validate the more novel laser ablation work.

Finally, the main set of 54 samples was selected from Mersey and Solway material to provide both a wide geographical and environmental distribution and in one instance to provide down-core data.

5.2.2 Multiple Collector Inductively Coupled Plasma Mass Spectrometry (MC-ICP-MS)

Multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS) is a new technique for the measurement of isotopic compositions at high precision. The method combines the outstanding ionisation efficiency of the ICP source with the superior peak shapes achievable from the ion optical focal plane of a large dispersion magnetic sector mass spectrometer, utilising simultaneous multiple collection to achieve the most precise isotopic measurements yet made for many elements, particularly those with high first ionisation potential. The analysis were carried out by means of a MC-ICP-MS manufactured by VG Elemental under the model name Plasma 54 (P54).

The MC-ICP-MS, is very different in concept from the conventional ICP-MS. It is a high precision, double-focusing instrument with extended geometry equipped with an array of Faraday collectors. The instrument is designed to do simultaneous measurements of all relevant ion beams over a restricted mass range.

The measurement of the lead isotopic ratios is subject to variations in detection efficiency for each isotope. This variation is mass dependant and conventionally known as mass bias. This bias can be determined externally, by measuring a known isotopic standard and then correcting sample values. However, because it can vary rapidly, some form of internal correction is preferable. In other isotopic systems i.e. Nd/Sm, a pair of isotopes of the elements of interest, which have a fixed and well characterised ratio may be used. However, for lead there is no suitable pair of isotope. The alternative is to spike the sample with another element of similar mass, excitation efficiency and chemical compatibility. In this study the element thallium was added as this has two isotopes at masses 203 & 205. An on-line mass bias correction was performed using these isotopes. Additionally, the Hg interference on ^{204}Pb was corrected by measuring the ^{202}Hg signal and subtracting the appropriate contribution to ^{204}Pb.

5.2.3 Laser Ablation Multiple Collector Inductively Coupled Plasma Mass Spectrometry (LA-MC-ICP-MS)

Laser ablation (LA) techniques for direct solid sample introduction into MC-ICP-MS are similar to those used for rapid multi-element determination in conventional ICP-MS. Laser ablation has been used as a sample introduction technique with ICP-AES for a number of years and the first application for solid sample introduction into ICP-MS was published in 1985. The application of laser ablation for sample introduction for MC-ICP-MS has been very limited so far (Halliday *et al.*, 1998).

The principles of laser ablation for sample introduction are that a pulse of laser light is focused onto the surface of a solid, in this case with a X5 objective lens to a spot size of less that 5 µm. This pulse of light although of low relative energy (mJ) has a high peak power 10^5 W, but when this is focused down to a small diameter (µm's) the power densities are huge - 1 $X10^{14}$ J m^2. This powerful pulse then rapidly heats the sample, expelling from the surface a mixture of solid, liquid and vapour - process known as ablation. If this process is performed in an enclosed cell with argon gas flowing through it, the ablated material may be transported to the MC-ICP-MS for analysis.

The laser ablation system used in the current study was the MicroProbe 2 by VG Elemental. This used a 266 nm ultra-violet laser, with a pulse length of 10 ns and a maximum energy of 5 mJ.

Detection capabilities and quality of isotopic ratio are directly related to the amount of material ablated and vary inversely with the volume of the material removed. The laser beam was rastered over the sample surface of the XRF pellet by continuously moving the sample cell/stage. The laser conditions and the rate of stage movement optimised to produce from low concentration samples, a large enough signal to calculate isotope ratios of adequate precision and for the high concentration samples a maximum signal within detector linearity.

To allow on-line corrections to the isotope ratios for mass bias a continuous aerosol of thallium, produced by normal nebulisation, was mixed with the gas from the laser ablation cell, prior to introduction into the ICP-MS. In addition, for quality control purposes a solution of the NIST lead isotopic standard SRM981 was analysed and an in-house solid reference material NG2 that is currently in development for use with LA-MC-ICP-MS.

5.2.4. Solution Multiple Collector Inductively Coupled Plasma Mass Spectrometry (Sol-MC-ICP-MS)

Prior to isotope ratio determination by solution MC-ICP-MS, the samples require significant sample preparation. The following well established procedure was followed:

1. Powdered sample was decomposed in covered (but not sealed) PFA bombs with a mixed acid attack consisting of $HF/HClO_4/HNO_3$ concentrated acids.
2. The samples were then dried out and re-dissolved in 1M HBr (Romil UPA grade). The Br combines with the lead in the sample to produce an anionic complex.
3. The solutions were then put onto Dowex AG1 anion exchange resin, a majority of the sample passed immediately through while the lead complex was held on the column.
4. The lead was then eluted in 6MHCl, re-dried and stored.
5. Before isotope ratio determination on the MC-ICP-MS the samples were dissolved in 1% HNO3 and a thallium 'spike' added.

5.3 Results And Discussion

5.3.1 Initial Sample Set

Lead isotopic ratios and the lead concentrations (as determined by XRF) for the analysed samples are given in Table 14 below.

Table 14. Lead isotopic ratios and the lead concentrations (as determined by XRF) for the analysed samples

Sample	Location	Concentration mg/kg	207/206 Pb	208/206 Pb	206/204 Pb	207/204 Pb	208/204 Pb
6146-19	Mersey	12	0.8638	2.103	18.05	15.59	37.95
6146-16	Mersey	18	0.8652	2.106	18.01	15.58	37.92
6146-17	Mersey	18	0.8668	2.107	17.97	15.58	37.87
6146-26	Mersey	22	0.8685	2.110	17.93	15.57	37.84
6146-20	Mersey	55	0.8740	2.116	17.81	15.56	37.68
6146-18	Mersey	80	0.8756	2.119	17.77	15.56	37.64
6146-21	Mersey	161	0.8810	2.125	17.64	15.54	37.49
6146-23	Mersey	314	0.9002	2.148	17.20	15.48	36.93
6146-22	Mersey	2326	0.9399	2.197	16.46	15.47	36.17
6146-13	PML	31	0.8494	2.086	18.36	15.60	38.29
6146-14	PML	92	0.8592	2.092	18.14	15.59	37.95
6146-15	PML	261	0.8513	2.084	18.34	15.61	38.23
6146-04	Solway	21	0.8460	2.079	18.42	15.58	38.30

For comparison some typical lead isotope values for UK regions and world class lead deposits are given in Table 15 (Brown, 1962).

From the above initial data set it was observed that significant variations occur in the samples analysed both between and within river systems. Within the R. Mersey samples the isotopic ratios appeared to be related to the concentration. This is demonstrated in Figure 39 where $^{208/206}$Pb is plotted against the reciprocal of the Pb concentration. This is done to aid interpretation of source mixing. The lead isotope ratios of the R. Mersey samples with the highest concentration of lead were compared to the typical ore values in Table 15 and it was concluded that they had significant 'Broken Hill type' (BHT) lead derived from overseas. Therefore the more detailed study was performed.

5.3.2 Validation of LA-MC-ICP-MS with solution ICP-MS

A comparison of lead isotope ratios obtained on 8 samples from the R. Mersey by both solution and LA-MC -ICP-MS are given below in Tables 16a and 16b respectively.

Table 15. Typical lead isotope values for UK regions and world class lead deposits (Brown, 1962).

	207/206Pb	208/206Pb	206/204Pb	207/204Pb	208/204Pb
Derbyshire	0.847	2.09	18.57	15.67	38.83
Lead Hills, Scotland	0.855	2.08	18.52	15.84	38.60
Lake District	0.847	2.09	18.25	15.53	38.15
N. Pennines	0.855	2.09	18.23	15.53	38.07
Devon/Cornwall	0.855	2.09	18.20	15.51	37.96
Ab'dh's'h, Scotland	0.870	2.11	17.78	15.41	37.55
Mt Isa, Australia	0.962	2.24	16.10	15.52	36.06
Broken Hill, Australia	0.962	2.22	16.15	15.58	35.87
Franklin, N.J. USA	0.909	2.14	17.14	15.60	36.68
Joplin-Picher, MVT, USA	0.730	1.88	22.06	16.11	41.48

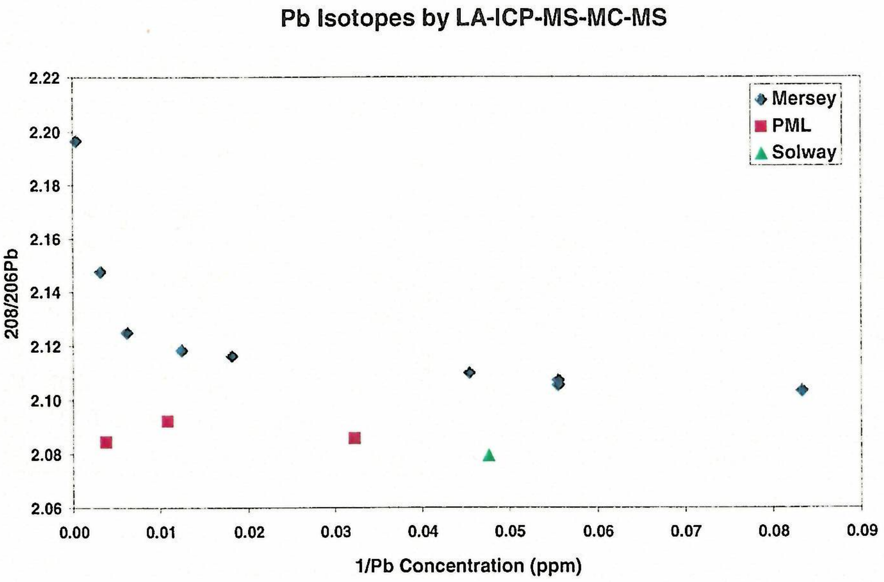

Figure 39. A plot of $^{208/206}$Pb isotope ratios (determined by LA-MC-ICP-MS) versus 1/Pb concentrations (determined by XRF) showing source mixing curve for R. Mersey samples.

Within the overall range of ratios found, the agreement between the to methods is very good. But close inspection of Figure 40 below, showed a small discrepancy between the two techniques. In particular this seemed to affect samples with low concentrations. Investigation as to the cause of this is on-going, but the data are still deemed 'fit for purpose'.

Table 16a Lead isotope ratios and their associated internal errors determined by Sol-MC-ICP-MS in 8 sediment samples from the Mersey.

	Mean					2 Standard Error of the Mean (SEM)				
	$^{206/204}$Pb	$^{207/204}$Pb	$^{208/204}$Pb	$^{207/206}$Pb	$^{208/206}$Pb	$^{206/204}$Pb	$^{207/204}$Pb	$^{208/204}$Pb	$^{207/206}$Pb	$^{208/206}$Pb
6146-16	18.10	15.59	38.01	0.8616	2.100	0.0017	0.0015	0.0037	0.0000	0.0001
6146-17	18.10	15.60	38.03	0.8617	2.101	0.0013	0.0011	0.0031	0.0000	0.0001
6146-19	18.12	15.60	38.04	0.8609	2.100	0.0024	0.0022	0.0053	0.0000	0.0001
6146-26	18.02	15.59	37.93	0.8652	2.105	0.0015	0.0013	0.0030	0.0000	0.0001
6146-20	17.88	15.58	37.78	0.8718	2.113	0.0017	0.0015	0.0034	0.0000	0.0001
6146-18	17.79	15.54	37.65	0.8735	2.116	0.0026	0.0024	0.0060	0.0000	0.0001
6146-21	17.68	15.56	37.56	0.8800	2.124	0.0012	0.0010	0.0025	0.0000	0.0000
6146-23	17.28	15.53	37.10	0.8988	2.147	0.0010	0.0010	0.0027	0.0000	0.0001

Table 16b Lead isotope ratios and their associated internal errors determined by LA-MC-ICP-MS in 8 sediment samples from the Mersey.

	Mean					2 Standard Error of the Mean (SEM)				
	$^{206/204}$Pb	$^{207/204}$Pb	$^{208/204}$Pb	$^{207/206}$Pb	$^{208/206}$Pb	$^{206/204}$Pb	$^{207/204}$Pb	$^{208/204}$Pb	$^{207/206}$Pb	$^{208/206}$Pb
6146-16	18.01	15.58	37.92	0.8652	2.105	0.0057	0.0031	0.0093	0.0002	0.0004
6146-17	17.97	15.58	37.87	0.8667	2.107	0.0058	0.0026	0.0085	0.0002	0.0005
6146-19	18.05	15.59	37.95	0.8636	2.103	0.0066	0.0031	0.0082	0.0002	0.0006
6146-26	17.93	15.58	37.85	0.8685	2.110	0.0072	0.0038	0.0142	0.0003	0.0007
6146-20	17.80	15.56	37.68	0.8741	2.116	0.0043	0.0022	0.0081	0.0002	0.0003
6146-18	17.77	15.56	37.65	0.8756	2.118	0.0040	0.0021	0.0079	0.0002	0.0003
6146-21	17.64	15.54	37.49	0.8810	2.125	0.0032	0.0023	0.0079	0.0001	0.0003
6146-23	17.19	15.48	36.92	0.9002	2.148	0.0063	0.0029	0.0097	0.0002	0.0004

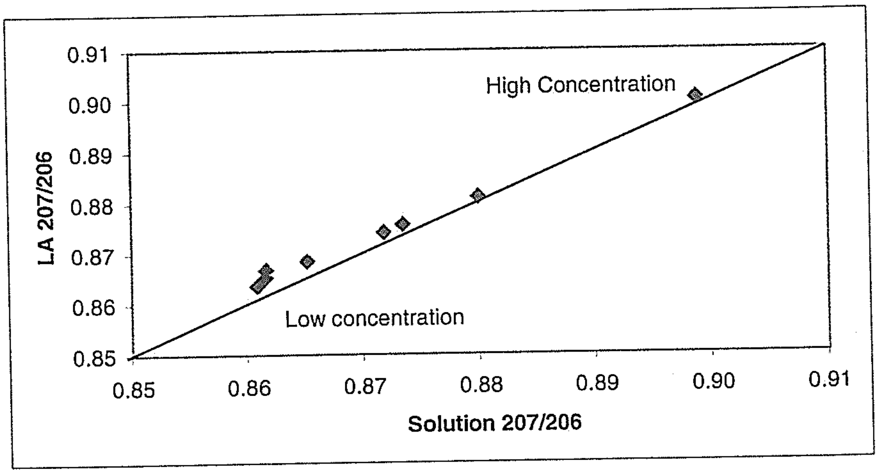

Figure 40 A plot of 207/206Pb isotope ratios of 8 samples from the R. Mersey determined by solution and laser ablation MC-ICP-MS. Note the small discrepancy at low concentrations

5.3.3 Main Sample Sets from Mersey and Solway Catchments

Tables 17a and 17b report the determined lead isotope ratios (and errors) in 30 samples from the river Mersey and 19 samples from the Solway catchment respectively. In addition to the acquisition of new data from the collected samples, an extensive literature review was made to determine representative lead isotope ratio values that might form the natural geogenic input to the Mersey and Solway. These consisted of values determined in galenas and reported in the recent past (typically since 1980), using established TIMS techniques from trusted laboratories. Thus much of the data is derived from the NIGL laboratories. A summary of this data is produced below in Table 18.

Table 17a. Lead concentrations and lead isotope ratios in sediments from the R. Mersey

Sample Number	Concentration (mg/kg)	$^{207/206}$Pb	$^{208/206}$Pb	$^{206/204}$Pb	$^{207/204}$Pb	$^{208/204}$Pb
6146-22	2326	0.9399	2.197	16.46	15.47	36.17
6146-23	314	0.9002	2.148	17.20	15.48	36.93
6462-10	265	0.8772	2.121	17.75	15.57	37.65
6462-81	177	0.8892	2.136	17.49	15.55	37.35
6146-21	161	0.8810	2.125	17.64	15.54	37.49
6462-33	136	0.8650	2.106	18.02	15.59	37.95
6462-30	114	0.8690	2.115	17.93	15.58	37.92
6462-146	94	0.8726	2.114	17.83	15.56	37.70
6146-18	80	0.8756	2.119	17.77	15.56	37.64
6462-125	79	0.8752	2.119	17.77	15.55	37.66
6462-152	74	0.8750	2.118	17.78	15.55	37.65
6462-140	69	0.8763	2.120	17.75	15.55	37.63
6462-113	56	0.8710	2.112	17.87	15.57	37.76
6146-20	55	0.8740	2.116	17.81	15.56	37.68
6462-110	48	0.8716	2.113	17.86	15.56	37.74
6462-162	47	0.8785	2.123	17.71	15.56	37.59
6462-2	35	0.8652	2.108	18.01	15.58	37.96
6462-119	34	0.8731	2.117	17.82	15.56	37.72
6462-83	29	0.8702	2.112	17.89	15.57	37.79
6462-56	27	0.8682	2.110	17.94	15.57	37.84
6146-26	22	0.8685	2.110	17.93	15.57	37.84
6146-25	19	0.8691	2.110	17.90	15.55	37.77
6146-16	18	0.8652	2.106	18.01	15.58	37.92
6146-17	18	0.8668	2.107	17.97	15.58	37.87
6146-24	18	0.8668	2.107	17.97	15.57	37.85
6462-131	17	0.8667	2.108	17.98	15.59	37.91
6146-27	16	0.8616	2.098	18.08	15.58	37.94
6462-75	15	0.8664	2.108	17.98	15.57	37.89
6146-19	12	0.8638	2.103	18.05	15.59	37.95
6462-134	10	0.8595	2.098	18.14	15.59	38.06

Table 17b. Lead concentrations and lead isotope ratios in sediments from the Solway catchment.

Sample Number	Concentration (mg/kg)	$^{207/206}$Pb	$^{208/206}$Pb	$^{206/204}$Pb	$^{207/204}$Pb	$^{208/204}$Pb
6462-6	182	0.8485	2.084	18.36	15.58	38.27
6462-7	178	0.8469	2.083	18.39	15.57	38.31
6462-49	178	0.8537	2.092	18.20	15.54	38.08
6462-47	125	0.8545	2.093	18.19	15.55	38.08
6462-18	78	0.8491	2.085	18.38	15.61	38.33
6462-14	69	0.8518	2.090	18.32	15.60	38.28
6462-26	29	0.8538	2.092	18.23	15.57	38.14
6462-41	27	0.8488	2.084	18.34	15.57	38.22
6462-25	25	0.8469	2.083	18.39	15.57	38.31
6146-04	21	0.8460	2.079	18.42	15.58	38.30
6462-55	17	0.8485	2.084	18.36	15.58	38.27
6462-29	14	0.8473	2.083	18.40	15.59	38.33
6462-19	14	0.8486	2.084	18.37	15.59	38.29
6146-5	13	0.8463	2.081	18.44	15.60	38.37
6146-9	13	0.8470	2.083	18.42	15.60	38.37
6146-2	12	0.8454	2.080	18.39	15.55	38.25
6146-10	12	0.8466	2.082	18.47	15.64	38.45
6146-12	12	0.8478	2.084	18.38	15.58	38.30
6146-1	10	0.8425	2.074	18.49	15.57	38.33

Table 18. Lead isotope ratios in galenas from relevant different ore provinces in the north of England and Scotland

		207/206Pb	208/206Pb	206/204Pb	207/204Pb	208/204Pb
Pennines (Barreiro, 1995; Barreiro and Spiro, 1997)	Mean	0.846	2.08	18.44	15.60	38.37
	2sd	0.007	0.01	0.14	0.07	0.25
Mendips (Haggerty *et al.*, 1996)	Mean	0.846	2.08	18.50	15.65	38.47
	2sd	0.005	0.01	0.13	0.03	0.12
Wales (Fletcher *et al.*, 1993)	Mean	0.856	2.10	18.30	15.65	38.38
	2sd	0.009	0.02	0.20	0.07	0.26
Orkney (Parnell and Swainbank, 1985)	Mean	0.8829	2.143	17.445	15.393	37.375
	2sd	0.0392	0.075	0.974	0.175	0.823
Southern Uplands (Parnell and Swainbank, 1984)	Mean	0.8514	2.090	18.286	15.564	38.208
	2sd	0.0095	0.012	0.241	0.057	0.361
Midland Valley (Parnell and Swainbank, 1984)	Mean	0.8536	2.094	18.215	15.547	38.134
	2sd	0.0094	0.018	0.252	0.094	0.281
Grampians (Parnell and Swainbank, 1984)	Mean	0.8680	2.113	17.833	15.477	37.668
	2sd	0.0218	0.039	0.526	0.091	0.523

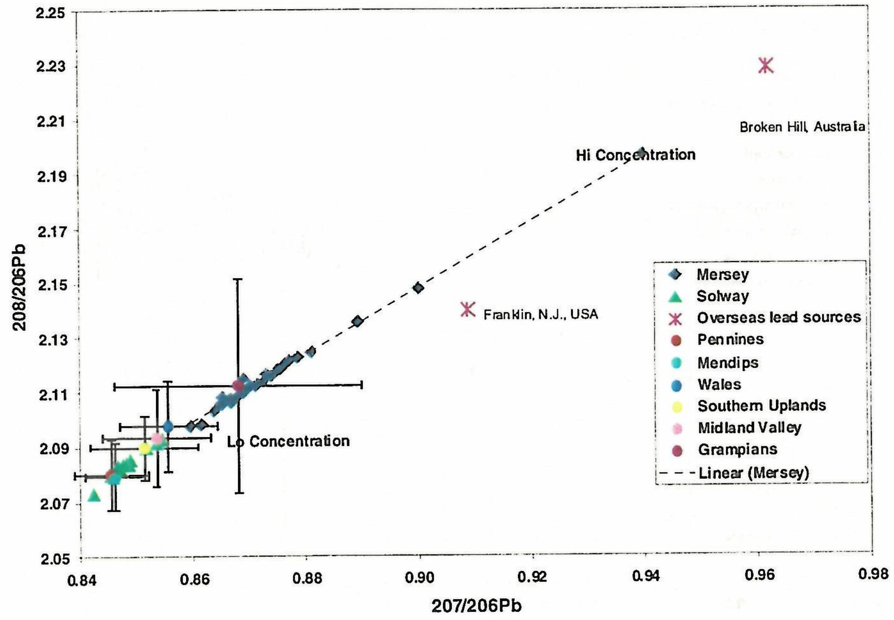

Figure 41a. A plot of $^{207/206}$Pb isotope ratio versus $^{208/206}$Pb isotope ratio for sediment samples from the R. Solway and R. Mersey catchments. Also shown, Pb isotope ratios from some British lead ore sources and likely world lead ore sources for comparison. Note, high concentrations in these river sediments have a significant Broken Hill Type (BHT) signature. See text for further explanation.

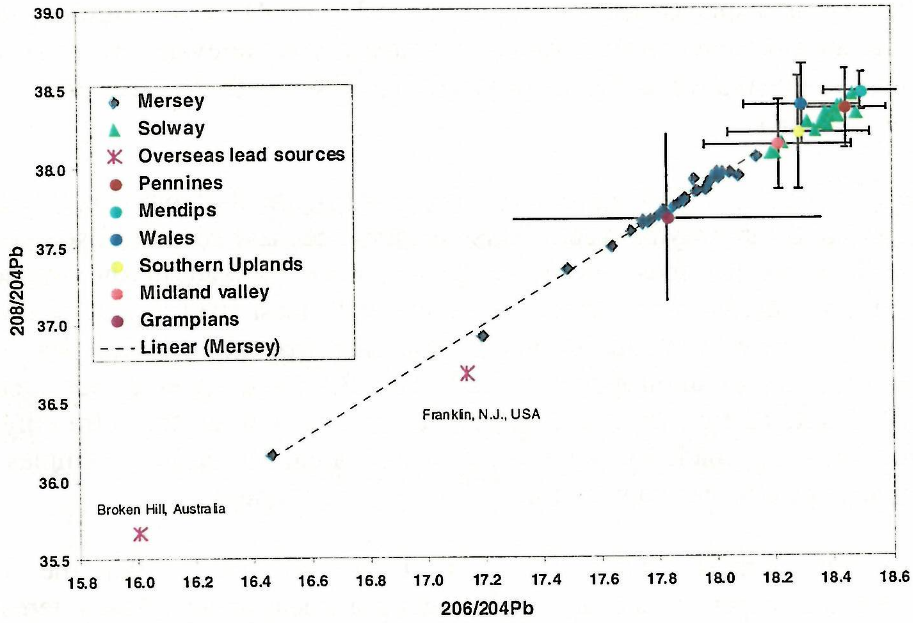

Figure 41b. A plot of $^{206/204}$Pb isotope ratio versus $^{208/204}$Pb isotope ratio for sediment samples from the R. Solway and R. Mersey catchments. Also shown, Pb isotope ratios from some British lead ore sources and likely world lead ore sources for comparison. Note, high concentrations in these river sediments have a significant Broken Hill Type (BHT) signature. See text for further explanation.

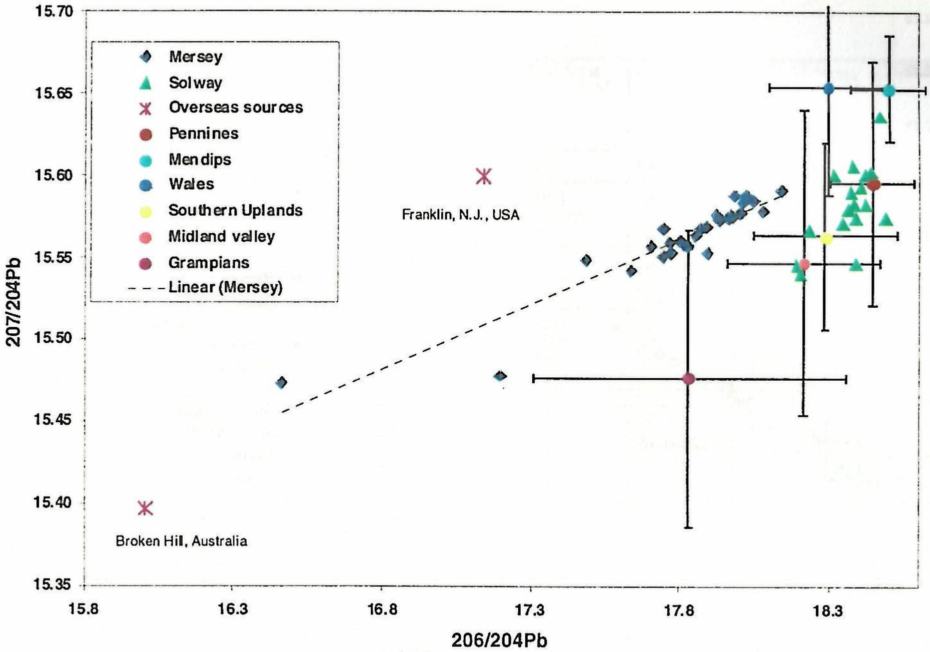

Figure 41c. A plot of $^{206/204}$Pb isotope ratio versus $^{207/204}$Pb isotope ratio for sediment samples from the R. Solway and R. Mersey catchments. Also shown, Pb isotope ratios from some British lead ore sources and likely world lead ore sources for comparison. Note, high concentrations in these river sediments have a significant Broken Hill Type (BHT) signature. See text for further explanation.

The full data set is displayed graphically above in Figure 41a-c. In addition the data from the literature of lead isotope ratios in galenas from relevant provenances are shown. These are displayed as means of several analyses with 2σ error bars to show likely range of values.

Using the $^{208/206}$Pb v $^{207/206}$Pb ratio plot (Figure 41a), the full data set for the R. Mersey shows a linear array between British lead sources and BHT lead sources. The Pennine lead seems the most likely geogenic source of lead in the Mersey on geographical grounds. However, even the sample with least BHT signature does not approach the Pennine signature in value, implying that all the samples have a component of overseas anthropogenic lead. The BHT source is almost certainly Broken Hill itself, as this was used extensively in the UK as the tetra-ethyl lead additive for petrol and made by Octel in the Mersey area. The Solway samples all fit within the range of UK lead sources for $^{208/206}$Pb v $^{207/206}$Pb ratios.

Figure 41b demonstrates similar features to Figure 41a except that the Solway samples are more dispersed and do not following a linear array. Most interestingly Figure 41c shows some structure within the Solway samples. A majority have a Pennine lead signature but trending towards the Southern Uplands and Midland Valley. However, one or two samples are offset towards overseas anthropogenic lead.

5.3.4 *Down-Core Lead Isotope Profile*

Seven samples from a core taken at Seaforth at the mouth of the Mersey Estuary were analysed to determine whether variations in lead concentrations were related to isotopic ratios and therefore lead sources. Results are given in Table 19 and the Pb concentration and $^{208/206}$Pb ratio plotted in Figure 42.

Table 19. Lead concentrations, $^{208/206}$Pb ratios and sample depths for the Seaforth 1 sediment core from the Mersey estuary.

Depth (cms)	Pb Concentration (mg/kg)	$^{206/204}$Pb	$^{207/204}$Pb	$^{208/204}$Pb	$^{207/206}$Pb	$^{208/206}$Pb
0-5	92	17.7992	15.5526	37.6552	0.8738	2.1156
5-10	94	17.7839	15.5394	37.6202	0.8738	2.1154
10-20	65	17.7757	15.5421	37.6106	0.8743	2.1158
20-30	69	17.7839	15.5406	37.6244	0.8739	2.1156
30-50	81	17.6739	15.5442	37.5174	0.8795	2.1228
50-70	109	17.5133	15.5201	37.3322	0.8862	2.1317
70-100	100	17.3995	15.5076	37.2243	0.8913	2.1394
Average 2sem errors		0.0076	0.0037	0.0120	0.0003	0.0005

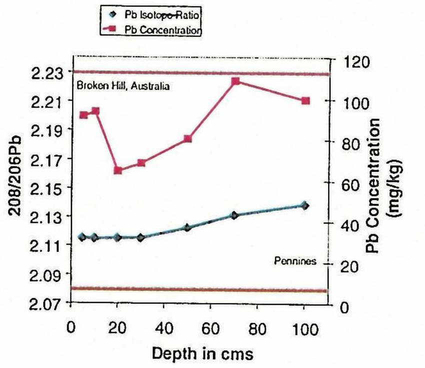

Figure 42. Plot of $^{208/206}$Pb against depth for a sediment core from Seaforth (see Fig. 32). End-member isotope ratios for Pennine and Broken Hill lead sources are shown as horizontal lines. See text for further explanation.

It can clearly be seen that although at 20 cms depth there is a significant drop in lead concentration and then an increase to a maximum at 70 cms depth, the lead isotope signature varies smoothly from a more geogenic Pennine signature at shallow depths to a more overseas BHT anthropogenic signature at a depth of 100 cms. This suggests that although the lead concentrations at Seaforth have not significantly improved in the most recent sediment, the original source was significantly different.

5.3.5 *Spatial Distribution of Lead Isotope Ratios*

The spatial distribution $^{208/206}$Pb isotope ratios and total Pb concentrations in selected Mersey basin samples are plotted in Figures 43a & b. As shown above the highest Pb concentrations are associated with a BHT lead signature. It is also apparent when considering the drainage and data that a simple diffuse contamination model is not appropriate and that point sources may be more significant. In particular the most contaminated sample i.e. highest lead concentration and best BHT signature is from next to an oil refinery in the Manchester Ship Canal. The second most contaminated sample, to the east, is also from the Manchester Ship Canal and the fourth, nearer the estuary mouth, is from near an oil terminal. Interestingly the third most contaminated site was somewhat different, being sited on the R. Tame (E or righthand side of figure 43a), just downstream of the M66 motorway and a sewage works. Both are likely sources of lead with a Broken Hill signature, either from petrol or industrial waste.

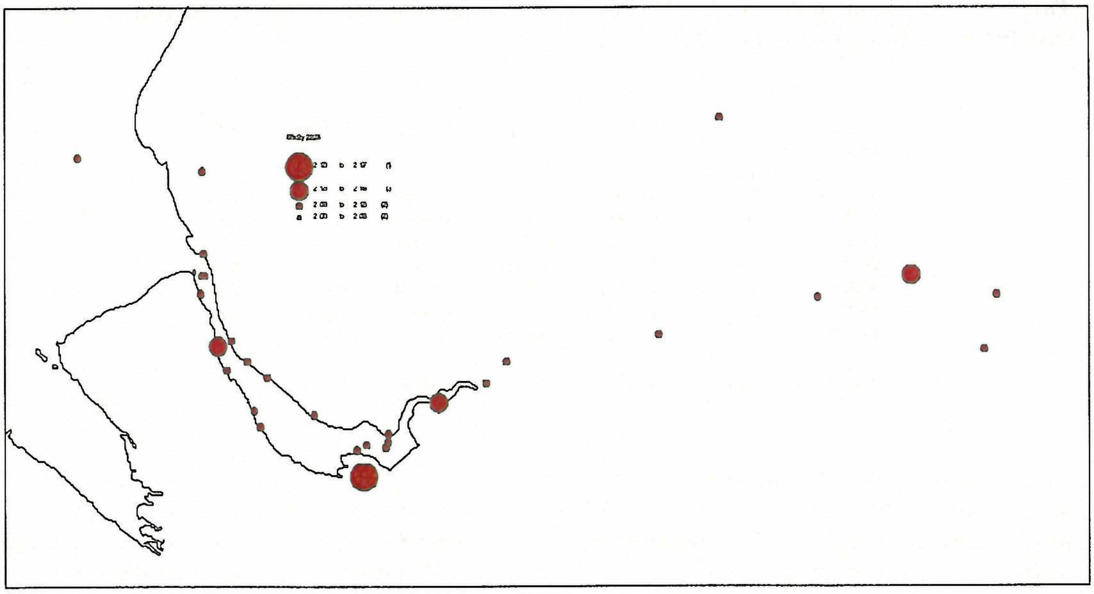

Figure 43a. Distribution of $^{208/206}$Pb ratios in selected samples from the Mersey drainage basin. See text for further information.

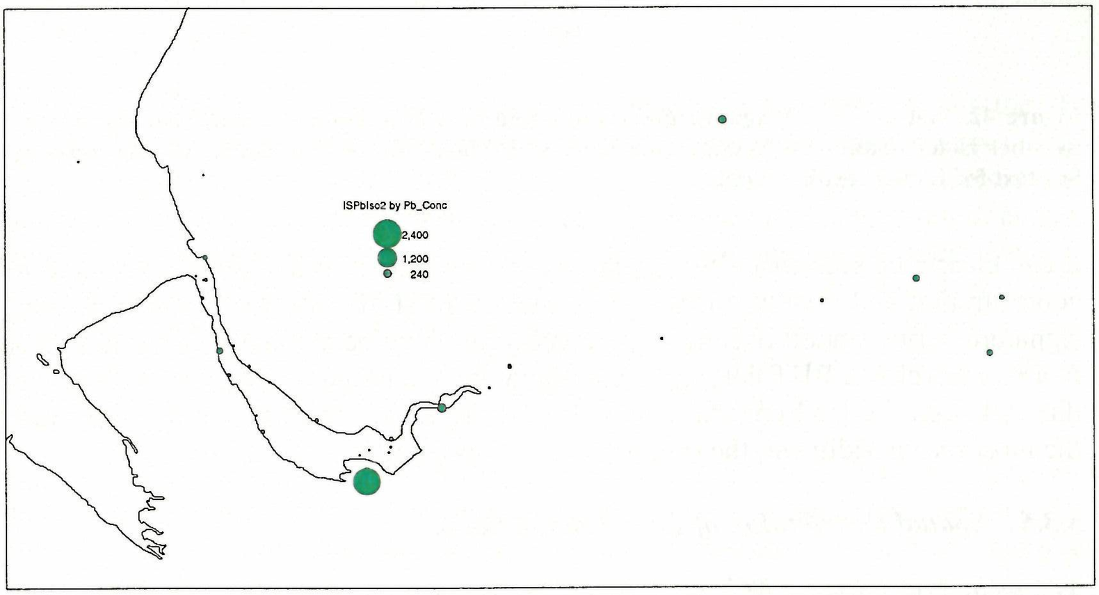

Figure 43b. Distribution of total Pb concentrations in selected samples from the Mersey drainage basin., for comparison with Figure 43a. See text for further information.

For comparison, the site with the least addition of BHT lead was at New Brighton. This is at the mouth of the river, adjacent to a domestic rather than industrial area. In addition, the sediments were more sandy than many. All these parameters have combined to minimise the contamination by overseas lead.

5.4 Summary: Lead Isotopes

It was originally envisaged that a majority of the analyses in this study would be performed using MC-ICP-MS after dissolution of powdered samples and chemical separation of the lead. The use of laser ablation techniques (LA) to determine Pb isotopic ratios only became a possibility after the study began. The LA results, validated by comparison with data generated using conventional dissolution techniques with solution based MC-ICP-MS, demonstrate that it is possible to rapidly obtain high quality lead isotopic information from sediments using LA-MC-ICP-MS on pressed powder pellets prepared for XRF. This produces significant savings in costs and time.

Specifically, it was observed that:

1. There are differences in Pb isotope ratios between samples from the Mersey, Solway and PML in-house reference materials as determined by LA-MC-ICP-MS. These differences are considered to reflect different sources of the sediments.
2. The isotopic composition of the samples from the Mersey formed an array between two Pb isotope end-members, one member similar to that expected from local geology (Pennines) and the other of Broken Hill Type (BHT), a major industrial source in the UK's recent past.
3. The highest lead concentrations in the Mersey samples were associated with high concentrations of the BHT end-member.
4. When integrated with other chemical and geographic information, Pb isotopic ratio data can provide important evidence on the sources of Pb in sediments. Thus relatively low absolute concentrations of Pb may nonetheless be linked to anthropogenic sources.

6 PART C BIOAVAILABILITY

6.1 Background and Rationale

There are various routes by which sediment metals reach the biota. For example, in sediment-dwelling bivalves, uptake may occur following the ingestion of particles, or by pinocytosis at the body surface. In addition, direct uptake of easily-desorbed forms may take place during contact between particles and surface tissues. The partitioning of metals among various sediment phases, and the quantity and nature of metal-binding ligands, will clearly have a significant bearing on bioaccumulation. In particular, the comparative rates of assimilation of anthropogenic and natural fractions are likely to be controlled by sediment characteristics. Sediments may even moderate uptake in species where bioaccumulation from solution appears the dominant pathway, since metals in pore water (or overlying water) may ultimately be controlled by equilibria with fractions adsorbed onto particulate phases (Langston and Bryan, 1984).

Understanding sedimentary processes is clearly a major long-term goal in pollution research and a significant factor in policy-making. The current project aims (which are strongly linked with those of the BGS component) contribute to this subject by addressing the following objectives:

1. To assess methods which effectively demonstrate whether the metals in estuarine and coastal sediments are biologically available.

2. To establish a means of distinguishing the relative contribution of the anthropogenic and natural sources of metals to any biological uptake or effect that may occur.

3. Hence to recommend methodology for use in other estuarine and coastal areas of the Irish Sea

6.2 Methodology

The project objectives were addressed by the following means:

1. Review of literature and information (including existing PML databases) to refine the protocols for characterising sediment-metals and assessing bioavailability.

2. Test protocols on new field material (sediment and biota) collected from estuarine and near-shore sites in the Mersey, Wyre, Ribble and Solway Firth.

3. A laboratory mesocosm experiment to look at uptake in sediment cores from these same sites

Briefly, the protocols adopted were as follows:

Under field conditions, identification of dominant processes which modify bioavailability can sometimes be achieved by observing the goodness-of-fit between metal concentrations in ubiquitous deposit-feeding species and levels in various types of sediment-extract over a wide spectrum of sediment types (Bryan and Langston, 1992). For the study of metal bioavailability in Irish Sea estuarine and near-shore sediments, such an approach has been be applied to field samples from the Mersey, Wyre, Ribble and Solway Firth systems. These were chosen to represent a range of river/estuarine/offshore systems with contrasting geological background, hydrodynamic and physico-chemical properties, and differing degrees of anthropogenic inputs. The Mersey is a major industrial estuary renowned for its history of contamination whilst the inner Solway has no major direct inputs of significance. The Ribble and Wyre were anticipated to represent estuaries of intermediate status in terms of metal sources. Information on previously published research and unpublished PML/MBA data, gathered during the initial phase of the current project, has been reviewed in an earlier section. 'In-house' data has been drawn upon here to supplement gaps and support conclusions from the current project and is considered to provide 'added-value', since techniques, sampling sites, bioindicator species and analytical methods are consistent throughout.

In order to test the goodness-of-fit between biota and their particulate environment the form of metals in the sediment were compared with body burdens. 'Chemical speciation' techniques, based on operationally-defined chemical extraction procedures (e.g. Tessier & Campbell, 1987), were applied to estuarine and marine sediments (to complement the geological fingerprinting scheme employed by BGS). Some surface water and pore-water determinations were also made at the study sites in order to evaluate their relationship with accumulated body burdens.

Normalisation procedures are usually considered essential when comparing sediment contamination, and several schemes were examined here in attempting to derive the most appropriate methodologies to forecast tissue burdens. Since anthropogenic concentrations and bioavailabilities of metals in sediments are often influenced by granulometry and physicochemical factors (such as the metal-binding components Fe/Mn oxyhydroxides, organics, salinity and redox) their roles were the subject of special consideration.

Estuarine inter-tidal surveys pose few problems, logistically, though extensive field sampling, particularly offshore, is costly. Moreover there is no 'universal bioindicator' which occurs naturally in both offshore and estuarine sediments. Therefore it was considered essential to adopt an experimental approach in order to compare the full range of sediment types in the Irish Sea. The methodology tested here involved exposure of benthic organisms to sediment cores of estuarine and marine nature (from the same suite of survey sites in the Mersey, Ribble, Wyre and Solway) in a laboratory mesocosm. Metal accumulation was determined after 6 months and compared with sediment characteristics in order to determine if this is a feasible technique to screen for sediment-metal bioavailability.

Thus, the field-survey element of the programme assesses, *in situ,* the effects of estuarine and coastal influences on bioaccumulation from Irish Sea estuary sediments. The laboratory (mesocosm) component is used partly to validate field observations, and partly to address, in a more generic fashion, whether or not sediment (irrespective of origin), represents a potential threat to biota in terms of enhanced bioaccumulation.

6.3 Field Sampling

The survey work was intended, primarily, to determine the influence of natural and anthropogenic sediment-metal loadings on accumulated metal levels in field populations. Sampling was based on a range estuaries bordering the Irish Sea and involved simultaneous collections of surface sediments and, where present, native benthic biota to act as bioindicators.

At the same time sampling also involved collection of intact cores at estuarine and offshore locations for the laboratory mesocosm experiment on metal bioavailability (see below).

The major sampling effort in the Mersey, Wyre, Ribble and Solway Firth regions took place between 18th and 21st July 1999. Two teams were involved, one working from the shore to sample the inter-tidal estuarine sites (upper and lower estuary) and the second team sampling from RV Roagan at offshore sites (outside the estuary mouth). The locations of these sites is indicated in Table 20 and in Figure 44.

Table 20. Sampling sites, Irish Sea, July 1999

SITE		SAMPLE TYPE	O.S. REF	LAT (N)	LONG (W)
Mersey lower (Rock Ferry)	M/L	Surface sed; cores; biota; water	sj340862		
Mersey upper (Eastham)	M/U	Surface sed; cores; biota; water	sj370812		
Mersey offshore	M/O	Surface sed; cores; water		53 32.00	03 18.39
Ribble lower (Lytham)	R/L	Surface sed; cores; biota; water	sd346270		
Ribble upper (Naze mount)	R/U	Surface sed; cores; biota; water	sd425269		
Ribble offshore	R/O	Surface sed; cores; water		53 42.73	03 18.96
Solway lower (Skinburness)	S/L	Surface sed; cores; biota; water	ny136564		
Solway upper (Port Carlisle)	S/U	Surface sed; cores; biota; water	ny232628		
Solway offshore	S/O	Surface sed; cores; water		54 36.70	03 42.47
Wyre lower (Knott End)	W/L	Surface sed; cores; biota; water	sd345485		
Wyre upper (Hambleton)	W/U	Surface sed; cores; biota; water	sd364429		
Wyre offshore	W/O	Surface sed; cores; water		53 59.27	03 00.26

At each of the offshore sites nine cores were obtained for the mesocosm study by deploying a box corer ($0.1m^2$) from the RV Roagan and sub-coring each box with a 300mm x 150mm (i.d.) plastic pipe. The ends of each pipe were capped and cores returned to PML. Particular attention was given to maintaining the integrity of the cores during collection and transport. Additional samples of surface sediment (100-200g) for metal analysis were scraped into sealable polythene bags and temporarily stored on ice in a vacuum flask for transport back to the laboratory, where they were sieved and processed immediately. Equivalent surface samples were also stored, frozen, for analysis by BGS. A further core was taken at each site and redox profiles measured using a platinum spear electrode inserted at measured depth intervals (see Appendix 5.1 for data).

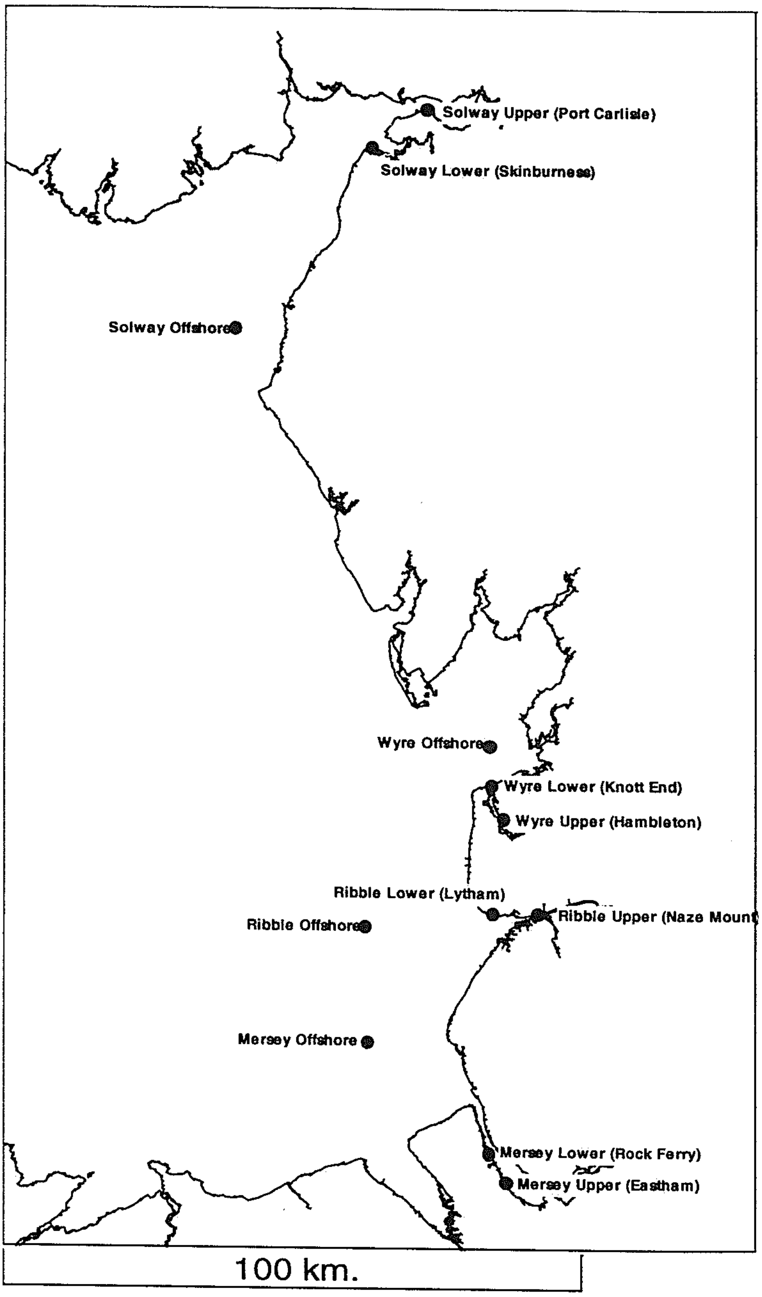

Figure 44. Irish Sea: sampling sites

At the 'upper' and 'lower' estuarine locations in each of four systems, six replicate cores were obtained, by sampling inter-tidally. The 300mm x 150mm (id) plastic pipe was pressed into the sediment and dug out by hand. These cores were capped for deployment in the mesocosm, and returned to Plymouth, along with additional samples of surface sediment (for analysis of metals).

At the majority of estuarine sites the deposit-feeding clam *Scrobicularia plana* (Fig. 45) was collected as an *in-situ* bioindicator of bioavailable sediment metal. *Scrobicularia plana* was chosen as the preferred bioindicator of sediment metal bioavailability in estuaries based on our own earlier evidence which suggests that *S.*

plana is responsive to most sediment metals (see, for example, Bryan *et al.,* 1985, from work supported by DoE under contract DGR/480 51). This deposit-feeding clam occurs in the majority of estuaries in England and Wales and is among the most salinity tolerant of molluscs. Previous records of the limits of distribution of *S. plana* were used to define the 'upper' and 'lower' estuarine sites in the current project

Where present, up to 30 *Scrobicularia plana* of similar size (3-4cm) were sampled at the 'upper' and 'lower' sites in the four estuaries. This level of replication has been shown to be capable of resolving differences in bioavailability of between 15 and 30%, depending the on metal (Bryan *et al.,* 1980). *S. plana* was not found in the upper Solway and was replaced here by a related, though slightly smaller deposit - feeding clam *Macoma balthica* (belonging to the same taxonomic group as *S. plana* - the Tellinacea- and believed to be a comparable bioindicator for most metals; see Fig. 45). Because of the small number of *Macoma* samples, data from the current project was combined with previous data from the Mersey, Ribble, Wyre and Solway estuaries to provide at least a preliminary evaluation of its responses to metals in sediments. These additional samples of *Macoma* were collected and analysed by identical methods during the 1990s.

A further candidate species for evaluating bioavailability *in situ*, the ragworm *Nereis diversicolor* (Fig. 45), was sampled at the estuarine sites. Approximately 100 *Nereis* were collected at each site.

All animals were maintained in sediment from the respective sites and transported live to PML in cool boxes for subsequent depuration of gut contents (which might otherwise contribute to body burdens and hence measures of bioavailability). The relative merits of clams and worms as bioindicators have been reviewed elsewhere (Bryan *et al.,* 1985; Langston and Spence, 1995).

Surface water samples were taken at each site (estuarine and offshore) to determine salinity, pH and a number of metals. Sub-samples of 1L were filtered immediately (0.45µm) for dissolved metal analysis and a further 1L retained for 'total' metals (particulate + dissolved). All samples were acidified with 1ml concentrated nitric acid (ARISTAR) to preserve them until analysed.

6.4 Mesocosm Experiment

The methodology being tested here involves seeding uncontaminated sediment-dwelling organisms into sediment cores from the Irish Sea. By observing accumulation of metals over time, in an environmentally-controlled system, and relating this to physico-chemical characteristics of the sediment it is hoped to glean further information on determinants of bioavailability, to complement field data. Laboratory-scale techniques such as this probably represent the only cost-effective means of assessing bioavailability in offshore sediments, since direct methods involving collection of native fauna in sufficient numbers, at appropriate locations, may be prohibitively expensive and impractical (Langston *et al.,* 1999).

The major obstacle in attempting to evolve a generic 'bioavailability' technique, for all Irish Sea sediment types and habitats is the salinity issue. There are no bioindicators which are appropriate or capable of tolerating both the fully marine conditions of the open sea and the lowered salinity regimes encountered in estuaries.

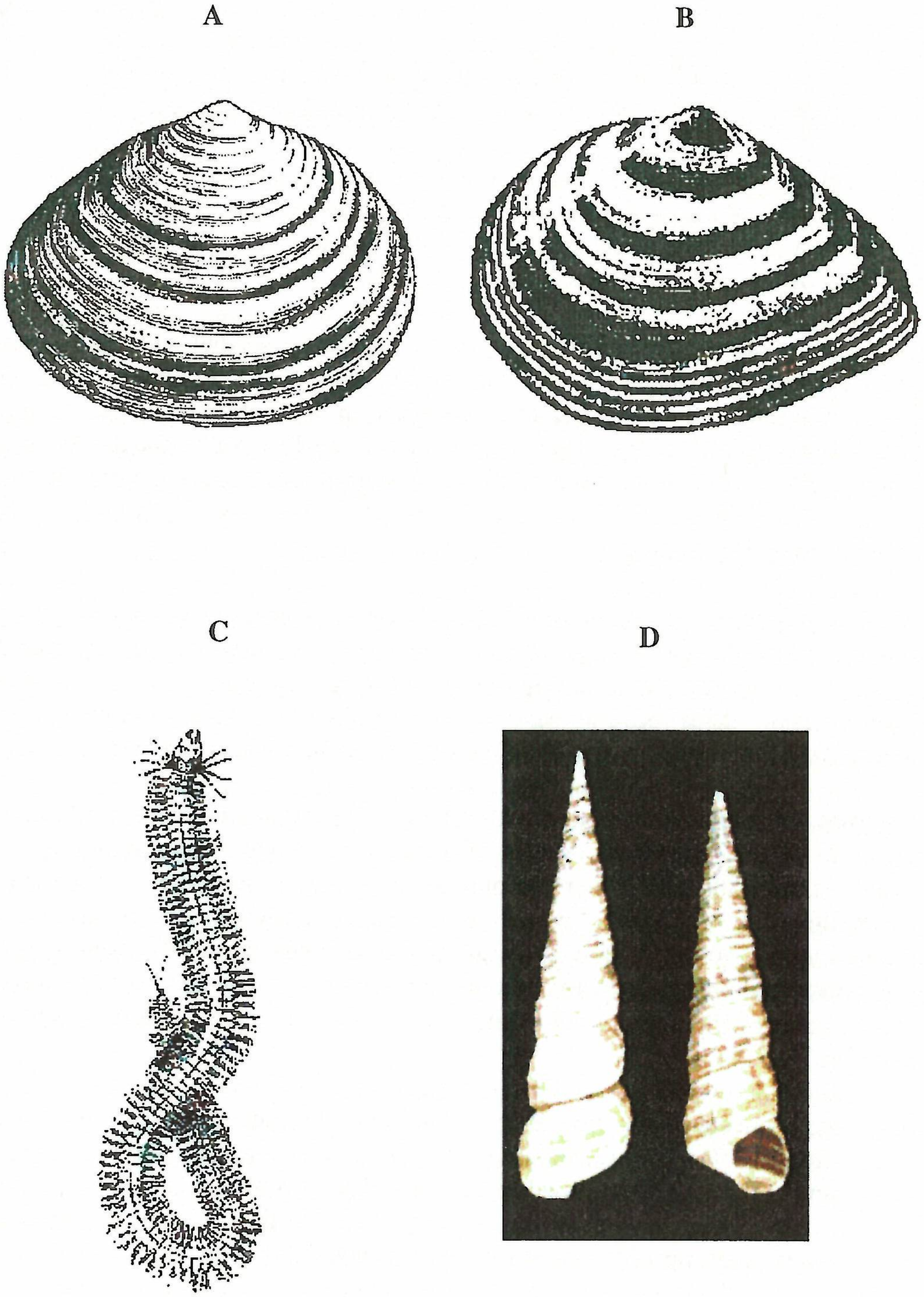

Figure 45. Species used as indicators of bioavailable sediment metal: *Scrobicularia plana* (A); *Macoma balthica* (B), *Nereis diversicolor* (C) and *Turritella communis* (D).

In an attempt to surmount the salinity problem and to compare metal bioavailability in offshore and estuarine sediments, two mesocosm systems were deployed, at 35 ‰ and 28 ‰, respectively. Each system housed a set of three replicate cores from upper, lower and offshore sites from each of the four study estuaries (Mersey, Ribble, Wyre, Solway). Any visible native macrofauna was firstly removed from the cores. Once installed in the mesocosm facility, the cores were maintained for two weeks in order to stabilise and condition them prior to seeding with macrofaunal species.

The lower salinity system (28 ‰) was maintained at temperature of 12 °C, and all cores were seeded with six specimens (2-3cm) of the estuarine clam *S. plana.* collected from a relatively metal-free site (Skern) at the mouth of the Torridge Estuary, North Devon. (OS reference SS442 308).

The higher salinity system (35 ‰) was also held at 12°C and seeded with the marine gastropod *Turritella communis* (Fig. 45). This species was used with some success in an earlier mesocosm study on metal bioavailability in sediments from the central North Sea (Langston *et al.*, 1999). *Turritella* were collected by Naturalist dredge and Agassiz trawl (*RV Squilla*) from a site relatively free from metal contamination in the English Channel, off Plymouth (Rame Head 50°16.50'N-4°14.10'W). Ten individuals were placed in each of the cores.

Before their introduction into cores, on 6th August 1999, *Scrobicularia* and *Turritella* were held for up to a week in clean sea water in the laboratory and any moribund animals discarded. Mortality rates during this period were negligible, however. At the start of the exposure three replicate samples of both *Turritella* (10 individuals) and *Scrobicularia* (six individuals) were taken for analysis as baselines (time zero).

The mesocosm systems were supplied with a flow of conditioned, oxygenated water (originating from the Eddystone Reef, off Plymouth) which was monitored for temperature, salinity and pH. Water samples were also taken periodically for metal analysis (unfiltered only). After a period of 6 months, redox profiles in sediments were checked again (no major changes were observed) and cores were then sieved. Retrieved organisms were allowed to depurate (removal of gut contents) for one week in clean sea water of the appropriate salinity, and stored at -20 °C, briefly, prior to metal analysis.

A further three replicate cores from each of the four offshore sites were held in a separate system at 35‰ and seeded with *S. plana*. The objectives of this sub-experiment were: 1) to test the survival and adaptability of *S. plana* as a bioindicator organism by determining accumulation characteristics of these clams at the two different salinities; 2) to provide insights on how bioavailability in sediments differs between estuarine and marine systems (i.e. mimicking the transition that particles undergo during their exchange between riverine sources and the sea); 3) assess the versatility of the methodology in extrapolating between sediment types and conditions.

6.5 Sample Preparation and Chemical Analysis

6.5.1 Sediments

Sieving. Metal contamination may vary with sediment granulometry, therefore standardisation of metal concentrations, with respect to grain size, has been employed by sieving samples prior to chemical analysis. Furthermore, anthropogenic loadings are often preferentially bound to fine silt and clay particles, i.e. those fractions which are processed preferentially by most filter-feeders and detritivors. Sieving therefore fulfils two functions - firstly, to normalise the data (making comparisons between sites more valid) and, secondly, to place emphasis on particles which are accepted by benthic organisms. Sieving at 100µm was the preferred option for biological work in this project, since it has precedents in our previous bioavailability studies and incorporates the range of particle types accepted by most deposit-feeders. In the laboratory the surface sediment samples were sieved through 100µm polypropylene mesh with 50% sea water (estuarine samples) or 100% sea water (marine samples) and the fines allowed to settle so that the water could be decanted. The resulting sediment slurry was well mixed before dispensing aliquots for metal analysis and determinations of water and organic content.

Other normalisation techniques. Additional, geochemical normalisation has further advantages over purely granulometric techniques, and may compensate for the mineralogical, as well as the size-dependant variability of the sediment. These techniques are referred to earlier in this report. Included among the mineralogical normalisers tested here were Al and Rb. Though they are not traditional geogenic normalising elements, iron (oxyhydroxides) and organic matter - two of the most important metal-binding ligands - have also been evaluated as normalisers in the current work. Because of their metal sequestration properties, Fe and organic coatings may also have an important influence on bioavailability. This hypothesis was investigated as part of the current programme.

The methods of sediment normalisation applied included the use of simple metal/normaliser ratios and the comparison of slopes from regression lines. An acknowledged problem with the latter however is the influence of significant intercept values for some metals.

Measurement of sediment organic matter was based on the loss in weight of dried (80°C) sediment after heating at 400°C for 6 h in a silica crucible. After both the preliminary drying and ashing stages, the sediment was allowed to cool for 1h in a desiccator before weighing. Since sediments had been treated with either 50% (estuarine samples) or 100% sea water (offshore samples), and their water content was known, the results were corrected for errors due to the loss in weight of seawater salts at 400°C.

6.5.2 Extraction and digestion of sediment-bound metals:

Three alternative sediment extraction techniques were tested as surrogate measures of bioavailable metal. In increasing order of strength (pH) these were:

1) 1M ammonium acetate (AmAc) (ion-exchangable, readily extractable forms)

2) 1M HCl (reducible forms, crystalline oxide phases)
3) concentrated HNO_3 digestion ('total metal')

In the 'total digest', wet-sieved (100μm) sediment samples were refluxed with concentrated nitric acid (HNO_3) using closed, pressurised microwave techniques. It should be noted that this may not extract all metals completely (though any remaining metal is unlikely to be bioavailable). Analysis of IAEA-356 reference sediment illustrates typical recoveries by this method, based on comparison with dissolution in hydrofluoric acid (Table 21). Recoveries for Co, Cr and Fe in sediment appear low because the HNO_3 digest does not remove highly refractory forms. For other metals >80% is extracted by HNO_3.

Table 21. Recovery of metals from reference sediment QC-IAEA-356 by digestion with concentrated HNO_3

	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn	As	Hg
Recovery %	60.7	72.6	97.7	73.3	83.1	82.1	93.4	100.4	87.6	86.3

Bearing in mind that some sediment-fractions which are probably *not* biologically available will be solubilised and analysed in this strong mineral acid matrix, the two weaker extracts (1M HCl and AmAc) were investigated as alternative 'mimics' of bioavailable sediment metal. In these less-aggressive treatments each sample (wet sediment) was continuously stirred with 1M HCl or 1M AmAc for two hours at room temperature, and the extract separated from sediment by pressure filtration through a 0.45μm membrane filter, prior to metals analysis.

6.5.3 Treatment of biological samples.

All biological samples from the field were returned in cool boxes to PML as quickly as possible. The organisms were held in clean sea water for one week to 'clean-up' prior to analysis (i.e. purging of sediment-bound metals from the digestive system to ensure only biologically incorporated metals are measured). *Scrobicularia plana* and *Macoma balthica* (deposit-feeding clams) were cleaned in 50% aerated sea water for 7 days. As far as possible, each sample for analysis comprised the soft parts 5 or 6 adult *S. plana* of 20-40mm shell length, or the soft parts of 10 or more *M. balthica* of 12 to 18 mm length. To remove sediment from the body surfaces and the gut of *Nereis diversicolor*, worms were kept in acid-washed sand covered with 50% sea water for 6 days followed by one day in water. Pooled samples containing about 20 worms were used for analysis and as far as possible animals having a dry weight of 20 to 40 mg were used.

Tissues were dissected from shells where necessary (molluscs), and pooled individuals from each site frozen whole in clean glass beakers at -20°C, prior to freeze-drying at -80°C and 10^{-3} torr. All samples were then homogenised by grinding to a fine powder in a ceramic mortar and pestle, and stored in glass vials. Sub-samples of freeze-dried homogenate were digested with concentrated HNO_3 for metal analysis, using the microwave-assisted procedures outlined for sediment 'totals'. These samples were diluted and made up to volume with distilled water for analysis. Triplicate samples form each site were analysed wherever possible.

6.5.3.1 Analysis

Metals, including arsenic, silver, cadmium, copper, chromium, iron, mercury, manganese, nickel, lead, selenium, and zinc were analysed in sediment and tissue digests and extracts by atomic absorption techniques.

Most determinations for Ag, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn were carried out by flame atomic absorption using an air-acetylene flame (Varian AA20). Background correction was employed for all metals except Cu, Fe, Mn and Zn. Low concentrations of metals such as Ag and Cd were determined by graphite furnace atomic absorption using standard addition methods (Varian 300 Zeeman).

Flameless AA methods were used in the measurement of volatile or hydride-forming elements, using either stannous chloride (Hg) or sodium borohydride (As, Se) as reducing agents (Perkin-Elmer FIAS and MHS-20 hydride system). Concentrations of all elements were expressed on a dry weight basis.

In water samples, elevated concentrations of Mn, Fe, Zn and Cu were measured by flame AAS. Other metals were analysed by graphite furnace atomic absorption spectrometry. For low levels of Cu, Fe, Pb, Cd, Ni and Co, 100ml subsamples were extracted using the method of Danielsson *et al.* (1982). Briefly, metals were sequestered using a mixed buffer/complexing reagent (APDC/DDDC), extracted into Freon-TF, and back extracted into nitric acid solution for analysis by flame or furnace AA. Thus, low levels of metals were separated from the saline matrix, and concentrated by a factor of 20, prior to analysis. Arsenic was determined by hydride generation, after reducing any As present in the water samples to As^{3+} in 5% hydrochloric acid (HCl) and 1% potassium iodide (KI) solution at 70°C. All concentrations in waters are expressed as µg/l.

Analysis of spiked seawater samples gave recoveries >90% for Cu, Pb, Cd, Ni and Co. Recoveries from reference seawater (SLEW) are shown in Table 22.

Table 22. Recovery of metals from reference sea water SLEW

	Co	**Cu**	**Fe**	**Mn**	**Ni**	**Zn**	**As**
% recovery	86	123	68	117	86	107	87

6.6 Results

6.6.1 Sediment characterisation: trends and normalisation routines

Sediment geochemistry and metal distributions in Irish Sea samples have been characterised in several ways with a view to testing which of them best represents bioavailable fractions in field and mesocosm studies. Raw data for 'total' and extractable sediment metals, water and biota are held by PML.

In comparing sediment metal concentrations between sites, differences due to bulk grain-size characteristics have been eliminated, to a large extent, by sieving (<100μm). Once granulometric effects are minimised using this procedure, distinctions in 'total' (HNO_3-extractable) sediment-metal concentrations between the stations reveal relevant information on contamination patterns. The most significant feature was the trend towards decreasing concentrations northwards, away from the Mersey, though for some metals gradients were less than anticipated (Fig. 46).

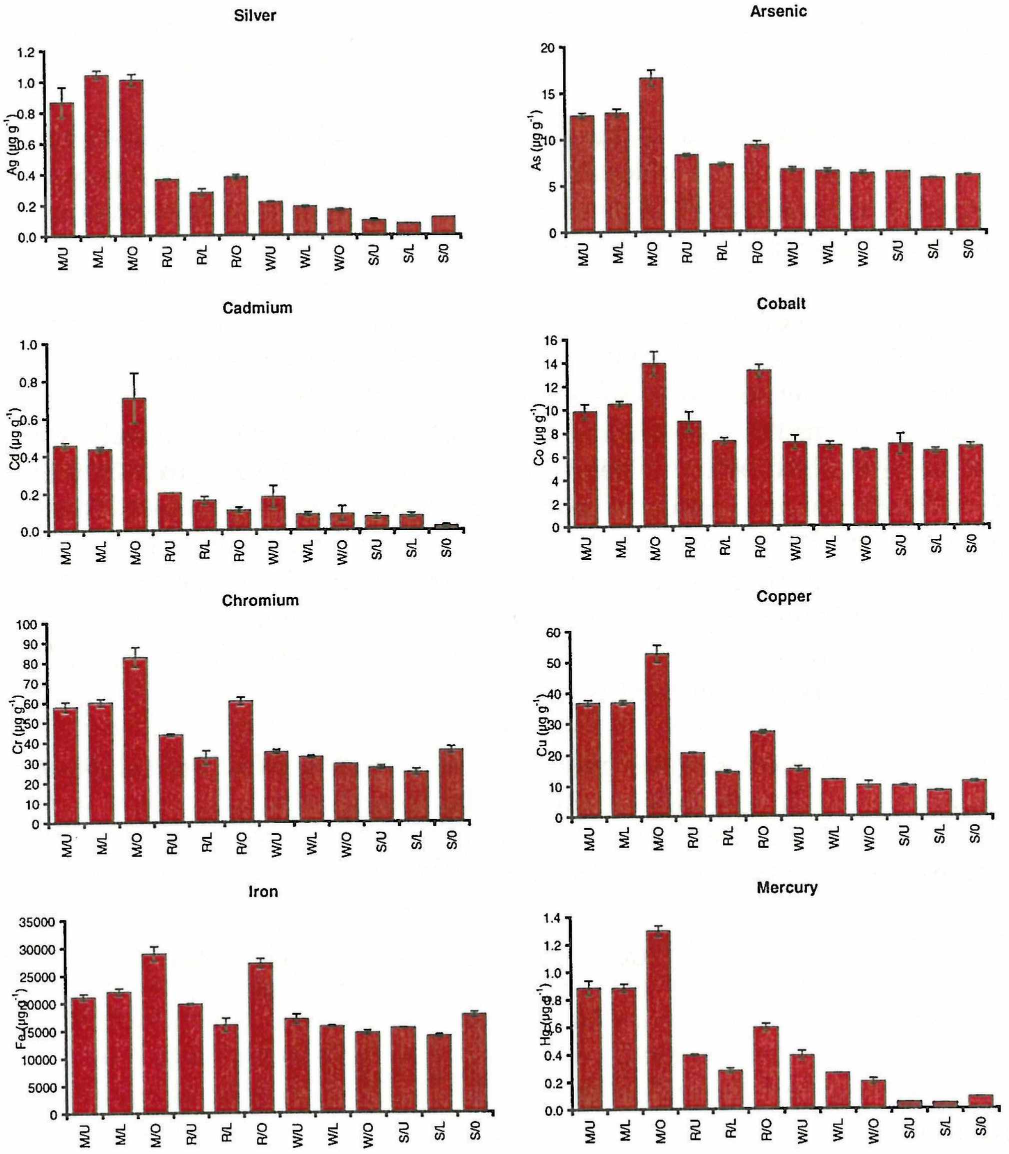

Fig 46. Total (HNO_3-digestable) metals (m ± sd, μg g^{-1}) in Mersey (M), Ribble (R), Wyre (W) and Solway (S) sediments (/U,/L,/O, - upper, lower and offshore sites). Continued....

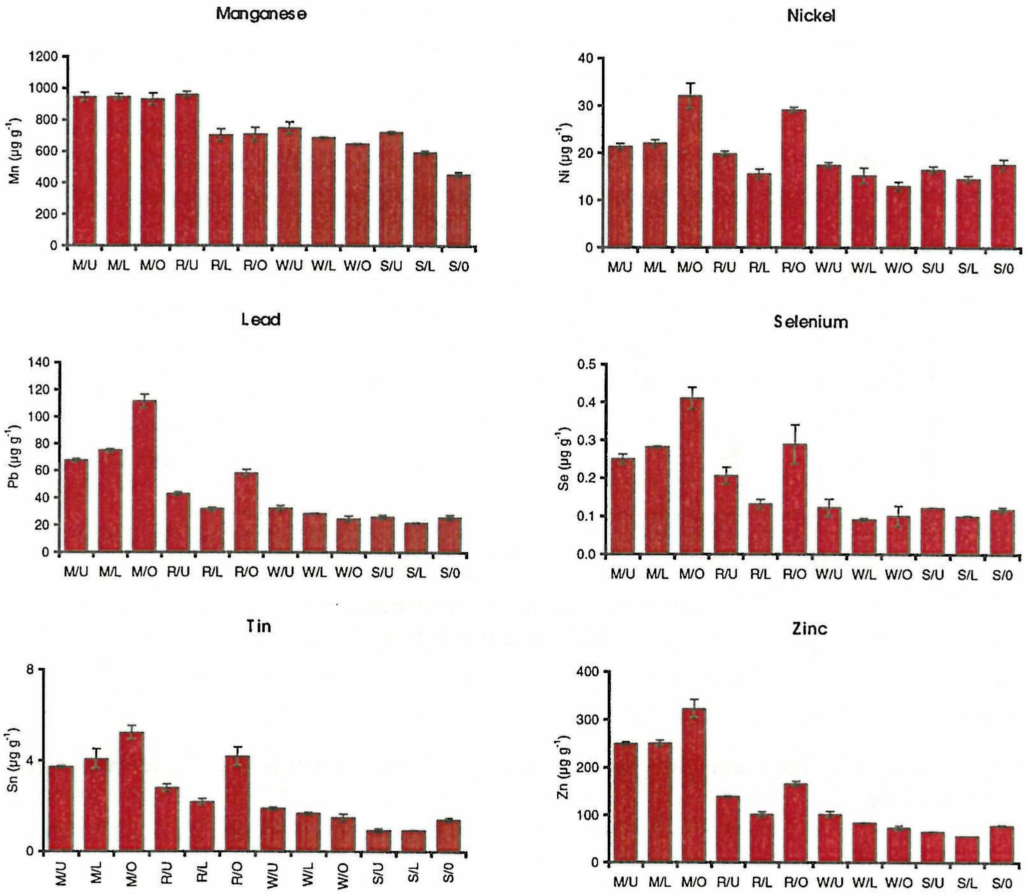

Fig 46. (cont). Total (HNO_3-digestable) metals (m ± sd, µg g^{-1}) in Mersey (M), Ribble (R), Wyre (W) and Solway (S) sediments (/U,/L,/O, - upper, lower and offshore sites).

It is worth noting here results from a comparison of sieving and analysis techniques between PML and BGS. In their procedure for analysis of sediment metals BGS traditionally uses the <150µm fraction for its data sets (analysed by OES/XRF) as compared to the <100µm fraction used at PML (analysed by AAS). This diversity might be suspected of introducing difficulty in data comparisons. However an intercalibration exercise between laboratories during this project indicated significant correlations for most metals, despite different sieving regimes and analytical methods (see linear regression equations, Table 23)[1]. The similarity in data for the majority of metals tested shows that, provided some grain size standardisation is carried out, the exact mesh size selected for sieving may not be critical, particularly for estuarine and offshore muds which contain a high proportion of fine silts and clays. Results from the two laboratories are likely to give comparable impressions of contamination despite variations in techniques, as indicated in Figure 47 for Cu, and in the relationships shown in Table 23.

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[1] Note: Ag, Cd, Hg and Se were not quantified by BGS in the current comparison. Note also the slope of the regression line was <1 for Cr and Sn - HNO_3 probably underestimates the true total for these metals because of inability to extract highly refractory forms e.g. cassiterite, SnO_2

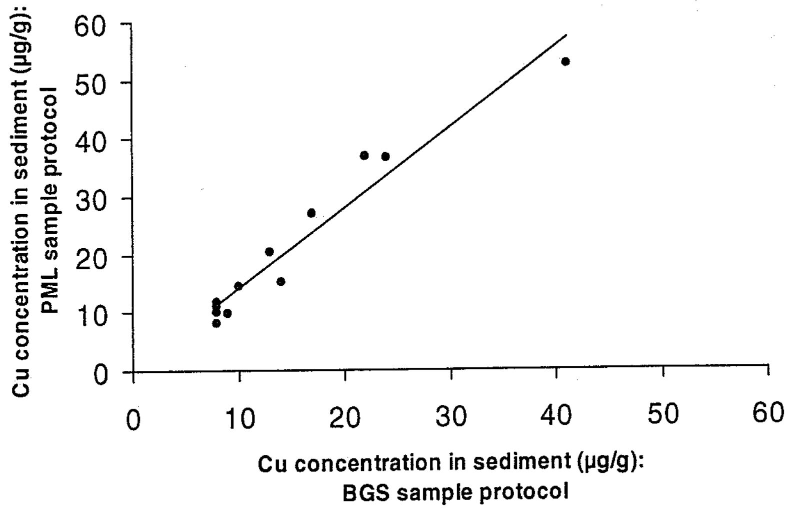

Figure 47. Comparison of PML and BGS methodology for Cu in sediments. For linear regression parameters see Table 23.

Table 23. Comparison of PML and BGS methodology: linear regression parameters

metal	regression equations	R^2	P
As	y = 1.5509x - 2.5641	0.904	P<0.00001
Cr	y = 0.7301x - 17.468	0.7687	0.00018
Cu	y = 1.3932x + 0.0623	0.9443	P<0.00001
Fe	y = 1.1067x - 890.8	0.7855	0.00012
Mn	y = 0.9161x + 172.9	0.4637	0.01477
Ni	y = 1.0638x + 1.3572	0.7289	0.00041
Pb	y = 1.4427x - 8.0122	0.9595	P<0.00001
Sn	y = 0.319x + 0.446	0.8474	0.00002
Zn	y = 1.1502x + 9.458	0.9595	P<0.00001

y= metal concentration after PML sieving and analysis protocol
x=metal concentration after BGS sieving and analysis protocol

Expected downstream gradients in metal concentrations between Mersey upper, lower and offshore sites were not detected. The reasonably homogenous distribution of metals in sediments throughout the area is consistent with the concept of a single population of fines, with a significant component of transport from Liverpool Bay back into the estuary, competing with the seaward movement of riverine particulates. Landward transport of Liverpool Bay fines (and perhaps more localised contaminated marine deposits), assisted by prevailing winds and residual currents, may also explain why sediments off the mouth of the Ribble (and, more remotely, the Solway) were, if anything, slightly higher than those upstream. In contrast the gradients of metal contamination (and bioavailability) in the less-exposed Wyre Estuary were more consistent with seaward transport and sedimentation of riverine/land-based particulates within the estuary. Here metal enhancement was highest upstream.

This overall pattern of sediment origin, movement and deposition is supported by the geological fingerprinting evidence provided by BGS. However their suggested interpretation of slightly higher values at outer estuary sites in the Solway and Ribble invokes winnowing of metal rich particulates in the inner estuary and re-deposition further towards the sea. It would be interesting to pursue the mechanisms of enrichment further in future studies.

Distinctions in size-normalised values between the four Irish Sea estuaries were greatest for 'pollutant' metals (Hg, Ag, Cd, Sn, Zn, Cu, Pb, As, Cr and Se), reflecting their anthropogenic origins, and less so for the more common 'geological' elements such as Fe, Mn, Co and Ni. Enhancement of each metal in Mersey, Ribble and Wyre sediment relative to the Solway (assumed to represent baseline values for the region) is shown in Figure 48 for upper and lower estuarine sites and for the offshore station. Though Mersey sediments were consistently most elevated above baselines, for all pollutant metals (notably for Hg by up to 22-fold), the ranking of enrichment of metals in each of the estuaries was broadly similar.

Across the entire data-set there was significant co-variance between nearly all metals ($P<0.05$ in 89 out of a possible 91 permutations, Table 24) which suggests that their distributions are determined by a combination of common sources of metal inputs (dominated by the Mersey) and shared geological/geochemical attributes.

Table 24. Correlation matrix for metals in Irish Sea sediments. All values are significant ($P<0.05$) except for those marked*

	ORG	Ag	As	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Se	Sn	Zn
ORG	1														
Ag	0.708	1.000													
As	0.768	0.963	1.000												
Cd	0.683	0.935	0.965	1.000											
Co	0.880	0.755	0.850	0.715	1.000										
Cr	0.829	0.885	0.951	0.862	0.951	1.000									
Cu	0.799	0.951	0.994	0.947	0.888	0.976	1.000								
Fe	0.850	0.741	0.839	0.706	0.986	0.961	0.884	1.000							
Hg	0.779	0.949	0.980	0.949	0.861	0.958	0.989	0.855	1.000						
Mn	0.803	0.797	0.758	0.784	0.593	0.661	0.752	*0.546**	0.768	1.000					
Ni	0.843	0.699	0.821	0.694	0.980	0.941	0.865	0.991	0.828	*0.516**	1.000				
Pb	0.811	0.928	0.989	0.940	0.902	0.978	0.994	0.897	0.978	0.721	0.885	1.000			
Se	0.879	0.868	0.944	0.853	0.966	0.982	0.964	0.957	0.932	0.695	0.949	0.973	1.000		
Sn	0.858	0.890	0.928	0.834	0.952	0.977	0.956	0.943	0.953	0.718	0.909	0.949	0.967	1.000	
Zn	0.778	0.973	0.993	0.951	0.856	0.960	0.996	0.853	0.988	0.775	0.825	0.982	0.943	0.948	1

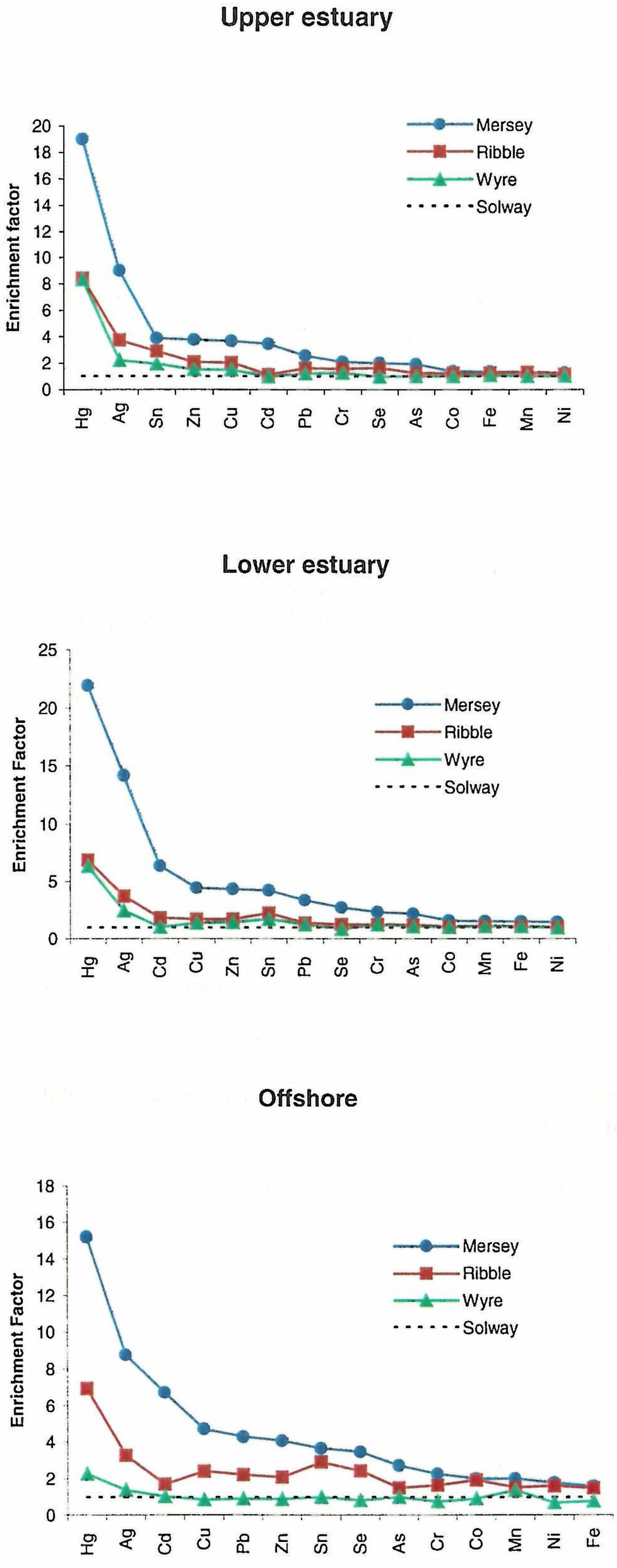

Figure 48. Comparison of metal enrichment in sediments (totals) from upper, lower estuary and offshore sites, relative to equivalent Solway baseline values.

To examine the influence of the latter, residual variation in metal loadings was investigated by looking at relationships with the major metal-binding substrates, Fe (oxyhydroxides) and organics, and also with Al and Rb (inert markers of fine-grained fractions, such as clays, which usually have a high natural metal content) - in effect performing additional geochemical 'normalisation' procedures to explain variation. Initial inspection of the normalised distributions, illustrated by Cu in the example shown in Figure 49, suggests that the selection of the normalising element may not be critical in sieved samples. A similar conclusion can be drawn for most metals, in that relative distribution patterns, between sites, did not change appreciably with the choice of normaliser. The only minor exceptions to this rule occurred with some of the geogenic metals, for example Co, where normalisation - particularly to Fe - tended to flatten out any gradient across sites because of the strong correlation between these two metals (Fig. 50).

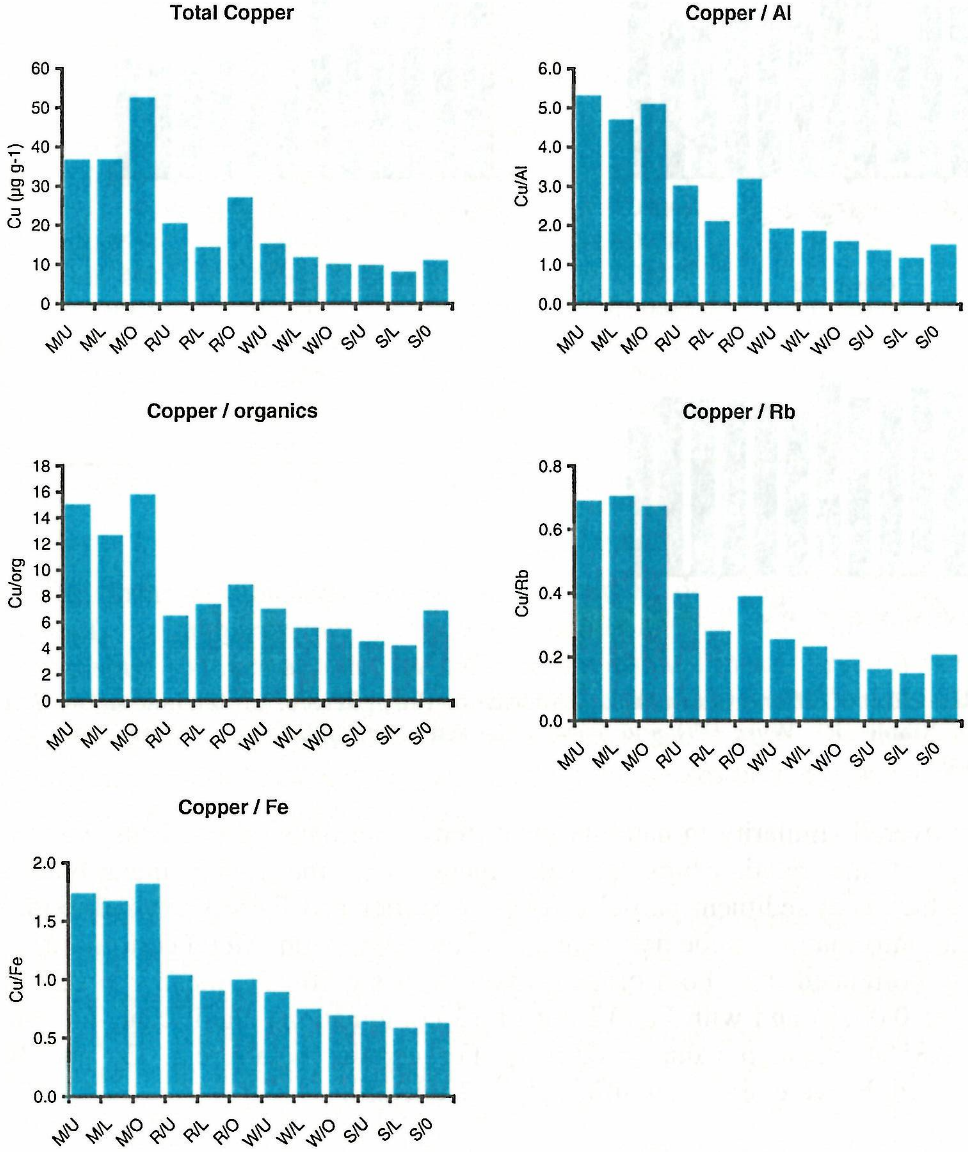

Figure 49. The effect of different normalising elements on the pattern of contamination for Cu in Mersey (M), Ribble (R), Wyre (W) and Solway (S) sediments (/U,/L,/O, - upper, lower and offshore sites)

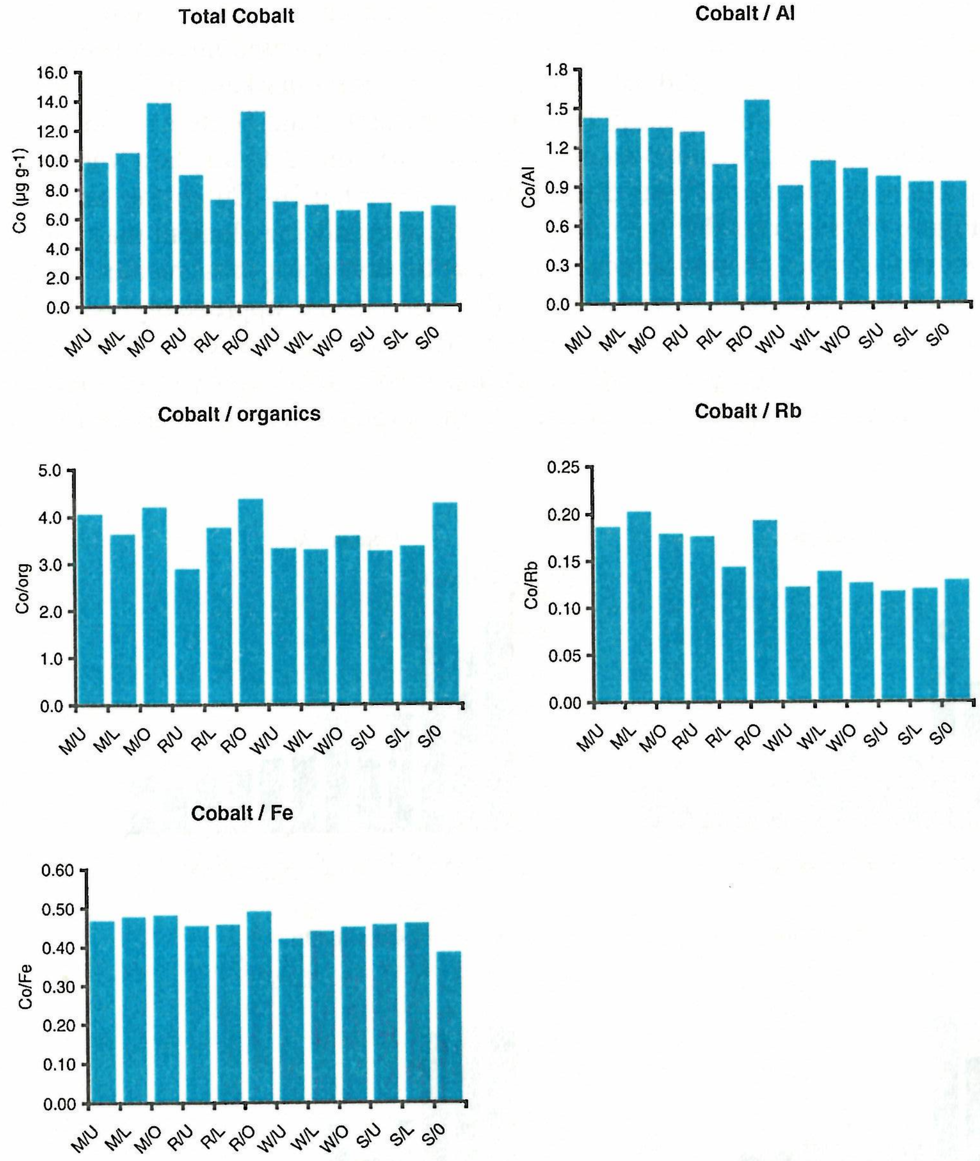

Figure 50. The effect of different normalising elements on the pattern of contamination for Co in Mersey (M), Ribble (R), Wyre (W) and Solway (S) sediments (/U,/L,/O, - upper, lower and offshore sites).

Despite the overall similarity in patterns for different normalising elements, detailed comparisons of the relationships between metals and the major metal-binding substrates which coat sediment particles (organic matter and Fe/Mn oxyhydroxides) reveal further information on the determinants of contamination. Metal concentrations were widely correlated with both organic matter (all significant, mean r = 0.8049, mean p value 0.0029) and with Fe (12 out of 13 combinations significant -not Mn- mean r = 0.8584, mean p value = 0.0064). For certain metals, e.g. Co and Ni, correlations with Fe were highly significant (see Table 25).

Whilst most metals (except Ni and Fe) covaried with Mn (oxyhydroxide), the mean r of 0.6988, and mean p value of 0.025 (Table 25), suggests this phase was less significant than organics and Fe in influencing trace element distributions (confirmed by paired t-test , $P<0.05$).

It is important to stress that the current results concern benthic sediments (mainly of geogenic origin). Metals associated with suspended particles (often predominantly biogenic) may have different affinities including a greater organic association (notably, those metals such as Cd and Cu, which have a strong affinity for microalgae).

Table 25. Comparison of r, P values for relationships between metals vs Fe, organics and Mn in Irish Sea sediment samples (whole data-set)

	Fe		**organics**		**Mn**	
	r	p	r	p	r	p
Ag	0.7405	0.0059	0.7082	0.01	0.7966	0.0019
As	0.8388	0.00065	0.7677	0.0036	0.7584	0.0043
Cd	0.7056	0.0104	0.6829	0.014	0.7841	0.0025
Co	0.9858	4.4E-09	0.8803	0.00016	0.5931	0.042
Cr	0.9608	0.000001	0.8292	0.00085	0.6606	0.019
Cu	0.8844	0.00013	0.7989	0.0018	0.7522	0.0048
Fe	-	-	0.8500	0.00046	0.5468	0.066
Hg	0.8554	0.00039	0.7792	0.0028	0.7678	0.0035
Mn	0.5468	0.066	0.8034	0.0017		-
Ni	0.9908	5E-10	0.8426	0.00058	0.5164	0.086
Pb	0.8967	0.000078	0.8114	0.0014	0.7207	0.082
Se	0.9574	0.000001	0.8791	0.00017	0.6949	0.012
Sn	0.9434	0.000004	0.8579	0.00036	0.7182	0.0085
Zn	0.8526	0.00043	0.7777	0.0029	0.7749	0.0031
mean	0.8584	0.0064	0.8049	0.0029	0.6988	0.026

Specific linear relationships between metals and Fe or organics were also observed frequently in samples from individual estuaries and illustrate further how simple 'normalising' routines account for much of the residual metal variability in Irish Sea samples (see examples for Hg, Figure 51). These associations reflect the fact that Fe (and to a lesser extent Mn) oxyhydroxide phases and organic coatings are a major determinant of metal levels in surface fines. These phases probably account for a high proportion of anthropogenic loadings.

Consequently, the slopes of regression lines varied between estuaries (depending on the degree of contamination) and were invariably greatest in the Mersey (see example for Hg in Figure 51 and regression data in Table 26). The slope parameter is, therefore, potentially, a means of quantifying the extent of anthropogenic influence. In the current data-set the relationships between metals and Fe were generally better than those with organics (compare statistically significant, highlighted, entries in Table 26), though this may partly have been influenced by the smaller range in organic values in some estuaries. The application of regression models may be confounded further by the varying intercept value which may necessitate more sophisticated treatment (e.g. through the use of residuals (Rowlatt and Lovell, 1994b). In the current project, the simple normalised ratio of metal : Fe (or organics) will serve as a marker of anthropogenic enrichment in attempting to derive the most suitable surrogate measures of sediment metal-bioavailability (see later section).

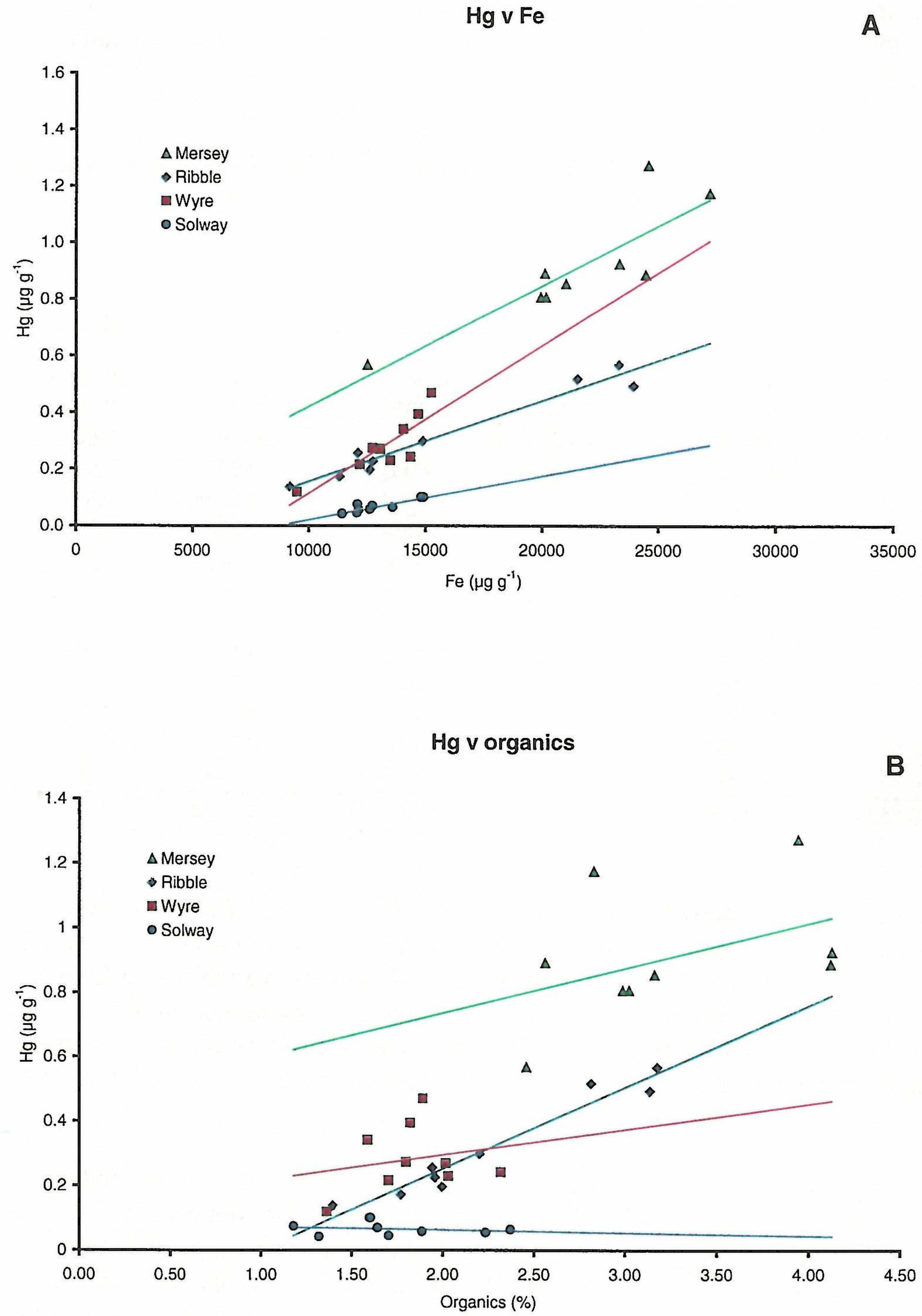

Figure 51. Linear regression models showing relationships between Hg vs Fe (A) and organics (B) in sediments from individual estuaries

Table 26. Regression model parameters for metals vs Fe and organics in sediments from individual Irish Sea estuaries. Highlighted values are statistically significant.

Relationships between metals and Fe in sediments

	Mersey			Ribble			Wyre			Solway		
	slope x 10^{-5}	r	P	slope x 10^{-5}	r	P	slope x 10^{-5}	r	P	slope x 10^{-5}	r	P
Ag	1.5	0.606	n.s.	2.3	0.956	***	2.9	0.976	***	2.4	0.686	*
As	44.2	0.829	**	32.6	0.983	***	39.4	0.661	n.s.	34.5	0.789	*
Cd	3.7	0.838	**	-0.4	-0.787	*	2.3	0.641	n.s.	-1.5	-0.314	n.s.
Co	31.2	0.892	**	48.0	0.983	***	36.0	0.801	**	61.3	0.777	*
Cr	285	0.960	***	273	0.991	***	245	0.986	***	265	0.915	***
Cu	166	0.932	***	117	0.992	***	137	0.977	***	99.8	0.915	***
Hg	4.3	0.861	***	2.8	0.979	***	5.2	0.853	**	1.5	0.892	**
Mn	2900	0.875	**	1120	0.788	*	2900	0.605	n.s.	1000	0.187	n.s.
Ni	117	0.972	***	122	0.995	***	127	0.957	***	100	0.901	***
Pb	379	0.975	***	275	0.979	***	298	0.952	***	110	0.629	n.s.
Se	1.0	0.713	*	0.7	0.930	***	0.8	0.923	***	1.1	0.75	*
Sn	19.7	0.840	**	12.7	0.993	***	14.4	0.936	***	10.6	0.932	***
Zn	1090	0.839	**	680	0.986	***	884	0.985	***	550	0.891	**

Relationships between metals and organics in sediments

	Mersey			Ribble			Wyre			Solway		
	slope	r	P	slope	r	P	slope	r	P	slope	r	P
Ag	0.068	0.439	n.s.	0.204	0.950	***	0.125	0.694	*	-0.019	-0.166	n.s.
As	0.629	0.184	n.s.	2.92	0.983	***	3.181	0.864	**	-0.152	-0.109	n.s.
Cd	0.024	0.084	n.s.	-0.042	-0.839	**	-0.001	-0.006	n.s.	0.116	0.749	*
Co	0.503	0.224	n.s.	4.224	0.967	***	1.394	0.501	n.s.	-0.687	-0.272	n.s.
Cr	7.552	0.396	n.s.	24.31	0.987	***	10.59	0.689	*	1.465	0.158	n.s.
Cu	4.120	0.360	n.s.	10.4	0.988	***	4.137	0.476	n.s.	1.144	0.328	n.s.
Fe	3728	0.581	n.s.	8873	0.992	***	3849	0.622	n.s.	496	0.155	n.s.
Hg	0.139	0.437	n.s.	0.253	0.973	***	0.079	0.209	n.s.	-0.009	-0.170	n.s.
Mn	38.45	0.180	n.s.	97.87	0.771	**	160	0.543	n.s.	-43	-0.250	n.s.
Ni	3.91	0.505	n.s.	10.81	0.985	***	3.630	0.442	n.s.	1.107	0.311	n.s.
Pb	16.28	0.654	n.s.	24.45	0.975	***	15.78	0.816	**	3.923	0.680	*
Se	0.049	0.547	n.s.	0.059	0.933	***	0.035	0.671	*	0.033	0.682	*
Sn	1.180	0.784	*	1.138	0.993	***	0.740	0.776	*	0.121	0.333	n.s.
Zn	6.772	0.081	n.s.	60.91	0.987	***	28.42	0.512	n.s.	7.980	0.404	n.s.

Key:		
	slope	slope of linear regression line
	r	correlation coefficient
	n.s.	Not significant ($P>0.05$)
	*	$P<0.05$
	**	$P<0.01$
	***	$P<0.001$

6.6.2 Sediment extracts as a measure of anthropogenic (non-residual) metal.

Chemical extracts have, in previous studies, often proved to be preferable as surrogate measures of bioavailable metal than total dissolutions. To test this possibility in Irish Sea samples, metal concentrations were determined in selective extracts from the Mersey, Ribble, Wyre and Solway sediments. Superficially, the patterns for 1M HCl-extractable metal were similar to those for 'total' metals (see Fig. 46). Examples of these distributions, for 1M HCl-extractable Cd, Cr Pb and Zn are shown in Figure 52. Proportions of metal extracted by 1MHCl varied from 17% for Ni, to 83% for Pb

(Fig. 53), with a mean value of 49±12% for the suite of metals analysed here (Se and Hg in 1M HCl extracts were below detection limits).

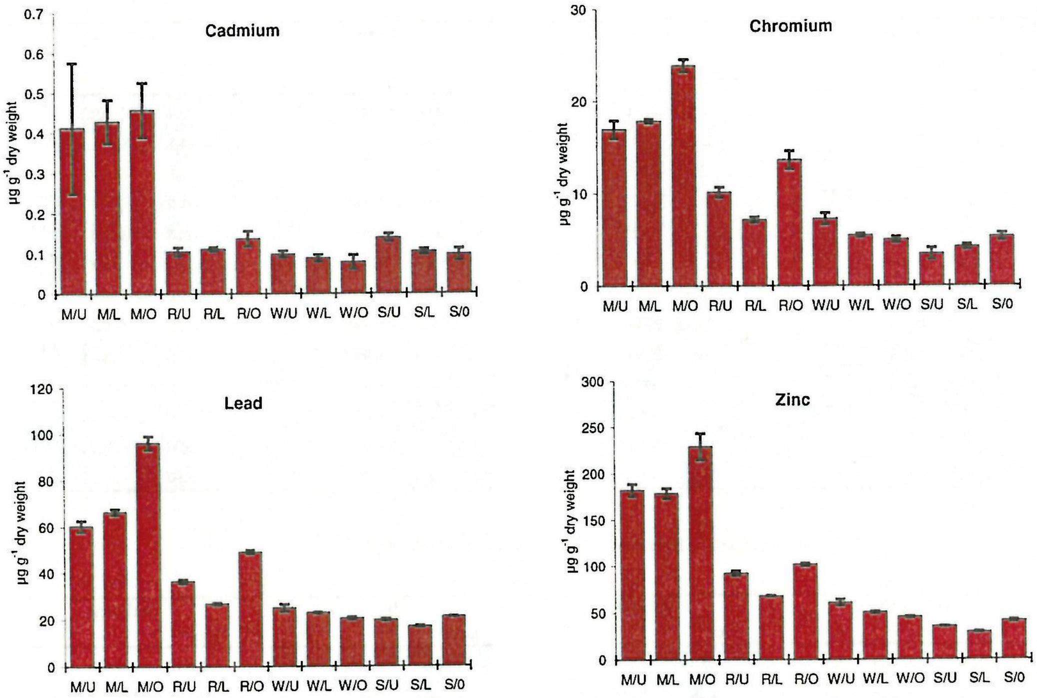

Figure 52. Cd, Cr, Pb and Zn in 1MHCl sediment extracts, illustrating distributions similar, superficially, to 'total' digests. Mersey (M), Ribble (R), Wyre (W) and Solway (S) sediments (/U,/L,/O, - upper, lower and offshore sites).

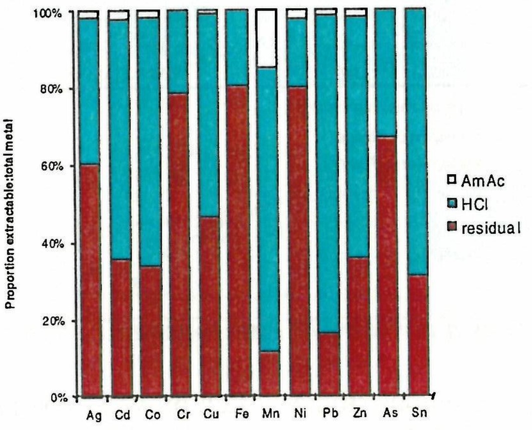

Figure 53. Proportion of total* metal extracted by 1M AmAc, 1MHCl, and remaining residual fraction. (*HNO_3 digest)

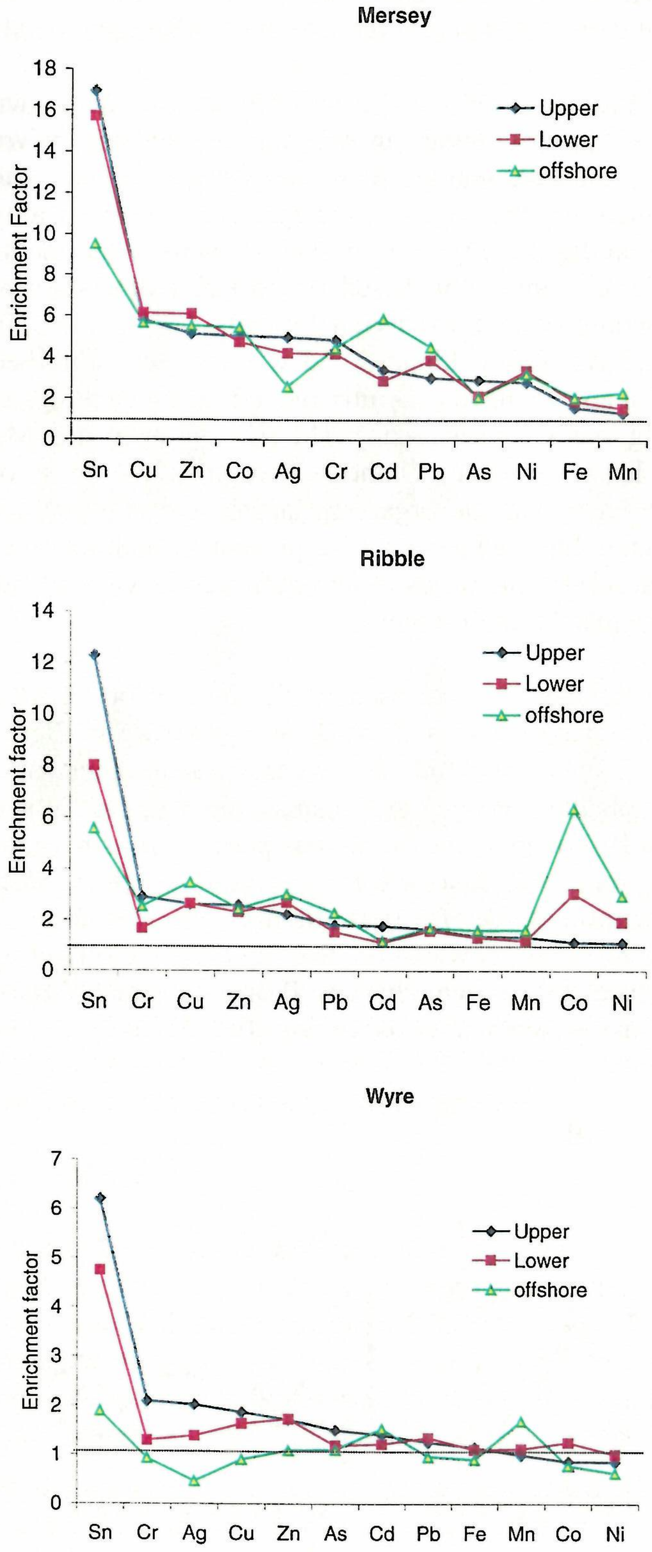

Figure 54. Comparison of metal enrichment in 1M sediment-extracts from Mersey, Ribble and Wyre Estuaries (upper, lower estuary and offshore sites), relative to Solway baseline values (horizontal dashed line).

1M HCl removes easily reducible metal, such as that adsorbed to Fe (Mn) oxyhydroxide phases, and does not attack the mineral lattice. As an extractant of surface-bound (non-residual) material it may well be a better measure of anthropogenic enrichment than total digests which also include more refractory metal.

With this possibility in mind, metal Enrichment Factors in 1MHCl extracts, are shown in Figure 54. These represent the ratio of values in Mersey, Ribble and Wyre sediments (upper, lower and offshore sites), relative to the equivalent Solway site (assumed to represent baseline values for the region). Though these were broadly similar to enrichment patterns for total digests (Fig. 48) - in that the Mersey sediments were consistently most elevated - Enrichment factors based on 1M HCl extracts reveal some differences in the scale of contamination for individual metals. For example, in contrast to sediment 'totals' (Hg and Ag ranked highest), Sn was the most enriched metal in 1MHCl extracts, and Cr, Cu and Zn have generally moved up the rankings at the expense of Cd and Ag (note Hg was not measured in 1M HCl extracts). Fe, Mn and Ni remained among the least enriched elements. Possible sources of anthropogenic Sn in the Mersey Estuary include organotin antifouling compounds, such as tributyl tin (TBT) and metabolites, which may be present in sediments in adsorbed form or as small paint particles. This needs to be confirmed in view of the known adverse effects of TBT in the marine environment.

An illustration of how anthropogenic metal - expressed as the proportion of total metal which is extractable in1M HCl - varied across the study area is shown in Figure 55. For Cr, Cu, Ni, Pb, Sn, Zn (Fig. 55A) and Co (not shown), this fraction increased, generally from north to south, towards the Mersey (with a small increase for Cu and Ni in the lower Ribble also indicated). The gradient for Sn was particularly strong, as indicated above. In contrast, the trend was reversed for Cd and Ag (Fig. 55B) implying the proportion in the anthropogenic fraction (though not the absolute concentration) was more important, relatively, towards the Solway (perhaps reflecting localised sources such as the phosphate plant at Whitehaven). Proportions of 1M HCl-extractable Fe, Mn and As did not vary greatly across the region (Fig. 55C).

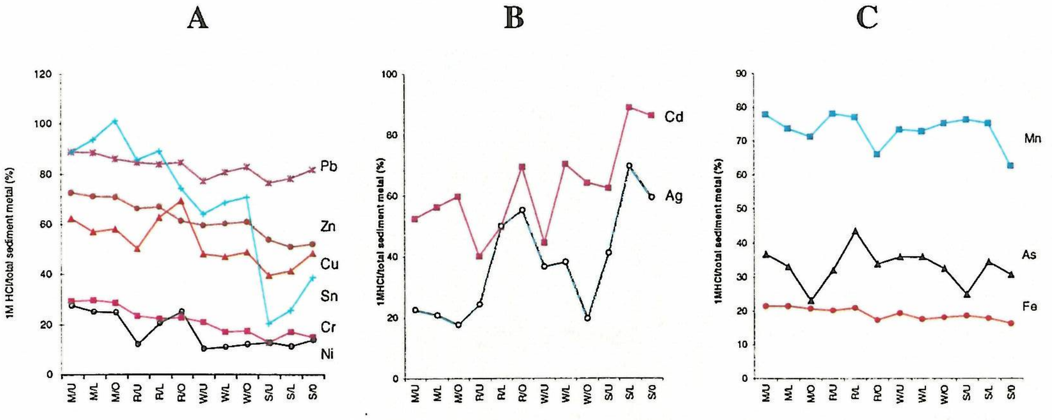

Figure 55. Proportion of anthropogenic metal (1M HCl extractable, expressed as the proportion of total metal) across the study area: Mersey, Ribble and Wyre Estuaries (upper, lower estuary and offshore sites). Key to site names as in legend Figure 56.

The weakest extract used here (1M AmAc) is a measure of readily-exchangeable metal. Concentrations in 1M AmAc extracts of Irish Sea sediments were generally very low, especially for some of the less abundant metals (As, Sn, Se and Hg were not detectable). For the majority of elements this represented a minor proportion of the total sediment metal (1.2 ±1.1%; Fig. 53). One exception was Mn, which was present in greater proportions in the exchangeable-metal fraction (15±7%). Distribution gradients for metals in 1M AmAc-extracts, across the study sites, were generally less distinct than those displayed for 'total' and 1M HCl extracts, and variability was higher, as illustrated by examples for Mn, Ni, Pb and Zn in Figure 56.

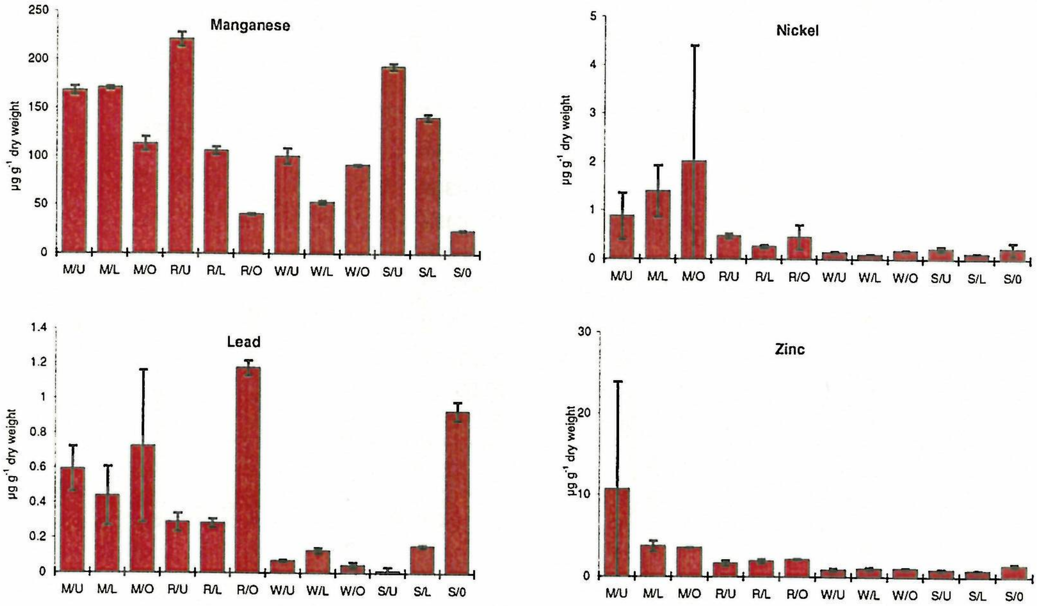

Figure 56. Mn, Ni, Pb and Zn in 1M ammonium acetate sediment extracts. Mersey (M), Ribble (R), Wyre (W) and Solway (S) sediments (/U,/L,/O, - upper, lower and offshore sites).

In a subsequent section of this report we evaluate how these variable patterns of total and extractable metal in sediments (including normalising routines), relate to trends in body burdens across the region, and discuss which, if any, are adequate surrogate measures of sediment metal bioavailability.

6.6.3 Metals in water

Despite the fact that water samples are subject to temporal and spatial variability, and though the emphasis in this study is on sediments, surface water samples were taken at each site. This was done to provide information on possible inputs of metals to the sediments in each estuary, and as ancillary factor to explain bioavailability (where relationships with sediment metals could not account for bioaccumulation patterns). Metal concentrations in filtered and unfiltered samples are listed in Appendix 5.2.

The distribution of dissolved metals resembled that in sediments, broadly, though concentrations in the two phases were significantly related only for As, Pb, Zn and Ni (Table 27). For the first three of these elements, concentrations were highest in the Mersey and decreased, generally, in a northerly direction (Fig. 57). A similar trend was seen for Cu (Fig. 57), but not so obviously for Cd ,Ni, Fe and Co (Fig. 58): distributions of Fe and Co were probably dominated by natural geochemical sources. Dissolved Mn distributions were unusual in that concentrations were highest in the two most northerly estuaries (Solway and Wyre, Fig. 59), possibly as a result of historical sources in that area (e.g. mining, and ore import and steel production along the Cumbrian coastline). However, salinity (and redox) undoubtedly has an influence on Mn concentrations in these and other estuaries. Indeed, concentrations of most metals were inversely related to salinity, as indicated by the profiles in Figures 57-59, implying that in most cases the principal sources of dissolved metals are in freshwater or low salinity regions of estuaries.

Table 27. Correlations between dissolved and sediment-bound metals at Irish Sea study sites (estuaries and offshore)

	r	P
As	0.73746	0.0062
Cd	0.25808	0.44355
Co	0.33446	0.34487
Cu	0.54973	0.06409
Fe	0.22812	0.47579
Mn	0.52321	0.08088
Ni	0.65374	0.02913
Pb	0.893	0.0005
Zn	0.87745	0.00018

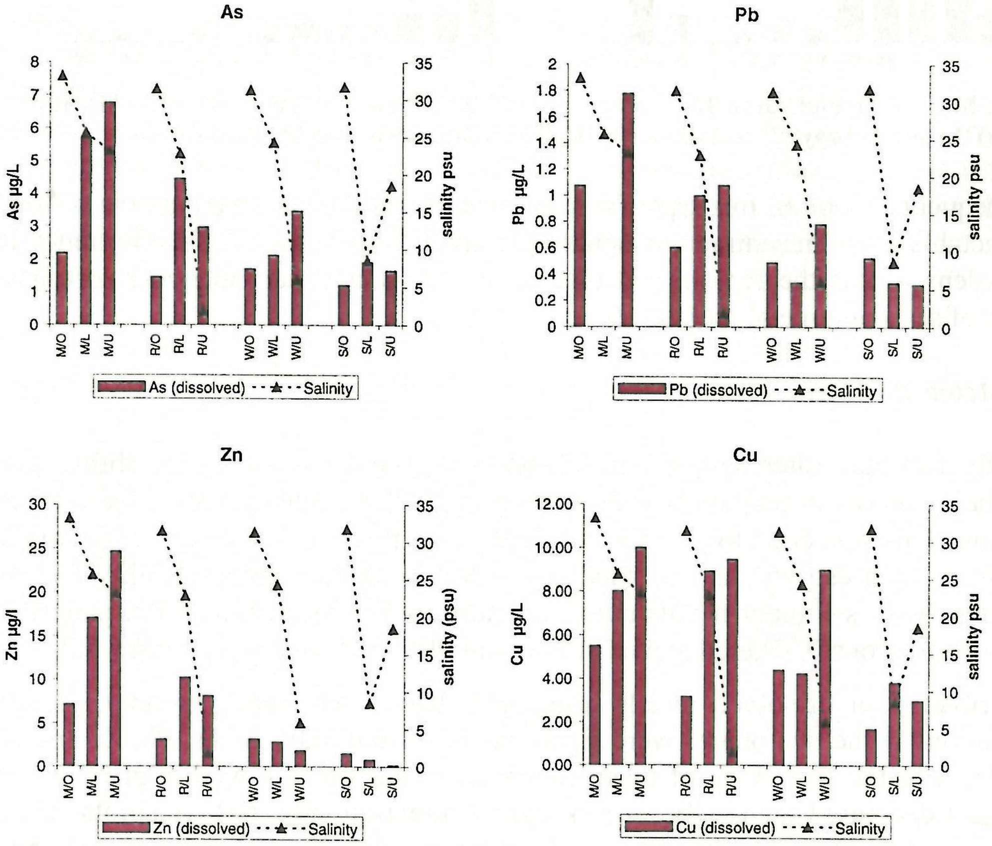

Figure 57. Distributions of dissolved As*, Cu* , Zn* and Pb (* significantly correlated with particulate metals). Salinity also plotted. Key to site names as in legend to Figure 56.

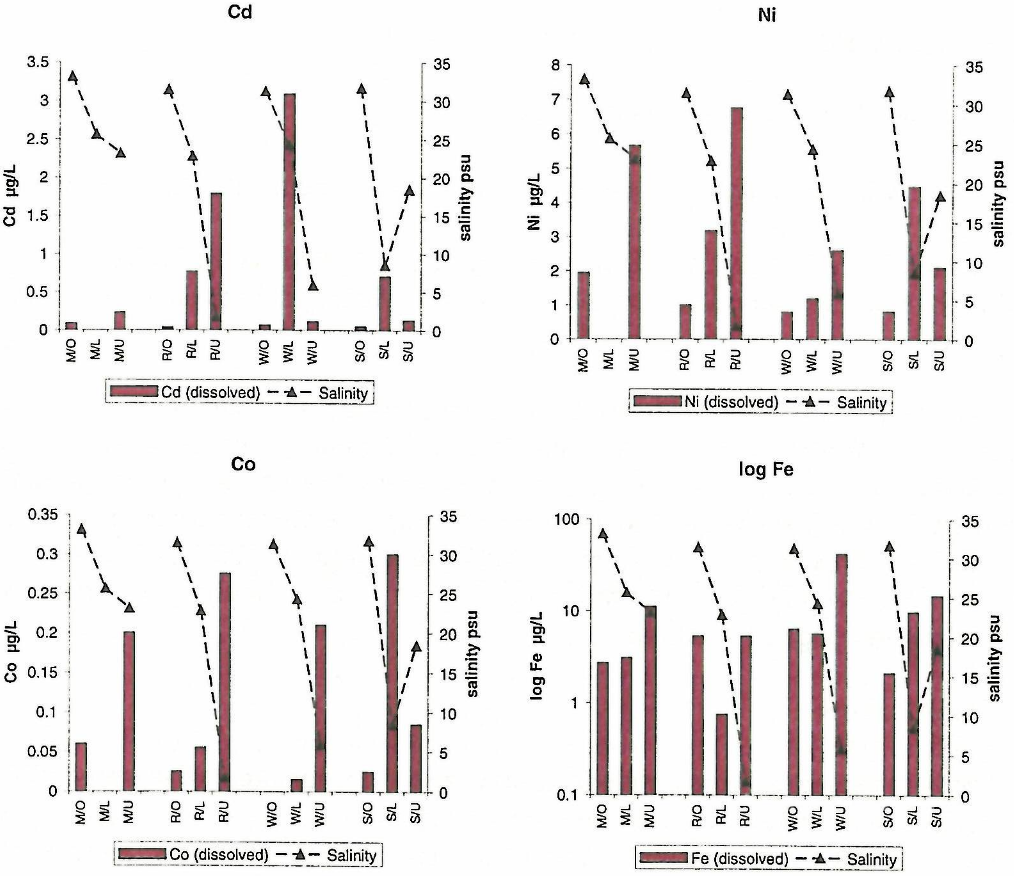

Figure 58. Distributions of dissolved Cd, Ni Co and Fe (none significantly correlated with particulate metals). Salinity also plotted. NB log scale for Fe. Key to site names as in legend to Figure 56.

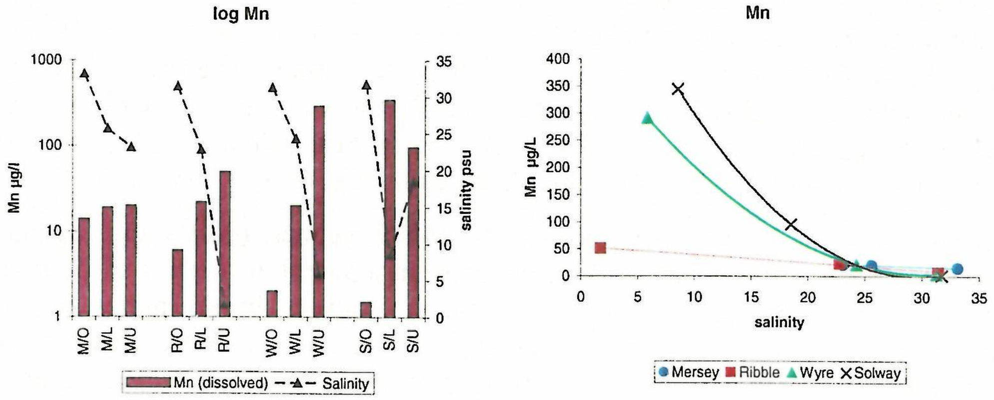

Figure 59. (A) - Distributions of dissolved Mn at Irish Sea sites (not significantly correlated with particulate metals). (B) - Dissolved Mn plotted as a function of salinity. NB log scale for Mn in (A). Key to site names as in legend to Figure 56.

6.6.4 Bioavailability

Objectives 2 and 3 of this project were:

- To assess whether metals in estuarine and coastal sediments are biologically available.
- To establish a means of distinguishing the relative contribution of the anthropogenic and natural sources of metals to any biological uptake or effect that may occur

These two objectives were addressed by a programme of field surveys (using estuarine clams *Scrobicularia plana* (and *Macoma balthica*) and ragworm *Nereis diversicolor* as bioindicators) and by exposing representative species (*S. plana* and a marine snail *Turritella communis*) to estuarine and marine sediment cores in the PML Mesocosm. Attempts were made to relate bioaccumulation in field and mesocosm studies with sediment geochemistry, with a view to defining bioavailable/anthropogenic fractions.

6.6.4.1 Field Surveys

Distributions of estuarine metal contamination across the study area, as represented by concentrations in bioindicators, often resembled, superficially, those in sediments - in that concentrations were usually highest in the Mersey. However patterns in bioaccumulation were sufficiently diverse (between species and metals) to confirm that other variables, beside total sediment metal, were important in modifying bioavailability in the Irish Sea. Bioaccumulation data for native fauna are therefore presented individually.

Scrobicularia plana : A generalised assessment of the bioavailability of different metals throughout the study area was made by determining Enrichment Factors (EF) in these clams (Fig. 60): i.e. by comparing values from the Mersey, Wyre and Ribble with 'baseline' values (assumed, as in the sediment study, to be the Solway). These biological Enrichment Factors were relatively high for a number of metals in clams from the Mersey Estuary (Fig. 60), as might be expected from sediment data treated similarly (Figs. 48 and 54). Across the range of metals measured, however, enrichment factors in total sediment digests (conc HNO_3) were not particularly well-matched to $EF_{S.\ plana}$ (R = 0.176, n.s.; Fig. 61A). In contrast, values for EF_{1MHCl} were more closely related to $EF_{S.plana}$ (R= 0.8687, P<0.001, Fig. 61B).

If, as seems likely, the enrichment of metals in 1MHCl extracts reflects the degree of anthropogenic input, the overall correlation with enrichment in tissues of *S. plana* supports the contention that anthropogenic metal loadings in sediments directly influence accumulation in these deposit-feeding bivalves. Furthermore, these results suggest that EFs in 1MHCl extracts may provide at least a preliminary classification of those metals which are likely to be of concern, biologically. As will be evident from Figure 61, however, there were several examples where residual variation was relatively large and more rigorous treatment of data on a metal-by-metal basis may be necessary to account for the effects of modifying factors on bioavailability (*see* next section on *sediment geochemistry - surrogate measures of contamination*).

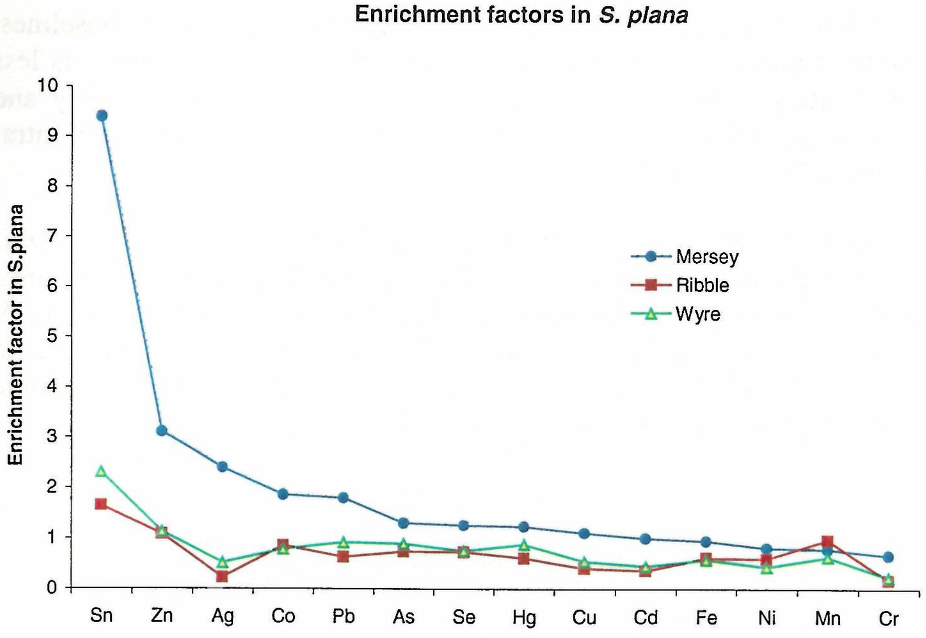

Figure 60. ***Scrobicularia plana*. Metal Enrichment Factors in clams from Mersey, Ribble and Wyre Estuaries (means, upper and lower estuary sites), relative to Solway baseline values.**

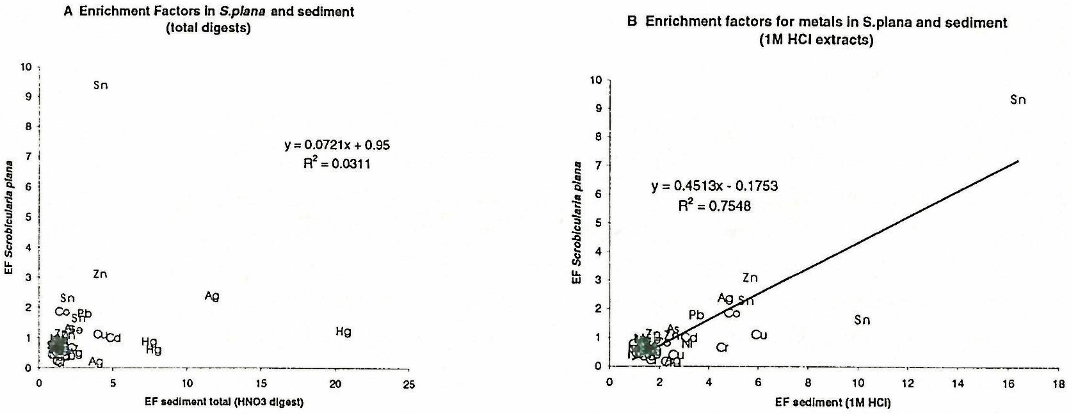

Figure 61. Relationship between Enrichment Factors (EF) in *Scrobicularia plana* and EF in sediment (A - totals, B - 1MHCl extracts). EF = concentration in Mersey, Ribble and Wyre clam or sediment ÷ corresponding regional baseline value (Solway)

Nereis diversicolor: The picture of contamination and anthropogenic influence in Irish Sea sediments portrayed by tissue residues in ragworm *Nereis diversicolor* was similar, generally, to that in *S. plana*, in so far as bioavailability of a broad spectrum of metals was elevated in the Mersey Estuary. Results are summarised, as EF_{Nereis} (using Solway worms as baselines), in Figure 62. However, some interesting species differences were evident for certain elements. For example, the relative bioavailability of Ag, Sn and Hg in the Wyre estuary, expressed as EF_{Nereis} (Fig. 62), were higher than in comparable assessments using *S. plana* (Fig. 60). Ni was also ranked more highly in *Nereis*, whilst, in contrast, EF values for Zn were lower - Zn body burdens in worms from all Irish Sea estuaries were in fact comparable with Solway baselines. *Nereis* is known to regulate Zn concentrations, and compared with molluscs, is less efficient at accumulating most metals. Subtle differences in diet, permeability and metal assimilation rates, almost certainly account for these and other observed intra-specific differences in EF sequences.

Comparatively low levels of bioaccumulation and regulatory mechanisms in *Nereis* may also explain why the relationship between $EF_{sediment}$ and EF_{Nereis}, across the range of metals (Fig. 63), was subject to more scatter than the corresponding plot in *S. plana*. Once again, however, 1MHCl extracts (EFs) were more representative of accumulated burdens ($r=0.4332$; $p < 0.01$) than total digests ($r=0.2584$;n.s) and should be considered a better general guide to anthropogenic influence.

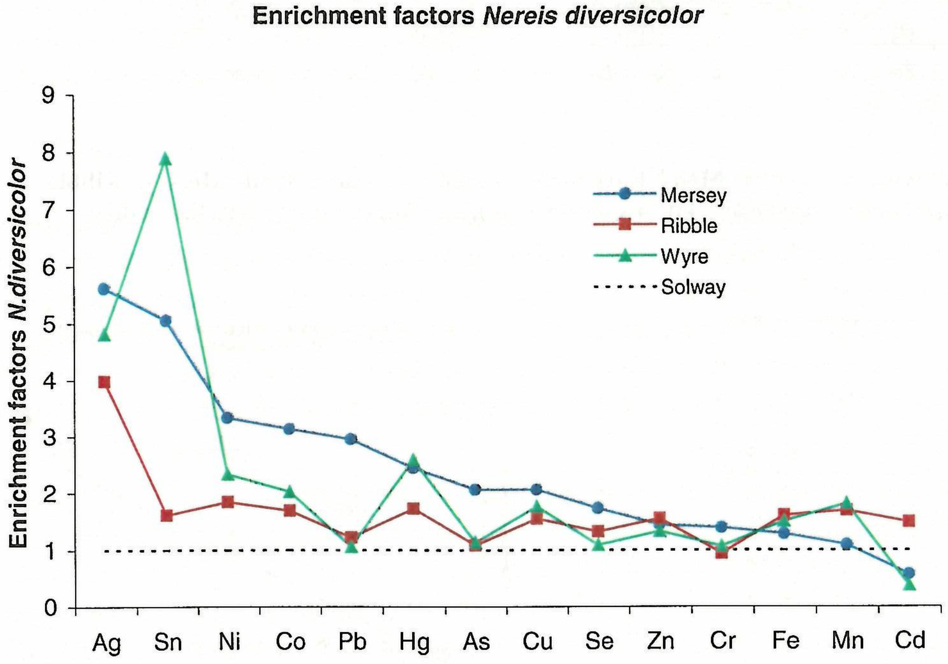

Figure 62. *Nereis diversicolor*. Metal enrichment factors in worms from Mersey, Ribble and Wyre Estuaries (means upper and lower estuary sites), relative to Solway baseline values.

Macoma balthica. This infaunal clam belongs to the same superfamily as *S. plana*, (Tellinacea), and gradually replaces it's less cold-tolerant relative towards the north of the region, notably in the Solway. Due to its small size and less predictable occurrence *Macoma* was collected on an opportunistic basis in the current project (Mersey and Solway only). However because *Macoma* is, potentially, a useful alternative to *Scrobicularia* in the northern sector, we have combined current results with other *Macoma* data from the Mersey, Ribble, Wyre and Solway Estuaries collected and analysed by identical methods during the 1990s. This synthesis is provided only as a preliminary guideline for the future use of *Macoma*.

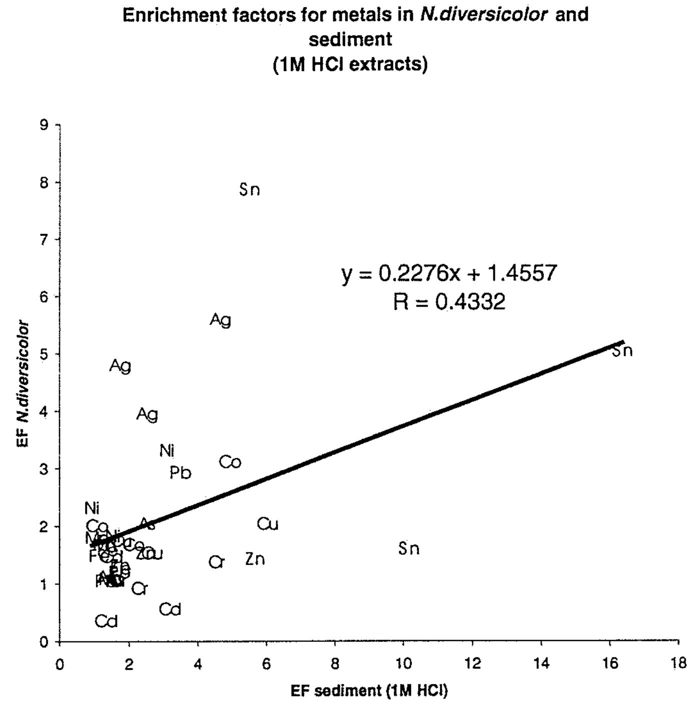

Figure 63. Relationship between metal Enrichment Factors (EF) in *Nereis diversicolor* and sediments (1MHCl extracts). EF = concentration in Mersey Ribble and Wyre clam or sediment ÷ corresponding regional baseline value (Solway).

Bearing in mind these caveats the pattern of enrichment factors in *Macoma* resembled those in other biondicators, highlighting the Mersey, but with Hg dominating the rankings and Sn somewhat less prominent (Fig. 64). The reason for this inter-specific variation is largely temporal: rankings for *Macoma* in Figure 64 were generated from earlier data, in part, and hence were influenced by historical inputs which are now diminishing (e.g. Hg in the Mersey). In contrast to *S. plana* or *N. diversicolor* the resulting pattern of contamination depicted by *Macoma* is not contemporary. *Macoma* is capable of both suspension- and deposit-feeding and it is possible that differences in dietary sources, metal assimilation routes and metabolism could also contribute to variations in body burden patterns.

Nevertheless, there was a significant correlation between the enrichment of elements in *Macoma* and $EF_{sediment}$ ($r=0.769$; $P<0.001$ in total digests), and it would appear that *Macoma* is a suitable substitute for *S. plana* as a bioindicator in the Irish Sea region. The fit with EF_{1MHCl} extracts was less distinct in *Macoma* ($r=0.314$, $P=0.06$) as a result of the smaller data set. Further validation is required to define, accurately, the relationship between anthropogenic sediment loadings and body burdens in this species.

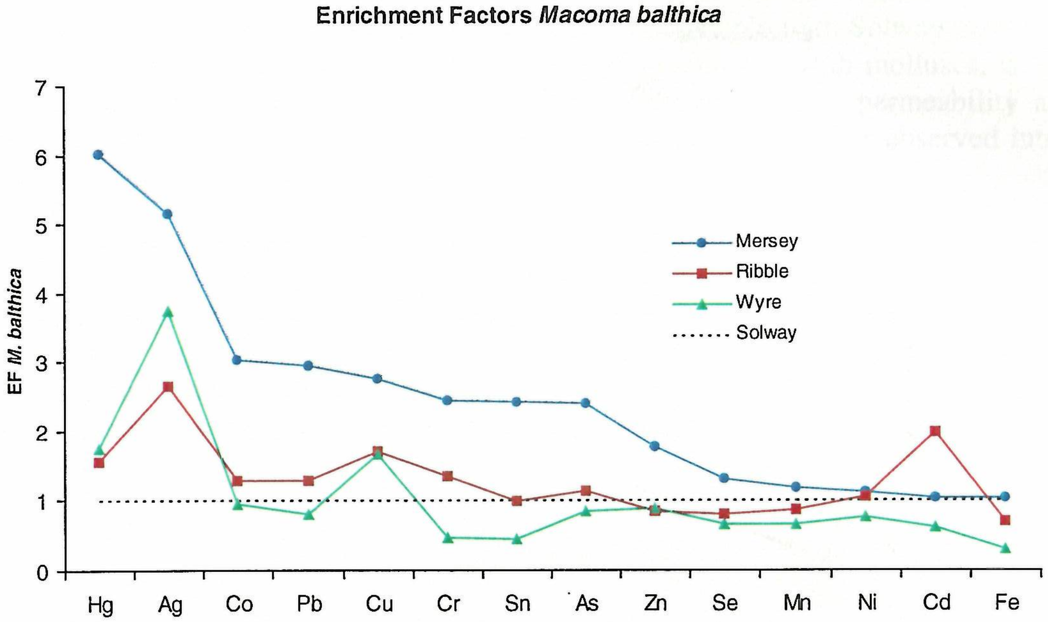

Figure 64. ***Macoma balthica.*** **Metal enrichment factors in clams from Mersey, Ribble and Wyre Estuaries (means, upper and lower estuary sites including previous data collected during the 1990s), relative to Solway baseline values.**

In accordance with objective (2), the field survey element of the programme has demonstrated that biological availability of metals in Irish Sea sediments can be assessed directly, by analysis of suitable bioindicators such as *Scrobicularia plana, Nereis diversicolor* and *Macoma balthica* - provided that adequate baseline values are obtained. Furthermore, the relative degree of enrichment in these organisms reflects, superficially at least, anthropogenic contributions in sediments - operationally defined by 1MHCl extractable metal - thereby helping to fulfil objective (3). It is important to recognize, however, that 'bioavailability', as represented by tissue residue data, will be modified by a multitude of biological factors (e.g. feeding habit, quantity and quality of diet, growth, season, sex and metabolism): although similar contamination trends may be exhibited across taxonomic groups, precise responses will vary between species and between metals, according to the summation of these modifying factors. The observed differences in bioaccumulation patterns between *Scrobicularia plana, Macoma balthica* and *Nereis diversicolor* serve as an example of the likely extent of this variability.

6.7 Relationships between metals in biota and sediment geochemistry: surrogate measures of contamination.

Inherently, any scheme which sets out to mimic, chemically, the 'biologically available' fraction suffers from a comparable dilemma to that described above, in terms of accounting for biological variability: no single determination can accurately predict uptake of all metals in all species. More realistically, however, characterisation of sediments may help to identify features which modify biological responses, predictably, in the environment. In future this approach may assist in the construction of more widely applicable models.

In the current project the most viable option was to apply a selective range of sediment measurements, to individual metal-organism combinations, to see if such measures could be used to describe bioavailable fractions, quantitatively. To demonstrate the feasibility of such a course of action in Irish Sea samples, bioaccumulation data from the field (and, below, the mesocosm experiment) were compared with sediment data, on a metal-by-metal basis. Geochemical characteristics considered included distribution of metals in various sediment extracts, together with the modifying influence of particulate Fe and organic matter.

Table 28 summarises those incidences in the 1999 data set where simple linear relationships existed between metal levels in sediments and biota.

Best fit relationships for native *Scrobicularia* and *Nereis* encompassed a combination of total digests, 1MHCl and 1M AmAc leaches (Table 28, examples in Fig. 65, and Appendix 5.3). There were also a number of examples where 'normalisation' of sediment metals with respect to the metal-binding components Fe (oxyhydroxides) or organic matter improved the strength of relationships, indicating that the degree and type of complexation was sometimes a significant modifying feature in sediments.

Table 28. Incidences in the current study where relationships between metals in sediments and biota were statistically significant. Upper half of table summarises results for native *Scrobicularia plana* and *Nereis diversicolor* (full list of r, and p values in Appendix 5.3); lower half (shaded) shows results for mesocosm experiment with *S. plana* and *Turritella communis*.

	Ag	As	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Se	Zn
	Native biota												
Native *Scrobicularia*	T T/Fe T/O	T/Fe T/O HCl/Fe		T HCl HCl/Fe AmAc	T/Fe T/O HCl/Fe AmAc					HCl HCl/Fe	ALL	T/O	ALL
Native *Nereis*		T T/Fe T/O HCl HCl/Fe		T/O HCl HCl/Fe						T/O	ALL	T T/Fe T/O	
	Transplanted biota (mesocosm)												
Scrobicularia (28‰)	HCl	n.a.	T T/Fe T/O HCl HCl/Fe		T T/Fe T/O HCl HCl/Fe						T/Fe T/O		T/Fe T/O HCL/Fe AmAc
Turritella (35‰)		n.a.			T T/Fe HCl HCl/Fe				T/O HCl/Fe	T/Fe	T T/Fe T/O HCl HCl/Fe		

Key:

T	Total (HNO_3 extractable metal)	/Fe	normalised to Fe
HCl	1M HCl extractable metal	/O	normalised to organic fraction
AmAc	1M Ammonium acetate extractable		

Only those relationships of statistical significance ($P<0.05$) have been included in Table 28 but there were several examples which were only marginally below this level: a slightly larger sample size would probably result in their inclusion in Table 28 (see Appendix 5.3 for full list of r values). Altogether there were 32 significant relationships for *S. plana* in the 1999 field data set (out of a possible 74 combinations). Correlations with sediment were particularly strong for Pb and Zn. Co, Cr, Ag, As, Sn and Ni were significant in some treatments but not all (see examples, Fig. 65 A,B,C). In *Nereis*, 18 out of 74 relationships were significant, with Pb, As and Se outstanding (Fig. 65 D,E,F). Unlike *S. plana*, Zn body burdens in *Nereis* were not related to sediments because of it's Zn regulating ability, described above.

To demonstrate the value of a larger sampling effort in establishing predictive relationships between metals in sediments and organisms, we have examined extensive records (n>100 sites) for Irish Sea estuaries in our own data base, collected over a 20 year period. Metal concentrations in *Nereis* and *Scrobicularia* were compared with total (HNO_3) and 1M HCl sediment extracts (including values normalised to organic and Fe content).

For *S. plana*, 44 out of 76 combinations were statistically significant. Bioavailability, based on chemical determinations of sediments, was most predictable for Cd, Pb, Zn, Se, Hg>Cr>Ag>As, Sn, Mn>Co, but was unreliable for Ni and Cu. Uptake of the latter metal in clams is suspected of being influenced to a large extent by the degree of anoxia in the surrounding sediment (Bryan and Langston, 1992). Eight of the significant relationships involved normalisation of sediment metals to Fe and eleven to organics.

For *N. diversicolor* there were 57 significant relationships with sediment metal extracts, out of a possible total of 76. Significance decreased in the sequence: Cd, Co, Cu, Hg, Pb, Se, Zn>Cr, As>Ag>Mn>Fe (not significant for Sn). Ten of these relationships involved normalisation of sediment metals to Fe and three to organics. The inability to predict Sn body burdens in worms, satisfactorily, from measurements of sediment Sn, probably reflects the importance of organic forms, such as TBT, and particularly the ability of *Nereis* to metabolise this compound. In contrast, TBT metabolism is relatively slow in clams (Langston *et al* 1990, 1994; Langston and Burt, 1991). Though TBT is present in relatively minor amounts in sediment compared with inorganic tin bioavailability of the organic form is considered to be disproportionately high. Specific measurements of organic tin are required to evaluate the significance of anthropogenic contributions of this metal in the Irish Sea sediments.

Relationships between dissolved metal levels and body burdens were significant for Zn in *S. plana* ($r= 0.8926$, $P<0.01$) and As and Pb in *Nereis* ($r= 0.87, 0.85$, $P<0.01$) and might reflect a significant dissolved component for uptake in these examples.

It is concluded that, while there is no single surrogate measure of bioavailability, by combining several procedures a fairly comprehensive appraisal is possible, applicable to a broad range of estuarine sites in the Irish Sea. These measures will, at the very least, provide opportunities to screen sediments and make some prediction of biological consequences, based on fairly simple chemical determinations.

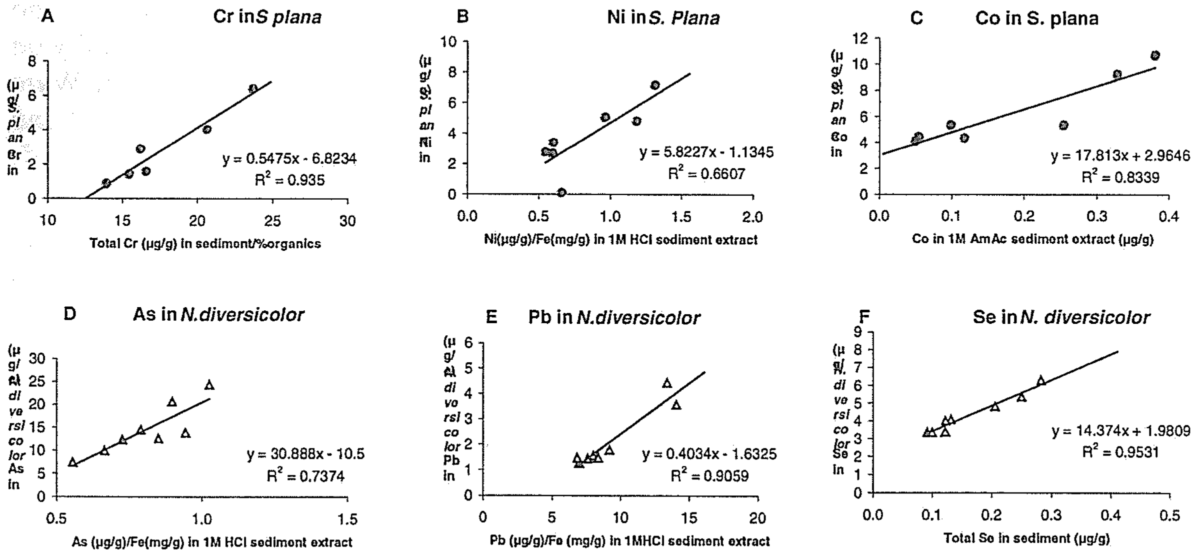

Figure 65. ***Scrobicularia plana*** **(A,B,C) and** ***Nereis divesicolor*** **(D,E,F): Relationships between metals in various sediment extracts and native animals from Irish Sea estuaries, July 1999. Note some sediment values are best normalised with respect to particulate Fe or organic content.**

6.8 Mesocosm experiment

At the end of the six month mesocosm experiment, sediments were re-analysed and metal concentrations compared to those at the start. Average recoveries are shown in Table 29 and indicate little variation in sediment loadings during this time (overall average recovery, for all metals, was 96%). Cd recoveries appear to be high, principally due to results for Solway sediments. This may be partly analytical - due to the low levels in these sediments - or perhaps reflecting some diagenetic mobility of this element. At the other extreme, average Se values were apparently somewhat lower (52%) by the end of the experiment.

Table 29. Comparison of metal concentrations in sediment at end and start of mesocosm experiment.

	Ag	As	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Se	Sn	Zn
% recovery	120	93	202	68	87	87	83	97	86	88	90	52	86	100

The decision to sacrifice cores and retrieve biota after six months was driven partly by the time constraints of the project, balanced by concerns that organisms would survive, accumulate metals and achieve steady state within that timescale.

Survival rates of *S. plana* were variable as indicated in Figure 66 and ranged from zero in Mersey and Solway offshore cores up to 78% in cores from the lower Solway. Poor survival in offshore sediments may have been attributable to the effect of reduced salinity (28 ‰) on sediment characteristics. However, in separate trials at 35 ‰, although survival in Solway offshore cores rose to >30%, there was no improvement in survival of *S. plana* in the Mersey cores. The influence of salinity on bioaccumulation was tested by comparing body burdens in *S. plana* held in Wyre offshore cores at 28 ‰ and 35 ‰. The only significant differences were for Cd and Ni, which where accumulated to slightly higher levels at the lower salinity ($P<0.05$; Fig. 67).

For the entire subset of estuarine cores (held at 28 ‰), average survival was 45% with a maximum of 61% in the Solway sediments. This might imply some relationship between survival and contaminant loadings but current evidence was insufficient to test this, rigorously.

The results for metal accumulation in *S. plana* indicate that a number of elements (Ag, Cd, Co, Cr, Hg, Mn, Ni, Pb and Zn) were accumulated significantly from various Irish Sea cores. The estuarine sites at which significant ($p<0.05$, student t test) uptake took place are listed in Appendix 5.4 (offshore cores not included in this exercise because of poor survival of *S. plana*). As with field data, the distinctions in bioavailability between the Irish Sea cores reflected by mesocosm exposures were not as large as anticipated and were masked to an extent by variability (relatively small sample sizes). Thus although mean uptake was almost invariably highest in Mersey cores, this was not always confirmed by statistical analysis. Larger sample sizes would help to resolve this problem in future studies.

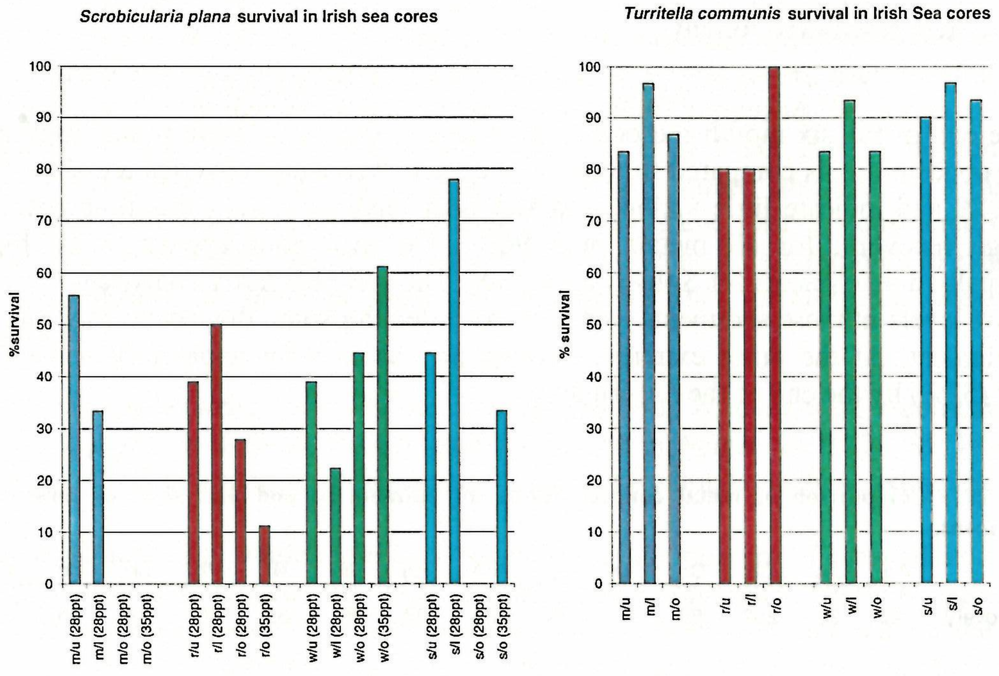

Figure 66. *Scrobicularia plana* and *Turritella communis*: survival rates after six months exposure to sediment cores in a mesocosm.

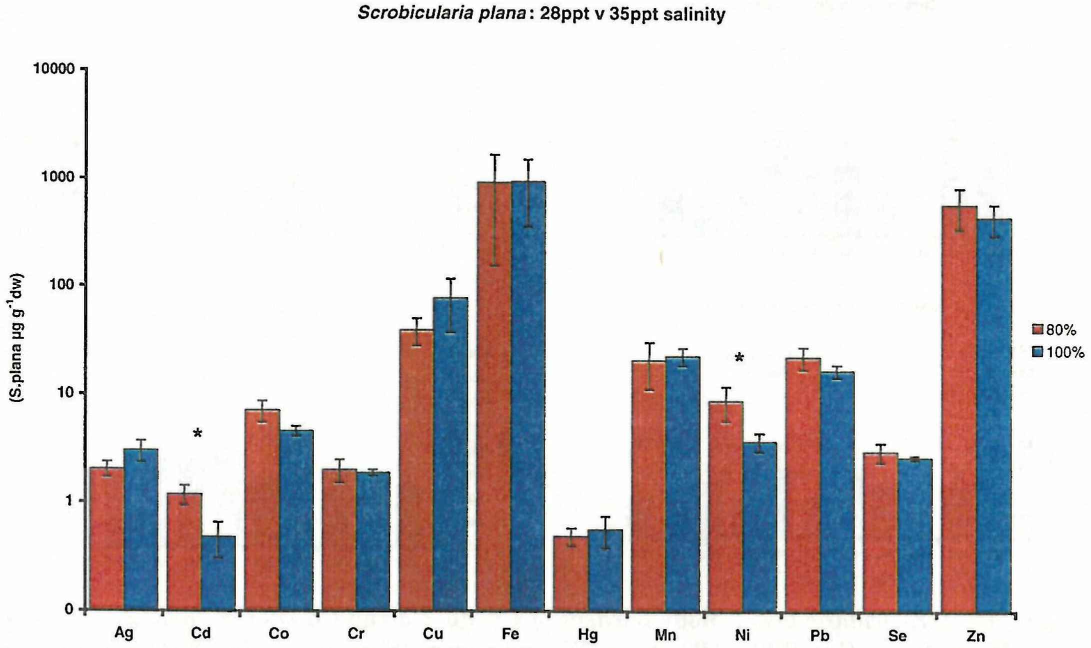

Figure 67. ***Scrobicularia plana*****. Comparison of accumulated metal burdens in clams held in sediment cores (Wyre offshore) at 28 ‰ and 35 ‰ for six months.**
*** significantly different (P<0.05, student 't' test).**

Another constraint highlighted by the current results stems from the observation that *S. plana* held in sediment cores in the mesocosm for six-months may not always achieve body burdens equivalent to those of native animals residing in the same sediments in the field. This was most evident for clams placed in the more contaminated Mersey cores, where, for a range of metals, accumulated burdens were often only a proportion of those present in native clams from the estuary (notably Ag, Mn, Pb, Se, Zn and to a lesser extent Hg and Cr). Examples of the uptake patterns of Cr, Pb and Zn are shown in Figure 68, and compared with Co (where concentrations in *S. plana* taken from mesocosm cores were more representative of natives).

Because of the limited ranges in bioavailability, and small sample replication used, separation of impact between the Irish Sea estuaries, based on body burdens in transplanted *S. plana*, was demonstrated, statistically, for only about half the elements analysed (Ag, Co, Cr, Hg, Fe, Pb and Se; $p<0.05$, ANOVA). Nevertheless, patterns of uptake of several pollutant metals were consistent with trends from field data and depicted similar south to north gradients, as indicated by the examples for Cr, Pb, Zn in Figure 68.

Thus, amounts of metal accumulated by *S. plana* after six months need not be numerically equivalent to natives in order to depict comparative trends in bioavailability. It may be that longer exposure times would help to achieve the approach of steady-state, though this is likely to be at the expense of even higher mortality rates. Greater replication would be advantageous in terms of resolving trends, statistically, though there is sufficient evidence here to indicate the scale of differences in bioavailability in the Irish Sea estuarine sediments studied her was comparatively small: further sample replication would not alter this conclusion.

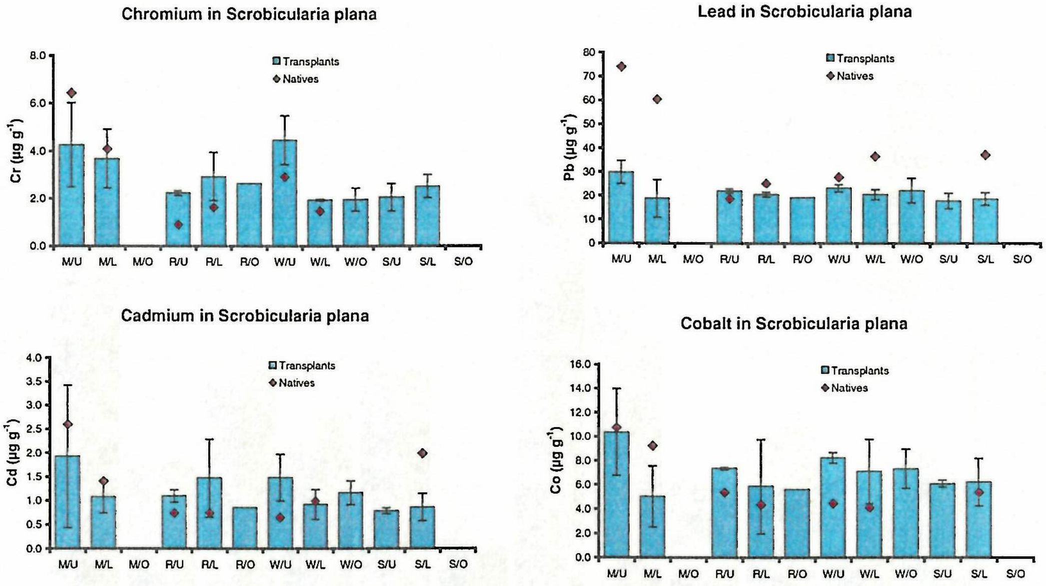

Figure 68. ***Scrobicularia plana*****: Body burdens of Cr, Pb, Cd and Co after six months exposure to cores from Mersey (M), Ribble (R), Wyre (W) and Solway (S) sediments (/U,/L,/O, - upper, lower and offshore sites) in the mesocosm (illustrated by bars). Concentrations in native animals from these sites are included (diamonds).**

Expressing metal uptake in mesocosm clams through the use of Enrichment Factors - this time comparing accumulated burdens in *Scrobicularia plana* held in Mersey, Ribble, Wyre and Solway cores with the Appledore 'baselines' (time zero) - produces plots which superficially resemble the patterns obtained by field data. $EF_{S.\ plana}$ tended to be highest in Mersey cores, though differences between Irish Sea estuaries were relatively small, perhaps because steady state had not been reached (Fig. 69). Nevertheless, it would seem that for a suite of metals (Cd, Hg, Ag, Zn, Co) the mesocosm study confirmed the presence of elevated bioavailability in the Irish Sea sediments, relative to that in Appledore sediments. It would be interesting in future, to compare results from a broader range of sediment types, in order to fully appreciate the influence of geochemistry on bioavailable fractions.

Survival rates of the marine snail *Turritella communis* were similar in each of the sets of cores and were consistently >80% suggesting this animal was more tolerant of experimental conditions than *S. plana* over the six-month exposure period (Fig. 66). In this respect it may be considered a more suitable choice for studying long-term exposure to metals. To its detriment, however, *Turritella* possesses naturally high body burdens of a number of elements which may have masked the relatively small net increases accumulated from the current range of test sediments.

Several metals (Cd, Co, Cr, Cu, Fe, Hg, Mn Se and Zn) were accumulated in *Turritella* from Irish Sea cores, relative to time -zero animals from Rame (and also relative to the Solway outer 'reference' core). The cores in which significant uptake took place are summarised in Appendix 5.5 ($p<0.05$, student t test). However, although evidence of the expected south-north gradient in contamination was apparent for some metals, clear separation between the Irish Sea estuaries was impossible to establish for Ag, Co, Cu, Fe, Hg, Se and Zn ($p>0.05$, ANOVA). The only element where variance in uptake in cores was highly significant was Cr ($P<0.001$; Fig. 70).

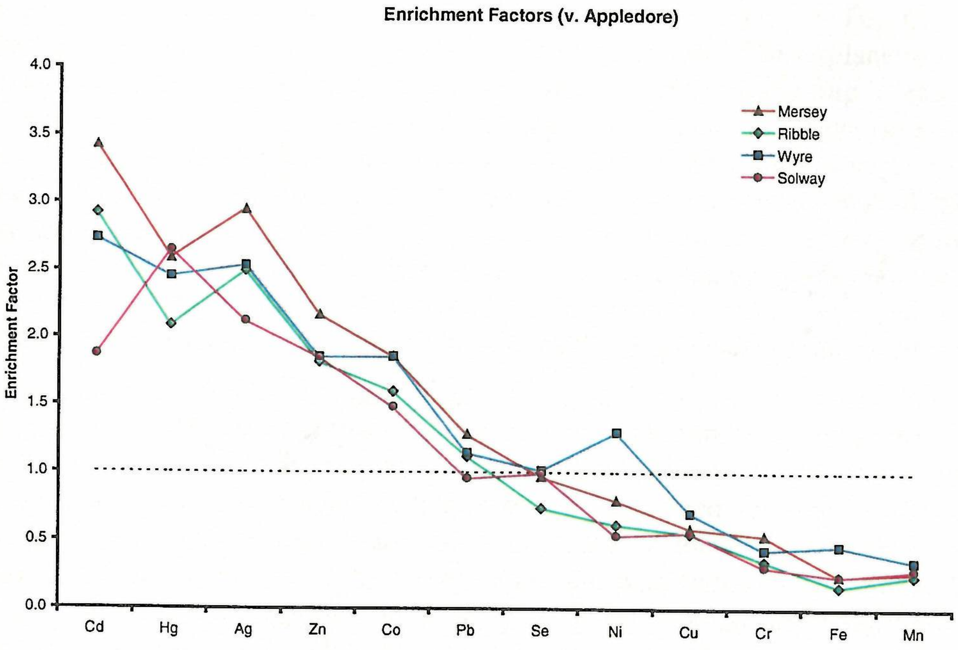

Figure 69. ***Scrobicularia plana.*** **Metal enrichment factors in clams from Mersey, Ribble, Wyre and Solway estuarine cores (after 6months exposure in the mesocosm), relative to Appledore baseline (time zero) values.**

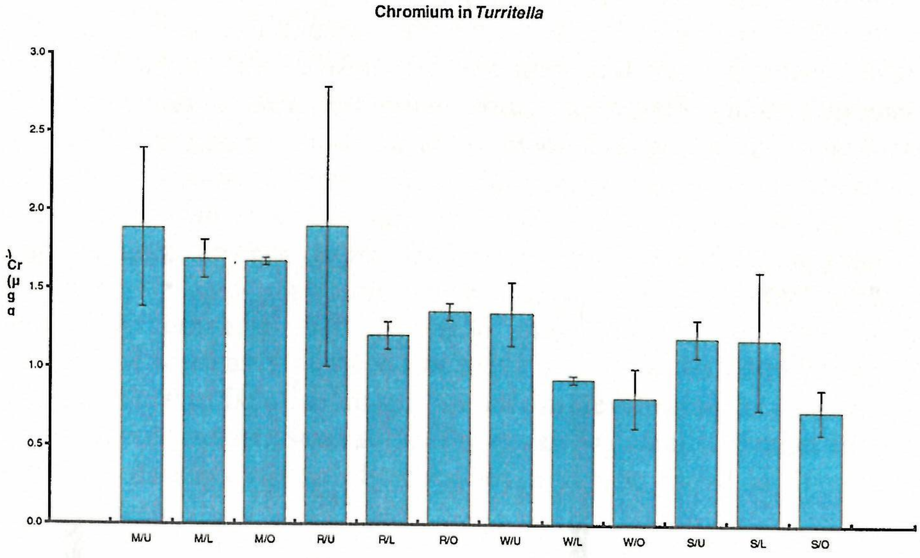

Figure 70. ***Turritella communis.*** **Patterns of Cr uptake from Mersey, Ribble, Wyre and Solway sediment cores (after 6 months exposure in the mesocosm).**

Expressing the uptake of metals in mesocosm-exposed *Turritella* through the use of enrichment factors - comparing accumulated burdens in Mersey, Ribble, Wyre and Solway cores with 'time zero' values - suggests there was little variation between Irish Sea estuaries (Fig. 71). Rather, increased bioavailability (to *Turritella*) of certain sediment metals is indicated to be a widespread across the region, albeit at low levels.

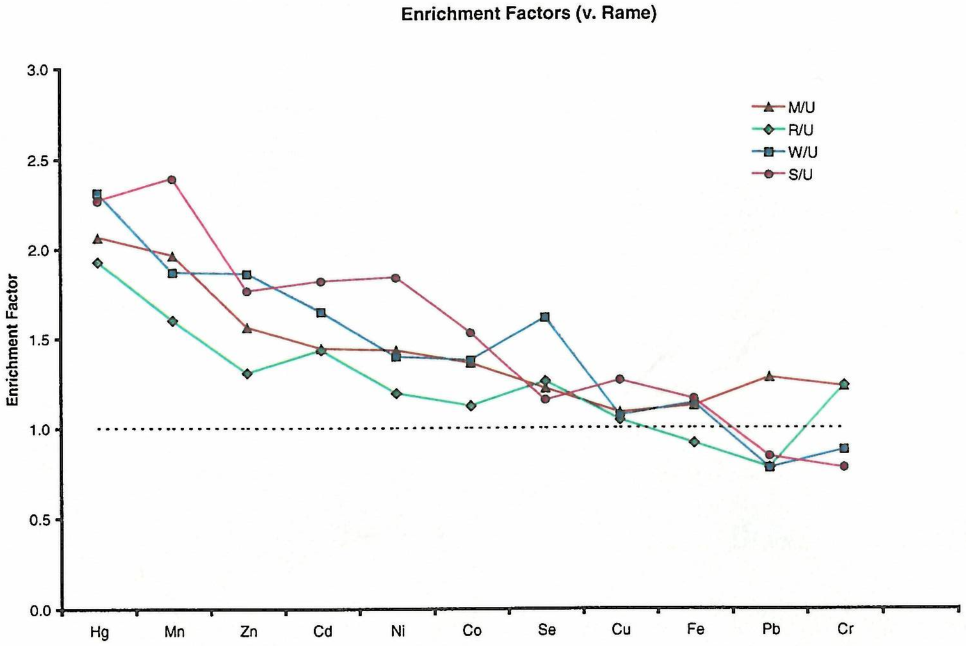

Figure 71. ***Turritella communis*. Metal enrichment factors in snails from Mersey (M), Ribble (R), Wyre (W) and Solway (S) sediments (/U,/L,/O, - upper, lower and offshore sites) after 6 months exposure in the mesocosm, relative to Rame baseline (time zero) values.**

Describing 'bioavailability' in general terms is clearly difficult, and any synthesis will involve compromise, since different species accumulate metals according their individual physiology and biochemistry. To illustrate this natural 'biodiversity' in metal handling ability, Figure 72 compares baseline metal concentrations in the two species tested here, *Turritella* and *Scrobicularia*.

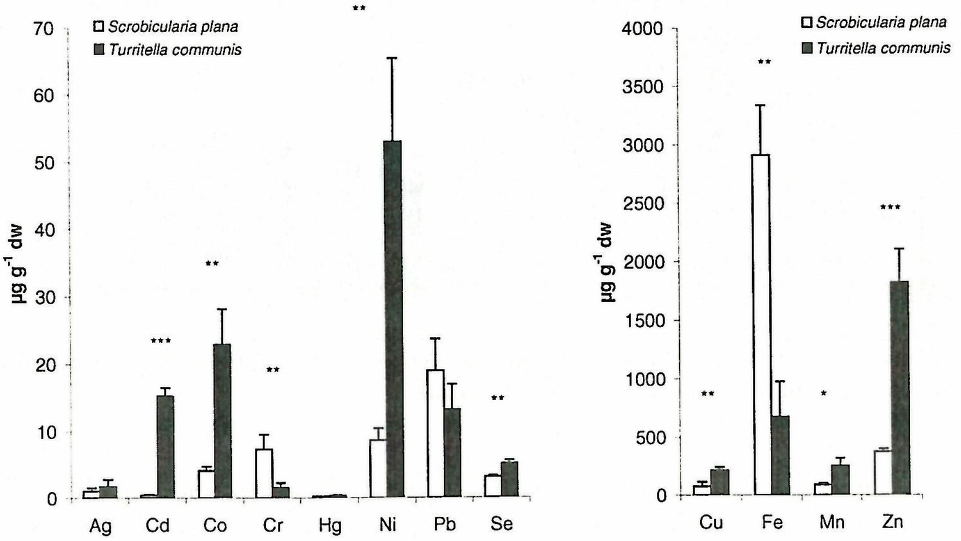

Figure 72. *Scrobicularia plana* and *Turritella communis*: comparison of baseline metal concentrations (*,, ***, values significantly different at P<0.05, <0.01 and <0.001, respectively; student t test).**

Whilst *Scrobicularia plana* contains higher concentrations of Fe, Cr and Pb, *Turritella* is a natural accumulator of most other metals. The explanation for high metal burdens in *Turritella* stems from the presence of metal-binding ligand systems, notably Ca/Mg phosphate granules in the digestive system. We have determined the metal composition of these granules in animals from different cores in the mesocosm study, using X-ray microanalysis, but attempts to equate sediment bioavailability with the metal content of these insoluble granules were unsuccessful. It may be that, as in whole animals, the inherently high metal content of these inclusions tended to mask the relatively small net increases accumulated from the current suite of sediments. More work is needed over a wider range of sediments to evaluate this possibility.

Such natural variability in metal accumulating abilities will obviously confound the provision of uniform measures of bioavailability and anthropogenic influence, based on body burdens. Accompanying sediment characterisation might help to provide a simpler means of classifying contamination, as described for field samples, above. Accordingly, attempts were made to relate uptake of metals in *Scrobicularia plana* and *Turritella communis,* in the mesocosm study, with sediment chemistry. Although fewer significant correlations were observed than under steady-state conditions in nature, some reasonable relationships were observed in these experiments (Table 28 and Appendix 5.6). In *S. plana,* Cd, Cr, Pb and Zn accumulation in Irish Sea cores was consistently found to be a function of sediment enrichment (defined by various measures), as was Cr and Pb uptake in *Turritella* (Appendix 5.6). The fact that *Turritella* appeared to be less responsive to certain metals than *S. plana* was probably due to the summation of a number of biological factors - in particular the inherently high metal content of *Turritella* (masking relatively small increases of some elements). Differences in assimilation pathways may also contribute to the variation.

In summary, laboratory (mesocosm) studies seem promising as a screening method to determine whether sediments represent a source of bioavailable metal and whether they are a potential threat to biota, though they are best used to complement field observations, rather than as a substitute for surveys. *S. plana* was found to be less robust than *Turritella*, however lower baseline concentrations (for most metals) may make the use of clams preferable when trying to detect small changes in bioavailability. Experiments with *Turritella* must also be restricted to saline conditions (~35‰) whereas *S. plana* is tolerant of a much wider salinity range (down to ~10‰). As in the field approach, mesocosm evaluation of sediment-metal bioavailability should involve several types of organism, ideally. Further trials with a wider range of sediments and indicator species would be useful in developing this method of assessment.

6.9 Summary: Bioavailability

Though there is no single universal measure of biological impact, the majority of methodologies tested here combine to provide a useful overall assessment of the origins and bioavailability of contaminant metals in sediments. The project drew upon a combination of: 1) existing information (n.b. PML's own data-base); 2) new surveys of sediments and biota from the Mersey, Wyre, Ribble and Solway Firth systems; and 3) observation of bioaccumulation from these sediment cores in a laboratory mesocosm experiment.

The bioavailability of metals (Ag, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, Sn and Zn) in Irish Sea sediments has been assessed, and attempts made to test whether or not this varies according to their source (anthropogenic or natural).

The most meaningful and direct assessments of estuarine sediment impact are those involving field surveys with bioindicator species such as *Scrobicularia plana, Macoma balthica* and *Nereis diversicolor*. Selective sediment measurements can often be used to mimic and predict the 'biologically available' fraction in sediment, and to distinguish the relative importance for biota of natural *vs* pollutant loadings.

Several techniques aimed at characterising sediment contamination and providing surrogate measures of bioavailability were evaluated. Sieving is an important first step in comparing sediment loadings and establishing anthropogenic influence. Comparison of PML (<100µm) and BGS techniques (150µm) showed that, provided some-grain size standardisation is carried out, the exact mesh size selected for sieving may not be critical, particularly for estuarine and offshore muds which contain a high proportion of fine silts and clays. Results from the two laboratories gave comparable impressions of contamination despite variations in techniques (including analysis). For the majority of 'pollutant' metals, spatial trends in body burdens in the Irish Sea are a direct function of concentrations in the fine sediment fraction.

Additional information as to the relative degree of metal contamination in sediments was achieved by establishing relationships with, and normalisation to, metal binding substrates such as Fe (oxyhydroxides) and organic matter content. Traditional geogenic normalisers such as Al and Rb (Loring, 1991) also offered comparable information. For the range of Irish Sea sediment types analysed here, therefore, selection of the normalising element may not be critical in terms of comparing loadings, provided that samples have been sieved.

Normalisation techniques not only help to provide better measures of anthropogenic enrichment in the environment but, in cases where Fe- or organic-normalised sediment values can be shown to correlate significantly with body burdens, they may also denote the biological consequences of that enrichment. Careful application of this type of measurement in sediments can therefore be used to map or predict bioavailable metals and estimate the proportion which is not of a natural origin.

For parts of the sample set dealt with in this project, the suspected mixing of fine particles over relatively large areas, may be a factor masking the designation and impact of some anthropogenic sources. Also, there are undoubtedly other characteristics beside Fe and organic ligands which could modify availability: redox/ sulphide chemistry in sediments is probably one of the more important factors which needs to be examined in some detail.

Faced with variability in biological response, the use of weaker extracts is sometimes preferable to 'total' digests in providing information on bioavailable metal, althoughthe application of extractants such as 1M HCl to mimic and predict the 'biologically available' fraction, is clearly not a panacea (see also Martin *et al.*,1987; Tessier and Campbell, 1987; Campbell *et al.*, 1988). Ammonium acetate (exchangeable metal) offers no advantages over 1M HCl and is less versatile, analytically. Despite their limitations, however, these techniques at least provide a viable option for preliminary comparative estimations of bioavailability in sediments, particularly where bioindicator species are difficult to obtain.

Unfortunately, there is no 'universal bioindicator' present naturally in both offshore and estuarine sediments and an experimental approach had to be adopted to compare the full range of sediment types in the Irish Sea. Mesocosm studies with the estuarine clam *S.plana* (at 28 psu) and a marine gastropod *Turritella communis* (35 psu) were shown to provide a preliminary assessment of metal bioavailability. The main limitation of mesocosm studies, on current evidence, concerns the long equilibration times which may apply to the bioaccumulation of sediment metals, which may not reach steady state within the time frame examined here (6 months). Such mesocosm studies are therefore promising as a screening method to determine whether sediments represent a potential threat to biota, though at present they are best used to complement field observations, rather than as a substitute for surveys.

7 SUMMARY OF CONCLUSIONS

The methodologies outlined in sections 4-6 above have successfully addressed the main project objectives as set out in section 2.

Where detailed regional geochemistry is available, model geochemical signatures, based on combining the signatures of different geological lithologies in proportion to their presence in the drainage basin, provide an innovative technique for the estimation of natural background values, even when mining, industry and urban development are present in the catchment. No new data collection is needed and the methodology could be used to address government policy issues such as the definition of background values on which to base compliance with the OSPAR Strategy on Hazardous Substances. In 'pristine' catchments, a link between average catchment geochemistry and the chemistry of the representative major river/estuary sample has been established. Thus even where detailed regional geochemistry is not available, a relatively limited programme of river/estuary sampling should allow model/background signatures to be determined. In some cases, specific element values in model and catchment signatures were found to be at variance. It is thus best, from an environmental point of view to generate both signatures and then to err on the side of caution and set the natural background level at the lower of the two values. Further work to refine the modelling procedures would be valuable.

Measurement of Pb isotopic ratios using laser ablation techniques on pellets prepared for XRF analysis is another innovative and cost-cutting methodology which allows Pb from different natural and anthropogenic sources to be identified. Particularly when used in conjunction with multi-element geochemistry and GIS data, Pb isotopes have the potential to distinguish anthropogenic metal and also different natural sources, even where absolute values are relatively low.

The geochemistry of major river samples taken downstream of industrial activity, when compared with catchment and/or river samples upstream, allows industrial and mining metal inputs to be distinguished. Overall negative inputs to the estuaries, in comparison with catchment background levels, probably reflect loss of fine-grained material to the sea in suspension and the trapping of heavy mineral concentrates in the river basins.

Based on results from both geochemical and bioavailability studies there were few examples of natural enrichment or bioaccumulation in Irish Sea sediments (arising from catchment sources). Anthropogenic enrichment and bioavailability of pollutant elements (Sn, Hg, Ag, Pb, Cr and sometimes other metals) was observed in Mersey sediments, and occasionally elsewhere, in both field and mesocosm assessments. The scale of anthropogenic impact was, perhaps, unexpectedly small (less than a factor of ten for most metals), considering the industrial background of much of the region. No doubt this partly reflects successful efforts to reduce major inputs in recent years. However, the influence of contamination in Mersey sediments appears to be fairly extensive, albeit at low levels, and a more detailed survey is needed to resolve the dispersion of Liverpool Bay fines.

Multi-element geochemistry indicates that in inner estuary areas, hydraulic conditions may be such that some metal values are unusually depleted and a better estimate of metal inputs to the sea may be gained from samples taken nearer the estuary mouth. However, there is also evidence that fine sediments in the Mersey, Ribble and Solway estuaries are influenced to a significant extent by mixing with particulates from offshore. This has a significant effect on the observed gradients in metal contamination. For example, offshore surface fines in Liverpool Bay in the current study were equivalent in contamination (and sometimes slightly higher) than those within the Mersey Estuary. In contrast, in the 1980s, levels of a number of pollutant metals were highest in the inner estuary (Langston, 1986). It appears that, following recent improvements in quality within the Mersey, offshore sediments of Liverpool Bay may now be acting as a reservoir of contaminated particles with a significant transport component into the estuary. This inshore movement, coupled with northerly dispersion of Liverpool Bay fines may also explain why metal concentrations in sediments off the mouth of the Ribble (and, more remotely, perhaps, the Solway) were, if anything, slightly higher than those upstream in the respective estuary. In contrast, metal contamination (and bioavailability) gradients in the Wyre appear be less influenced by incursion and large scale mixing with marine sediments; metal enhancement was higher, upstream, in this estuary than offshore.

Biological availability of metals in different Irish Sea (estuarine) sediments can be assessed, directly, by analysing suitable bioindicators (such as *Scrobicularia plana*) and comparing body burdens with background values for the species. Use of selective extracts can also help to define biologically available sediment fractions, and their origin, for some organism/metal combinations. The degree of metal enrichment in tissues of *S.plana*, for example, reflects, superficially, anthropogenic contributions in sediments (operationally defined by 1MHCl-extractable metal). However, manifestation of the 'biologically-available metal fraction or phase', expressed as body burdens, will vary from species to species, and from metal to metal, because it is dependent, to an extent, on the physiology and biochemistry of the organism under investigation. In extreme cases, uptake of metals such as Cu and Zn can be regulated by some taxa to meet essential requirements, irrespective of environmental contamination. Comparisons of bioavailability, based on analyses of *Scrobicularia plana, Macoma balthica* and *Nereis diversicolor* at Irish Sea sites, have demonstrated the likely extent of this biological variability. For future assessments, the use of a small range of bioindicators would clearly be preferable to a single species approach.

Laboratory (mesocosm) studies seem promising as screening method to determine whether sediments represent a potential threat to biota, though they are best used to complement field observations, rather than as a substitute for surveys. In the long-term the mesocosm approach is likely to be most useful and cost-effective with respect to offshore sediments or materials destined for disposal at sea, where *in-situ* measures of bioavailability are usually impractical. Again, a combination of uptake experiments with species such as *Turritella communis* and *Scrobicularia plana*, and sediment characterisation, represent the most viable strategy. It is recommended that replication of cores is increased to a minimum of six to improve statistical treatment of data.

In summary, the most satisfactory options for establishing sediment-metal biovailability, and anthropogenic influences, involve a combination of analysis of bioindicators (*in situ*) and geochemical characterisation of sediments. By studying the relationships between the two it is possible to identify features which determine biological responses in the environment. Mesocosm style studies are useful as a complementary screening tool, particularly for offshore sediments and waste deposits, though this approach would benefit from wider validation. Other species and sediment types should be evaluated. Materials from metal-rich estuarine sites, contaminated dredge spoils, and artificially manipulated sediments would be ideal for testing the influence of modifying characteristics. The use of mesocosm-type studies could also be extended to incorporate biological effects. In order to examine the biological consequences of sediment loadings, at the subcellular-level, it would be opportune to assess the composition and role of metal-binding granules in species such as *Turritella,* over a range of sediment types, and to look at other indices of impact (e.g. metallothionein induction and immune function). These measures would indicate whether or not the organisms are susceptible, or able to adapt, to metal-induced stress. At the whole animal level, bioaccumulation, growth and condition could be measured as an overall indication of response, preferably in a range of key sediment-dwelling types. This would identify further suitable species for screening sediments, and also the most vulnerable.

The combination of approaches tested here represents a significant advance in interpreting the influence and origins of particulate metals. Both geochemical and bioavailability programmes were able to confirm, independently, the absence of extreme levels of pollution in Irish Sea sediments, but at the same time identified common gradients and examples of enrichment for some individual metals. Inputs into the Mersey Estuary/Liverpool Bay, were distributed fairly evenly in local sediments, but were, nevertheless, the dominant influence on trends in anthropogenic, bioavailable metal in sediments of the eastern Irish Sea basin. The Solway represented 'pristine' conditions for the region. Further use of this approach over a wider range of sediment types should provide revealing insights as to the overall significance of metal loadings around UK coastlines. A more extensive data-set, covering a wider range of estuarine conditions and geological backgrounds in the UK would also be valuable in testing the robustness of the methodologies described here.

8 RECOMMENDATIONS

A similar strategy to that outlined here could be applied in future, in whole or in part, to provide a more comprehensive and contemporary spatial assessment of sediment quality and anthropogenic inputs throughout the Irish Sea Basin and beyond to the whole of the UK. A first priority would be to establish natural background levels for inputs to the sea as a basis for government policy with respect to the OSPAR Strategy on Hazardous Substances. It would also act as a platform to establish long-term change. Refinement of the procedures for modelling geochemical signatures would form an integral part of any such study.

In future, more detailed attempts to define the origins and bioavailability of certain forms of pollutant metals (highlighted in this study) would be valuable. One example would be the more detailed examination of isotopic ratios of Pb in Mersey sediments in order to characterise Pb sources (natural or anthropogenic). Contemporary analysis of biota may reveal whether this source is reflected in accumulated body burdens. Sn also appears to be one of the more enriched elements in biota of the Mersey and to a lesser extent the Wyre and Ribble. Though present in relatively minor amounts in sediment, compared with inorganic tin, bioavailability of TBT is considered to be disproportionately high. Specific measurements of organic tin are therefore required to evaluate the significance of anthropogenic contributions of this metal in the Irish Sea sediments and biota.

Finally, it is important from a policy point of view to establish evidence for temporal trends in metals (particularly in Mersey sediments and biota). The use of shells as a marker of current and recent contamination history (using laser ablation ICP-MS techniques in relation to growth rings) would be worth investigating. The current collection (*Scrobicularia plana*) may be a useful starting point. Archived material (shells, soft tissues and sediment) and residue data are also available to provide a longer-term historical perspective.

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Appendix 2: Details of sample sites. 1 of 9

Collection Number	Material	Sample No.	Map	Grid Ref.
Beb1	SIEVED - in plastic bag	Beb1	108	340862
Beb1 - 0-5cm	UNSIEVED - in plastic bag	Beb1 - 0-5cm	108	340862
Beb1 - 10-20cm	UNSIEVED - in plastic bag	Beb1 - 10-20cm	108	340862
Beb1 - 20-27cm	UNSIEVED - in plastic bag	Beb1 - 20-27cm	108	340862
Beb1 - 5-10cm	UNSIEVED - in plastic bag	Beb1 - 5-10cm	108	340862
Bollin1	SIEVED - in plastic bag	Bollin1	109	698887
Bollin2	SIEVED - in plastic bag	Bollin2	109	882804
Calder1	SIEVED - in plastic bag	Calder1	103	726364
Calder2	SIEVED - in plastic bag	Calder2	103	727363
Calder2	<2mm in paper bag		103	727363
Caldew1 - R.Bank	SIEVED - in plastic bag	Caldew1	85	369488
CludenWater1 - R.Bank	SIEVED - in plastic bag	Cludenwater1	84	959787
CludenWater2	SIEVED - in plastic bag	Cludenwater2	84	947791
CludenWater3	SIEVED - in plastic bag	Cludenwater3	84	885798
Crole1 (L.Bank)	SIEVED - in plastic bag	Croal1	109	749065
Douglas1 - L.Bank	SIEVED - in plastic bag	Douglas1	102	445259
Douglas2A	SIEVED - in plastic bag	Douglas2A	108	466180
Douglas2B	SIEVED - in plastic bag	Douglas2B	108	466180
Eden1 - L.Bank	SIEVED - in plastic bag	Eden1	85	377580
Eden2 - R.Bank-GRAVEL	SIEVED - in plastic bag	Eden2	85	371579
Eden2B - R.Bank	<2mm in paper bag		85	371579
Eden2B - R.Bank-SAND	SIEVED - in plastic bag	Eden2B	85	371579
Eden3 - L.Bank	SIEVED - in plastic bag	Eden3	86	517494
Eden3 - L.Bank	<2mm in paper bag		86	517494
Eden4 - Centre	SIEVED - in plastic bag	Eden4	86	515484
Eden5	SIEVED - in plastic bag	Eden5	85	339617
Eden5B	SIEVED - in plastic bag	Eden5B	85	339617
Eden6 - L.Bank	SIEVED - in plastic bag	Eden6	85	328618
Egre1	SIEVED - in plastic bag	Egre1	108	319925
Egre1 - 0-5cm	UNSIEVED - in plastic bag	Egre1 - 0-5cm	108	319925
Egre1 - 10-20cm	UNSIEVED - in plastic bag	Egre1 - 10-20cm	108	319925
Egre1 5-10cm	UNSIEVED - in plastic bag	Egre1 5-10cm	108	319925
Ellen1	SIEVED - in plastic bag	Ellen1	89	069371
Esk 2 - L.Bank	SIEVED - in plastic bag	Esk2	79	350874
Esk1	SIEVED - in plastic bag	Esk1	79	354877
Esk3	SIEVED - in plastic bag	Esk3	85	385783
Esk4 - R.Bank	SIEVED - in plastic bag	Esk4	85	389729
Esk5	SIEVED - in plastic bag	Esk5	85	389730
Esk5	<2mm in paper bag		85	389730
Esk6 - L.Bank	SIEVED - in plastic bag	Esk6	85	334650
Etherow1	SIEVED - in plastic bag	Etherow1	109	976919
Etherow1	<2mm in paper bag		109	976919
Eweswater1	SIEVED - in plastic bag	Eweswater1	79	372868
Fiddlers Ferry1 - 0-5cm	UNSIEVED - in plastic bag	Fiddlers Ferry1 - 0-5cm	108	555849
Fiddlers Ferry1 - 10-20cm	UNSIEVED - in plastic bag	Fiddlers Ferry1 - 10-20cm	108	555849
Fiddlers Ferry1 - 20-30cm	UNSIEVED - in plastic bag	Fiddlers Ferry1 - 20-30cm	108	555849
Fiddlers Ferry1 - 30-50cm	UNSIEVED - in plastic bag	Fiddlers Ferry1 - 30-50cm	108	555849
Fiddlers Ferry1 - 50-70cm	UNSIEVED - in plastic bag	Fiddlers Ferry1 - 50-70cm	108	555849
Fiddlers Ferry1 - 5-10cm	UNSIEVED - in plastic bag	Fiddlers Ferry1 - 5-10cm	108	555849
Fiddlers Ferry1 - 70-90cm	UNSIEVED - in plastic bag	Fiddlers Ferry1 - 70-90cm	108	555849
Fiddlers Ferry2	SIEVED - in plastic bag	Fiddlers Ferry2	108	555849
Goyt1 - Centre bar	SIEVED - in plastic bag	Goyt1	109	966874
Hale1 - 0-5cm	UNSIEVED - in plastic bag	Hale1 - 0-5cm	108	473808
Hale1 - 10-20cm	UNSIEVED - in plastic bag	Hale1 - 10-20cm	108	473808
Hale1 - 20-30cm	UNSIEVED - in plastic bag	Hale1 - 20-30cm	108	473808

Appendix 2: Details of sample sites. 2 of 9

Collection Number	Material	Sample No.	Map	Grid Ref.
Hale1 - 30-45cm	UNSIEVED - in plastic bag	Hale1 - 30-45cm	108	473808
Hale1 - 5-10cm	UNSIEVED - in plastic bag	Hale1 - 5-10cm	108	473808
Hale2	SIEVED - in plastic bag	Hale2	108	473808
Hodder1	SIEVED - in plastic bag	Hodder1	103	704392
Ince Bank1 - 0-5cm	UNSIEVED - in plastic bag	Ince Bank1 - 0-5cm	117	447795
Ince Bank1 - 10-20cm	UNSIEVED - in plastic bag	Ince Bank1 - 10-20cm	117	447795
Ince Bank1 - 20-30cm	UNSIEVED - in plastic bag	Ince Bank1 - 20-30cm	117	447795
Ince Bank1 - 30-50cm	UNSIEVED - in plastic bag	Ince Bank1 - 30-50cm	117	447795
Ince Bank1 - 50-70cm	UNSIEVED - in plastic bag	Ince Bank1 - 50-70cm	117	447795
Ince Bank1 - 5-10cm	UNSIEVED - in plastic bag	Ince Bank1 - 5-10cm	117	447795
Ince Bank2	SIEVED - in plastic bag	Ince Bank2	117	447795
Irthing1 - Nr. R.Bank	SIEVED - in plastic bag	Irthing1	86	478581
Irwell1 - Centre river	SIEVED - in plastic bag	Irwell1	109	750061
Irwell2 (central)	SIEVED - in plastic bag	Irwell2	109	799080
LiddellWater1 - R.Bank	SIEVED - in plastic bag	Liddelwater1	85	433774
LiddellWater1-R.Bank	<2mm in paper bag		85	433774
LiddellWater2 - L.Bank	SIEVED - in plastic bag	Liddelwater2	85	432774
M/O	SIEVED - in plastic bag			340862
M/U	SIEVED - in plastic bag			370812
Mersey1	SIEVED - in plastic bag	Mersey1	109	823917
Mersey1	<2mm in paper bag		109	823917
MickleBrook1	SIEVED - in plastic bag	MickerBrook1	109	862879
NBright1 - 0-5cm	UNSIEVED - in plastic bag	NBright1 - 0-5cm	108	314943
NBright1 - 10-20cm	UNSIEVED - in plastic bag	NBright1 - 10-20cm	108	314943
NBright1 - 5-10cm	UNSIEVED - in plastic bag	NBright1 - 5-10cm	108	314943
New Brighton1	SIEVED - in plastic bag	New Brighton1	108	314943
Nith1	SIEVED - in plastic bag	Nith1	84	976749
Nith2	SIEVED - in plastic bag	Nith2	84	977749
Nith3 - L.Bank	SIEVED - in plastic bag	Nith3	84	978784
Nith4 (Centre bank)	SIEVED - in plastic bag	Nith4	84	979781
Nith4 (Centre bank)	<2mm - in plastic bag		84	979781
Nith4B	<2mm - in plastic bag		84	979781
Nith5	SIEVED - in plastic bag	Nith5	84	974724
Nith6	SIEVED - in plastic bag	Nith6	84	995661
Nith6B	SIEVED - in plastic bag	Nith6B	84	995661
Nith7 - L.Bank	SIEVED - in plastic bag	Nith7	84	994688
Otterspool1	SIEVED - in plastic bag	Otterspool1	108	357869
Petterel1	SIEVED - in plastic bag	Petteril1	85	437510
R/O	SIEVED - in plastic bag			
Ribble Lower Surface	SIEVED - in plastic bag			346270
Ribble Upper Surface	SIEVED - in plastic bag			425269
Ribble1	SIEVED - in plastic bag	Ribble1	103	762449
Ribble1	<2mm in paper bag		103	762449
Ribble2 - Centre	SIEVED - in plastic bag	Ribble2	103	651351
Ribble3 - R.Bank	SIEVED - in plastic bag	Ribble3	102	367265
Ribble4 - R.Bank	SIEVED - in plastic bag	Ribble4	102	432270
Ribble5	<2mm in paper bag		102	432270
Ribble5 - R.Bank	SIEVED - in plastic bag	Ribble5	102	432270
Ribble5B	SIEVED - in plastic bag	Ribble5B	102	432270
Ribble6 - L.Bank	SIEVED - in plastic bag	Ribble6	102	421265
Ribble7 - L.Bank	SIEVED - in plastic bag	Ribble7	102	497290
Ribble8 - R.Bank	SIEVED - in plastic bag	Ribble8	102	517293
Richmond Bank1 - 0-5cm	UNSIEVED - in plastic bag	Richmond Bank1 - 0-5cm	108	572866
Richmond Bank1 - 10-20cm	UNSIEVED - in plastic bag	Richmond Bank1 - 10-20cm	108	572866
Richmond Bank1 - 20-30cm	UNSIEVED - in plastic bag	Richmond Bank1 - 20-30cm	108	572866
Richmond Bank1 - 30-50cm	UNSIEVED - in plastic bag	Richmond Bank1 - 30-50cm	108	572866

Appendix 2: Details of sample sites. 3 of 9

Collection Number	**Material**	**Sample No.**	**Map**	**Grid Ref.**
Richmond Bank1 - 50-75cm	UNSIEVED - in plastic bag	Richmond Bank1 - 50-75cm	108	572866
Richmond Bank1 - 5-10cm	UNSIEVED - in plastic bag	Richmond Bank1 - 5-10cm	108	572866
Richmond Bank2	SIEVED - in plastic bag	Richmond Bank2	108	572866
Roch1	SIEVED - in plastic bag	Roch1	109	813095
Runcorn Sands1	SIEVED - in plastic bag	Runcorn Sands1	108	527841
Runcorn Sands1	<2mm in paper bag		108	527841
S.Hale1	SIEVED - in plastic bag	S.Hale1	108	471797
S/O	SIEVED - in plastic bag			
Seaforth1	SIEVED - in plastic bag	Seaforth1	108	322958
Seaforth1	<2mm in paper bag	Seaforth1	108	322958
Seaforth1 - 0-5cm	UNSIEVED - in plastic bag	Seaforth1 - 0-5cm	108	322958
Seaforth1 - 10-20cm	UNSIEVED - in plastic bag	Seaforth1 - 10-20cm	108	322958
Seaforth1 - 20-30cm	UNSIEVED - in plastic bag	Seaforth1 - 20-30cm	108	322958
Seaforth1 - 30-50cm	UNSIEVED - in plastic bag	Seaforth1 - 30-50cm	108	322958
Seaforth1 - 50-70cm	UNSIEVED - in plastic bag	Seaforth1 - 50-70cm	108	322958
Seaforth1 - 5-10cm	UNSIEVED - in plastic bag	Seaforth1 - 5-10cm	108	322958
Seaforth1 - 70-100cm	UNSIEVED - in plastic bag	Seaforth1 - 70-100cm	108	322958
Solway Lower Surface	SIEVED - in plastic bag			ny136564
Solway Upper Surface	SIEVED - in plastic bag			ny232628
Speke1	SIEVED - in plastic bag	Speke1	108	412824
Speke1 - 0-5cm	UNSIEVED - in plastic bag	Speke1 - 0-5cm	108	412824
Speke1 - 10-20cm	UNSIEVED - in plastic bag	Speke1 - 10-20cm	108	412824
Speke1 - 20-30cm	UNSIEVED - in plastic bag	Speke1 - 20-30cm	108	412824
Speke1 - 30-46cm	UNSIEVED - in plastic bag	Speke1 - 30-46cm	108	412824
Speke1 - 5-10cm	UNSIEVED - in plastic bag	Speke1 - 5-10cm	108	412824
Tame1	SIEVED - in plastic bag	Tame1	109	906935
W/O	SIEVED - in plastic bag			
Waters1 - 0-5cm	UNSIEVED - in plastic bag	Waters1 - 0-5cm	108	344886
Waters1 - 10-20cm	UNSIEVED - in plastic bag	Waters1 - 10-20cm	108	344886
Waters1 - 5-10cm	UNSIEVED - in plastic bag	Waters1 - 5-10cm	108	344886
Waterside1	SIEVED - in plastic bag	Waterside1	108	344886
Waterside1B	SIEVED - in plastic bag	Waterside1B	108	344886
Waver1	SIEVED - in plastic bag	Waver1	85	179504
Weaver1	SIEVED - in plastic bag	Weaver1	118	629738
Wyre Lower Surface	SIEVED - in plastic bag			sd345485
Wyre Upper Surface	SIEVED - in plastic bag			sd364429
Wyre1 - R.Bank	SIEVED - in plastic bag	Wyre1	102	369411
Wyre1B	SIEVED - in plastic bag	Wyre1B	102	369411
Wyre10 - R.Bank	SIEVED - in plastic bag	Wyre10	102	350449
Wyre11	SIEVED - in plastic bag	Wyre11	102	344471
Wyre11B	SIEVED - in plastic bag	Wyre11B	102	344471
Wyre12	SIEVED - in plastic bag	Wyre12	102	341471
Wyre12B	SIEVED - in plastic bag	Wyre12B	102	341471
Wyre13	SIEVED - in plastic bag	Wyre13	102	340484
Wyre2	SIEVED - in plastic bag	Wyre2	102	369411
Wyre3 - L.Bank	SIEVED - in plastic bag	Wyre3	102	369410
Wyre4 - L.Bank	SIEVED - in plastic bag	Wyre4	102	369410
Wyre5 - R.Bank	SIEVED - in plastic bag	Wyre5	102	369411
Wyre5 - R.Bank	<2mm in paper bag		102	369411
Wyre6	SIEVED - in plastic bag	Wyre6	102	463410
Wyre6	<2mm - in plastic bag		102	463410
Wyre6B	<2mm - in plastic bag		102	463410
Wyre7B	SIEVED - in plastic bag	Wyre7	102	343486
Wyre8 - R.Estuary	SIEVED - in plastic bag	Wyre8	102	345485
Wyre9 - R.Bank	SIEVED - in plastic bag	Wyre9	102	349449
WyreLowerSurfaceB	SIEVED - in plastic bag			

Appendix 2: Details of sample sites. 4 of 9

Collection Number	Easting	Northing	Date	Description
Beb1	334000	386200	02-11-99	
Beb1 - 0-5cm	334000	386200	02-11-99	
Beb1 - 10-20cm	334000	386200	02-11-99	
Beb1 - 20-27cm	334000	386200	02-11-99	
Beb1 - 5-10cm	334000	386200	02-11-99	
Bollin1			16-09-99	<2mm
Bollin2			05-10-99	<2mm
Calder1			18-05-99	<150µm & <2mm
Calder2			18-05-99	<150µm & <2mm
Calder2			18-05-99	
Caldew1 - R.Bank			10-06-99	<2mm
CludenWater1 - R.Bank			08-06-99	
CludenWater2			08-06-99	<2mm
CludenWater3			08-06-99	<2mm
Crole1 (L.Bank)			15-07-99	<2mm
Douglas1 - L.Bank			14-07-99	Unsieved
Douglas2A			05-10-99	Unsieved
Douglas2B			05-10-99	
Eden1 - L.Bank			10-06-99	<2mm No sieving.
Eden2 - R.Bank-GRAVEL			10-06-99	
Eden2B - R.Bank			10-06-99	
Eden2B - R.Bank-SAND			10-06-99	
Eden3 - L.Bank			10-06-99	Sieved
Eden3 - L.Bank			10-06-99	
Eden4 - Centre			10-06-99	Unsieved
Eden5			23-06-99	Unsieved
Eden5B			23-06-99	
Eden6 - L.Bank			23-06-99	Unsieved
Egre1	331900	392500	02-11-99	
Egre1 - 0-5cm	331900	392500	02-11-99	
Egre1 - 10-20cm	331900	392500	02-11-99	
Egre1 5-10cm	331900	392500	02-11-99	
Ellen1			11-06-99	<2mm
Esk 2 - L.Bank			09-06-99	<2mm
Esk1			09-06-99	<2mm
Esk3			09-06-99	
Esk4 - R.Bank			09-06-99	<2mm
Esk5			09-06-99	<2mm No sieving.
Esk5			09-06-99	
Esk6 - L.Bank			23-06-99	Unsieved
Etherow1			16-07-99	<2mm
Etherow1			16-07-99	
Eweswater1			09-06-99	<2mm
Fiddlers Ferry1 - 0-5cm	355500	384900	03-11-99	
Fiddlers Ferry1 - 10-20cm	355500	384900	03-11-99	
Fiddlers Ferry1 - 20-30cm	355500	384900	03-11-99	
Fiddlers Ferry1 - 30-50cm	355500	384900	03-11-99	
Fiddlers Ferry1 - 50-70cm	355500	384900	03-11-99	
Fiddlers Ferry1 - 5-10cm	355500	384900	03-11-99	
Fiddlers Ferry1 - 70-90cm	355500	384900	03-11-99	
Fiddlers Ferry2	355500	384900	03-11-99	
Goyt1 - Centre bar			16-07-99	<2mm
Hale1 - 0-5cm	347300	380800	03-11-99	
Hale1 - 10-20cm	347300	380800	03-11-99	
Hale1 - 20-30cm	347300	380800	03-11-99	

Appendix 2: Details of sample sites. 5 of 9

Collection Number	Easting	Northing	Date	Description
Hale1 - 30-45cm	347300	380800	03-11-99	
Hale1 - 5-10cm	347300	380800	03-11-99	
Hale2	347300	380800	03-11-99	
Hodder1			14-07-99	<2mm
Ince Bank1 - 0-5cm	344700	379500	03-11-99	
Ince Bank1 - 10-20cm	344700	379500	03-11-99	
Ince Bank1 - 20-30cm	344700	379500	03-11-99	
Ince Bank1 - 30-50cm	344700	379500	03-11-99	
Ince Bank1 - 50-70cm	344700	379500	03-11-99	
Ince Bank1 - 5-10cm	344700	379500	03-11-99	
Ince Bank2	344700	379500	03-11-99	
Irthing1 - Nr. R.Bank			10-06-99	Sieved
Irwell1 - Centre river			15-07-99	<2mm
Irwell2 (central)			15-07-99	<2mm
LiddellWater1 - R.Bank			09-06-99	<2mm
LiddellWater1-R.Bank			09-06-99	
LiddellWater2 - L.Bank			09-06-99	<2mm
M/O	334000	386200		
M/U	337000	381200		
Mersey1			16-09-99	<2mm
Mersey1			16-09-99	
MickleBrook1			16-07-99	<2mm
NBright1 - 0-5cm	331400	394300	02-11-99	
NBright1 - 10-20cm	331400	394300	02-11-99	
NBright1 - 5-10cm	331400	394300	02-11-99	
New Brighton1	331400	394300	02-11-99	
Nith1			08-06-99	<2mm
Nith2			08-06-99	<2mm
Nith3 - L.Bank			08-06-99	<2mm
Nith4 (Centre bank)			08-06-99	<2mm
Nith4 (Centre bank)			08-06-99	
Nith4B			08-06-99	
Nith5			22-06-99	Van Veen grab
Nith6			23-06-99	Unsieved
Nith6B			23-06-99	
Nith7 - L.Bank			23-06-99	Unsieved
Otterspool1	335700	386900	02-11-99	
Petterel1			10-06-99	<2mm
R/O	313146	424807		
Ribble Lower Surface	334600	427000		
Ribble Upper Surface	342500	426900		
Ribble1			19-05-99	<150µm & <2mm
Ribble1			19-05-99	
Ribble2 - Centre			13-07-99	Sieved
Ribble3 - R.Bank			14-07-99	Unsieved
Ribble4 - R.Bank			14-07-99	Unsieved
Ribble5			14-07-99	Unsieved
Ribble5 - R.Bank			14-07-99	
Ribble5B			14-07-99	
Ribble6 - L.Bank			14-07-99	Unsieved
Ribble7 - L.Bank			14-07-99	Unsieved
Ribble8 - R.Bank			14-07-99	Unsieved
Richmond Bank1 - 0-5cm	357200	386600	03-11-99	
Richmond Bank1 - 10-20cm	357200	386600	03-11-99	
Richmond Bank1 - 20-30cm	357200	386600	03-11-99	
Richmond Bank1 - 30-50cm	357200	386600	03-11-99	

Appendix 2: Details of sample sites. 6 of 9

Collection Number	Easting	Northing	Date	Description
Richmond Bank1 - 50-75cm	357200	386600	03-11-99	
Richmond Bank1 - 5-10cm	357200	386600	03-11-99	
Richmond Bank2	357200	386600	03-11-99	
Roch1			15-07-99	<2mm
Runcorn Sands1	352700	384100	03-11-99	
Runcorn Sands1	352700	384100	03-11-99	
S.Hale1	347100	379700	03-11-99	
S/O				
Seaforth1	332200	395800	03-11-99	
Seaforth1	332200	395800	03-11-99	
Seaforth1 - 0-5cm	332200	395800	03-11-99	
Seaforth1 - 10-20cm	332200	395800	03-11-99	
Seaforth1 - 20-30cm	332200	395800	03-11-99	
Seaforth1 - 30-50cm	332200	395800	03-11-99	
Seaforth1 - 50-70cm	332200	395800	03-11-99	
Seaforth1 - 5-10cm	332200	395800	03-11-99	
Seaforth1 - 70-100cm	332200	395800	03-11-99	
Solway Lower Surface				
Solway Upper Surface				
Speke1	341200	382400	03-11-99	
Speke1 - 0-5cm	341200	382400	03-11-99	
Speke1 - 10-20cm	341200	382400	03-11-99	
Speke1 - 20-30cm	341200	382400	03-11-99	
Speke1 - 30-46cm	341200	382400	03-11-99	
Speke1 - 5-10cm	341200	382400	03-11-99	
Tame1			15-07-99	<2mm
W/O				
Waters1 - 0-5cm	334400	388600	03-11-99	
Waters1 - 10-20cm	334400	388600	03-11-99	
Waters1 - 5-10cm	334400	388600	03-11-99	
Waterside1	334400	388600	03-11-99	
Waterside1B	334400	388600	03-11-99	
Waver1			11-06-99	<2mm
Weaver1			16-09-99	Grab sample
Wyre Lower Surface				
Wyre Upper Surface				
Wyre1 - R.Bank			13-07-99	Unsieved
Wyre1B			13-07-99	
Wyre10 - R.Bank			13-07-99	Unsieved
Wyre11			13-07-99	Unsieved
Wyre11B			13-07-99	
Wyre12			13-07-99	Unsieved
Wyre12B			13-07-99	
Wyre13			13-07-99	Unsieved
Wyre2			13-07-99	Unsieved
Wyre3 - L.Bank			13-07-99	Unsieved
Wyre4 - L.Bank			13-07-99	Unsieved
Wyre5 - R.Bank			13-07-99	Unsieved
Wyre5 - R.Bank			13-07-99	
Wyre6			13-07-99	Sieved
Wyre6			13-07-99	
Wyre6B			13-07-99	
Wyre7B			13-07-99	Unsieved
Wyre8 - R.Estuary			13-07-99	Unsieved
Wyre9 - R.Bank			13-07-99	Unsieved
WyreLowerSurfaceB				

Appendix 2: Details of sample sites. 7 of 9

Collection Number	**Comments/notes**
Beb1	
Beb1 - 0-5cm	
Beb1 - 10-20cm	
Beb1 - 20-27cm	
Beb1 - 5-10cm	
Bollin1	sampled L bank to centre of channel, just above bridge
Bollin2	island in middle of 15m wide channel with gravelly bed. Fine sand from island + both sides + toe.
Calder1	L bank. gravel bed with bolders <2ft across
Calder2	R bank. gravel bed with bolders <2ft across. Evidence of contamination- glass, plastic etc.
Calder2	
Caldew1 - R.Bank	R bank, gravel patch sampled. L bank not sampled. River ~ 10m wide
CludenWater1 - R.Bank	ford nr. Hardlawbank, above Dumfries. Sand and cobble bottom, contaminated from track to ford?
CludenWater2	above roadbridge at Newbridge, above Dumfries. Mostly from R bank/centre. L impossible to sample
CludenWater3	Routin Bridge. 5m gravel bed channel
Crole1 (L.Bank)	L bank, Gravel bar Thick made ground above rock exposures
Douglas1 - L.Bank	L bank. Sample = muddy sand just inside steep side of channel.
Douglas2A	Probably still tidal and enclosed in artifical banks. Grad sample from bridge. D2A = from bridge. D2B = mud from L bank.
Douglas2B	
Eden1 - L.Bank	L bank, inside bend, rippled sand patch next to water. Rubbish close by - bricks,plastic,metal.
Eden2 - R.Bank-GRAVEL	R bank, inside bend, sampled gravel patch similar to present river bed (selved) + rippled sand upbank of the gravel
Eden2B - R.Bank	
Eden2B - R.Bank-SAND	
Eden3 - L.Bank	L bank, gravel patch. Wide fast flowing river
Eden3 - L.Bank	
Eden4 - Centre	Island upstream of Eden3, small patch of sand in centre, lots of root material.
Eden5	Cattletown House Demesne, island in centre of river. Rippled muddy sand over gravel, below tidal lt,fresh water at time of sampling (edd tide
Eden5B	
Eden6 - L.Bank	Inside bend of channel (L bank). W of Old Sandsfield ~ 500m. Well rippled sand
Egre1	
Egre1 - 0-5cm	
Egre1 - 10-20cm	
Egre1 5-10cm	
Ellen1	Sample from sandy gravel bank in middle of river. Just above road bridge, river ~ 10-15m wide.
Esk 2 - L.Bank	L bank. Sample of dry gravel/boulder bed on upside of bend
Esk1	R bank, L bank too fast flowing to sample. sample of dry gravel/boulder bed on upside of bend.
Esk3	sampled L and R bank sandy patches. Large fast flowing river exposing bedrock
Esk4 - R.Bank	R bank, just upstream from disused railway bridge, behind groyne of large blocks. Wide shallow river.
Esk5	L bank, opp. Esk4 ~50m upstream. Sampled dry rippled sand bank behind gravel bar.
Esk5	
Esk6 - L.Bank	Sarkfoot Pt. Sampled L bank, Inside bend. Muddy sands with still gravel patches.
Etherow1	Sample from centre of channel, nr White Hope farm, Etherow Country Park.
Etherow1	
Eweswater1	fast flowing boulder strewn stream
Fiddlers Ferry1 - 0-5cm	
Fiddlers Ferry1 - 10-20cm	
Fiddlers Ferry1 - 20-30cm	
Fiddlers Ferry1 - 30-50cm	
Fiddlers Ferry1 - 50-70cm	
Fiddlers Ferry1 - 5-10cm	
Fiddlers Ferry1 - 70-90cm	
Fiddlers Ferry2	
Goyt1 - Centre bar	Sample from gravel bar, R centre of channel. Strawberry Hill.
Hale1 - 0-5cm	
Hale1 - 10-20cm	
Hale1 - 20-30cm	

Appendix 2: Details of sample sites. 8 of 9

Collection Number	Comments/notes
Hale1 - 30-45cm	
Hale1 - 5-10cm	
Hale2	
Hodder1	Lower Hodder Bridge, sand from gravel bar above bridge
Ince Bank1 - 0-5cm	
Ince Bank1 - 10-20cm	
Ince Bank1 - 20-30cm	
Ince Bank1 - 30-50cm	
Ince Bank1 - 50-70cm	
Ince Bank1 - 5-10cm	
Ince Bank2	
Irthing1 - Nr. R.Bank	small grassed mid-channel bar nr R bank. Gravel samples from upstream end of bar
Irwell1 - Centre river	In lee of small linear island near L bank
Irwell2 (central)	Inside bend of river accessed via Sewage Works. Sample from nr centre of channel on small gravel bank
LiddellWater1 - R.Bank	sample from R bank, small dry gravel/boulder patch. deep river with exposed bedrock.
LiddellWater1-R.Bank	
LiddellWater2 - L.Bank	L bank, 50m downstream from LW1, below bridge. Bank with large boulders and bedrock exposed.
M/O	
M/U	
Mersey1	Sampled L bank to middle of channel, underneath bridge. According to Grab sampling, nr R bank = gravel and deep water.
Mersey1	
MickleBrook1	Sampled whole channel, nr Cheadle Golf Club.
NBright1 - 0-5cm	
NBright1 - 10-20cm	
NBright1 - 5-10cm	
New Brighton1	
Nith1	R bank. below Dumfries. gravel bed, with boulders ~10cm. close to tidal limit, maybe below.
Nith2	L bank. below Dumfries. faster flowing than at nith1.
Nith3 - L.Bank	L bank, above Dumfries. gravel bed, 5-10cm. appears to be less fine material.
Nith4 (Centre bank)	downstream of nith3 and roadbridge, above Dumfries. Samples from centre of river
Nith4 (Centre bank)	
Nith4B	
Nith5	sample from left centre of river at high tide, below tidal limit. Above confluence with Cargen Water.
Nith6	Between Scar Pt. & Airds Pt. Sample from channel, muddy sand.
Nith6B	
Nith7 - L.Bank	Glencaple, L bank. Sample of muddy sand, sampling interrupted by tidal bore
Otterspool1	
Petterel1	Reed covered island in centre of stream. Up and downstream ends sampled. Lots of organic matter, above M6 road bridge
R/O	
Ribble Lower Surface	
Ribble Upper Surface	
Ribble1	sampled whole width of stream as difficulties finding sed.
Ribble1	
Ribble2 - Centre	Island at centre of stream at Ribchester. Sample from muddy patches at downstream end. May be a lot of organic material in sample.
Ribble3 - R.Bank	Sample ~ 70m from end of jetty. St. Anne's RNLI station. Sample = muddy sand.
Ribble4 - R.Bank	Naze Farm nr. Fleckleton. Sand near low tide channel inside all training walls.
Ribble5	Naze Farm nr. Fleckleton, mud between training walls and saltmarsh very sticky and soft.
Ribble5 - R.Bank	
Ribble5B	
Ribble6 - L.Bank	Downstream of River Douglas, L bank. Due S of marsh, just upstream of creek. Sample = Mud below saltmarsh and above training walls.
Ribble7 - L.Bank	L bank. Marsh Farm. Sample from edge of channel - muddy sand.
Ribble8 - R.Bank	R bank, nr Riverside Marinar river walk, next to railway crossong. Sample = sandy mud.
Richmond Bank1 - 0-5cm	
Richmond Bank1 - 10-20cm	
Richmond Bank1 - 20-30cm	
Richmond Bank1 - 30-50cm	

Appendix 2: Details of sample sites. 9 of 9

Collection Number	Comments/notes
Richmond Bank1 - 50-75cm	
Richmond Bank1 - 5-10cm	
Richmond Bank2	
Roch1	Below weir and bridge, sample from R side of channel
Runcorn Sands1	
Runcorn Sands1	
S.Hale1	
S/O	
Seaforth1	
Seaforth1	
Seaforth1 - 0-5cm	
Seaforth1 - 10-20cm	
Seaforth1 - 20-30cm	
Seaforth1 - 30-50cm	
Seaforth1 - 50-70cm	
Seaforth1 - 5-10cm	
Seaforth1 - 70-100cm	
Solway Lower Surface	
Solway Upper Surface	
Speke1	
Speke1 - 0-5cm	
Speke1 - 10-20cm	
Speke1 - 20-30cm	
Speke1 - 30-46cm	
Speke1 - 5-10cm	
Tame1	Reddish Vale. Sample from gravel banks, just downstream from viaduct. All channel sampled
W/O	
Waters1 - 0-5cm	
Waters1 - 10-20cm	
Waters1 - 5-10cm	
Waterside1	
Waterside1B	
Waver1	Fine gravel to muddy sand bed. River 4-5m wide with relatively slow flow.
Weaver1	Grab sample from bridge, sampled across channel
Wyre Lower Surface	
Wyre Upper Surface	
Wyre1 - R.Bank	R bank, muds above central gravelly channel. Mud in mounds with clumps of seaweed, sediment is muddy sand.
Wyre1B	
Wyre10 - R.Bank	Saltmarsh channel nr sea wall. Sample = sand mud.
Wyre11	Sands nr centre of channel. Well rippled with dune like topography with filled pools infront of dunes. Ebb tide at time of sampling.
Wyre11B	
Wyre12	Muddy sands with regular ripples, no dune features. About 100m towards bank from Wyre11.
Wyre12B	
Wyre13	L bank at estuary mouth, nr jetties. Sample = laminated muddy sand nr edge of channel.
Wyre2	Centre channel bar, sand with some cobbles and boulders. Well rippled medium to coarse sand. Sample is muddy sand.
Wyre3 - L.Bank	L bank, same place as Wyre2. Rippled sand, sample is muddy sand.
Wyre4 - L.Bank	L bank ~ 40m downstream from Wyre3. Muds just below saltmarsh, well laminated mud with sand.
Wyre5 - R.Bank	R bank muds below saltmarsh, well laminated mud with sand. NB. More muddy than Wyre4
Wyre5 - R.Bank	
Wyre6	Upstream of weir at St. Michael's on Wyre, centre of stream. Sand and gravel with some large boulders and weeds.
Wyre6	
Wyre6B	
Wyre7B	Mouth of estuary (right), 100m beyond the end of jetty, just inside mussel bed.
Wyre8 - R.Estuary	R of estuary mouth, inside jetty.
Wyre9 - R.Bank	Edge of saltmarsh at Wellheads - Coatwalls, R bank. Sample = sandy mud.
WyreLowerSurfaceB	

Appendix 3: ED-XRF Data. 1 of 12

Sample	Na2O	MgO	Al2O3	SiO2	P2O5	SO3	K2O	CaO	Sc	TiO2	V	Cr	MnO	Fe2O3
Beb1	2.0	2.4	7.2	67.1	0.210	0.50	1.72	6.65	0.5	0.55	46	103	0.076	2.66
Beb1 - 0-5cm	2.5	2.3	7.8	65.3	0.240	0.50	1.80	6.56	17.0	0.56	60	115	0.086	3.14
Beb1 - 10-20cm	1.9	5.7	11.9	57.8	0.170	0.10	2.73	5.76	38.0	0.60	73	101	0.092	4.60
Beb1 - 20-27cm	1.6	4.8	10.4	63.2	0.150	0.20	2.35	5.56	13.0	0.57	77	114	0.081	4.02
Beb1 - 5-10cm	1.9	2.6	6.8	67.4	0.190	0.60	1.62	6.92	0.5	0.52	54	104	0.076	2.75
Bollin1	0.9	1.1	5.6	83.3	0.220	0.30	1.85	0.50	0.5	0.37	21	54	0.039	1.56
Bollin2	1.0	1.1	6.6	80.7	0.080	0.30	2.03	0.71	0.5	0.37	21	48	0.032	1.53
Calder1	0.7	1.0	7.3	78.7	0.190	0.20	1.11	1.59	0.5	0.36	38	64	0.060	3.60
Calder2	0.8	0.7	4.1	89.4	0.020	0.10	0.78	2.08	14.0	0.28	30	62	0.067	3.68
Calder2	0.6	0.7	4.0	78.0	0.210	0.20	0.70	2.40	0.5	0.14	45	43	0.126	8.89
Caldew1 - R.Bank	0.8	1.5	10.0	74.3	0.110	0.20	2.04	0.97	9.0	0.66	61	72	0.134	4.27
CludenWater1 - R.Bank	2.0	2.7	10.6	67.3	0.140	0.40	1.95	0.40	5.0	0.62	53	368	0.052	3.01
CludenWater2	1.6	2.7	10.8	70.7	0.150	0.20	2.02	0.45	6.0	0.60	71	255	0.081	3.43
CludenWater3	1.9	2.8	12.0	63.2	0.180	0.20	2.17	0.54	14.0	0.62	75	152	0.126	4.13
Crole1 (L.Bank)	1.1	1.4	9.8	64.3	0.500	1.20	1.64	1.82	10.0	0.54	71	197	0.153	5.94
Douglas1 - L.Bank	1.7	1.8	6.1	66.6	0.160	0.60	1.55	6.10	0.5	0.33	27	52	0.070	1.89
Douglas2A	1.0	1.7	7.4	73.2	1.210	0.60	1.67	2.30	3.0	0.52	57	169	0.114	4.24
Douglas2B	1.1	2.7	11.7	61.0	0.600	0.50	2.25	3.99	8.0	0.61	94	167	0.177	5.01
Eden1 - L.Bank	1.3	1.9	8.8	72.1	0.140	0.30	2.29	1.23	0.5	0.43	38	56	0.090	2.47
Eden2 - R.Bank-GRAVEL	1.2	2.0	7.7	76.1	0.090	0.20	2.19	1.22	0.5	0.39	30	52	0.075	2.38
Eden2B - R.Bank (<2mm)	0.9	1.5	6.2	88.7	0.005	0.05	1.43	0.51	2.0	0.30	35	31	0.054	2.45
Eden2B - R.Bank-SAND	1.1	2.3	9.1	66.5	0.180	0.40	2.19	1.39	2.0	0.42	39	56	0.088	2.80
Eden3 - L.Bank	0.9	1.7	8.0	65.9	0.150	0.70	1.77	1.63	0.5	0.41	25	53	0.092	2.40
Eden3 - L.Bank	1.1	1.5	6.9	85.8	0.040	0.10	1.39	0.43	5.0	0.30	40	35	0.073	2.94
Eden4 - Centre	1.0	1.4	6.9	69.6	0.120	0.70	1.64	1.30	0.5	0.35	25	53	0.067	2.09
Eden5	1.3	1.6	6.2	72.3	0.040	0.30	1.93	2.95	0.5	0.24	23	31	0.033	1.51
Eden5B	1.2	1.6	6.5	70.8	0.070	0.40	1.92	3.02	0.5	0.25	26	36	0.034	1.52
Eden6 - L.Bank	1.6	1.3	6.3	71.6	0.060	0.40	2.09	2.43	0.5	0.20	19	32	0.029	1.41
Egre1	3.2	2.0	6.1	68.5	0.180	0.40	1.67	6.39	0.5	0.45	39	86	0.062	2.32
Egre1 - 0-5cm	2.1	2.5	8.1	68.1	0.210	0.70	1.86	5.26	10.0	0.41	57	84	0.072	2.82
Egre1 - 10-20cm	2.1	2.1	6.7	66.3	0.220	1.00	1.63	5.38	0.5	0.30	37	59	0.063	2.08
Egre1 5-10cm	2.5	2.9	9.4	54.1	0.300	1.70	1.96	6.77	0.5	0.47	63	81	0.088	3.21
Ellen1	0.8	1.2	9.8	64.2	0.300	0.60	1.47	1.41	0.5	0.47	44	58	0.172	3.69
Esk 2 - L.Bank	1.8	3.5	13.1	66.4	0.140	0.10	1.98	0.49	16.0	0.75	91	145	0.069	4.90
Esk1	1.7	3.2	12.2	72.5	0.110	0.10	1.92	0.48	19.0	0.73	82	135	0.062	4.61
Esk3	1.2	2.7	10.7	74.3	0.070	0.10	2.25	0.64	6.0	0.67	65	178	0.061	3.91
Esk4 - R.Bank	1.5	2.5	10.5	73.8	0.120	0.10	2.29	0.79	6.0	0.64	58	118	0.068	3.44
Esk5	1.4	2.8	11.0	74.8	0.080	0.10	2.34	1.23	28.0	0.72	84	160	0.093	4.88
Esk5	1.3	2.5	8.1	82.6	0.005	0.05	1.65	0.38	5.0	0.42	55	70	0.049	3.54
Esk6 - L.Bank	1.3	1.7	6.8	75.2	0.060	0.20	2.00	3.65	0.5	0.28	24	45	0.037	1.71
Etherow1	1.4	1.5	12.3	68.9	0.160	0.20	1.87	0.72	13.0	0.65	54	162	0.106	4.62
Etherow1	0.7	0.8	5.2	87.9	0.040	0.10	0.89	0.35	2.0	0.20	38	50	0.054	4.25
Eweswater1	1.8	3.2	12.5	71.6	0.040	0.10	2.24	0.38	19.0	0.80	94	239	0.057	4.90
Fiddlers Ferry1 - 0-5cm	1.5	1.5	4.9	62.8	0.210	0.70	1.47	5.70	0.5	0.23	16	41	0.042	1.49
Fiddlers Ferry1 - 10-20cm	1.5	1.5	4.8	70.2	0.170	0.50	1.45	5.27	0.5	0.23	23	49	0.043	1.52
Fiddlers Ferry1 - 20-30cm	1.5	1.5	5.5	60.2	0.230	0.90	1.44	5.72	0.5	0.26	16	50	0.047	1.62
Fiddlers Ferry1 - 30-50cm	1.4	1.3	4.4	72.0	0.100	0.60	1.40	4.26	0.5	0.24	14	46	0.034	1.38
Fiddlers Ferry1 - 50-70cm	1.7	1.6	5.4	60.0	0.280	0.70	1.50	6.66	0.5	0.26	18	57	0.049	1.63
Fiddlers Ferry1 - 5-10cm	1.3	1.5	5.3	63.6	0.240	0.70	1.49	5.93	0.5	0.26	15	51	0.047	1.61
Fiddlers Ferry1 - 70-90cm	1.4	1.6	5.7	60.8	0.320	0.90	1.55	6.67	0.5	0.23	27	56	0.054	1.85
Fiddlers Ferry2	1.3	2.8	9.4	61.0	0.560	0.50	2.00	6.99	0.5	0.52	68	124	0.146	4.04
Goyt1 - Centre bar	0.9	1.3	9.9	69.6	0.250	0.40	1.58	0.84	4.0	0.56	45	99	0.099	4.32
Hale1 - 0-5cm	1.3	2.2	7.8	71.0	0.310	0.50	1.84	5.52	17.0	0.42	57	101	0.100	3.14
Hale1 - 10-20cm	1.9	2.0	6.9	71.0	0.270	0.60	1.72	5.40	0.5	0.35	44	81	0.080	2.53
Hale1 - 20-30cm	2.3	1.7	5.5	66.9	0.230	0.70	1.55	5.78	0.5	0.27	25	63	0.051	1.76
Hale1 - 30-45cm	1.7	1.9	6.1	65.6	0.300	1.10	1.64	6.48	0.5	0.30	40	74	0.071	2.33
Hale1 - 5-10cm	1.9	2.3	7.5	64.5	0.330	1.00	1.76	6.02	0.5	0.36	51	85	0.093	2.93

Appendix 3: ED-XRF Data. 2 of 12

Sample	**Na2O**	**MgO**	**Al2O3**	**SiO2**	**P2O5**	**SO3**	**K2O**	**CaO**	**Sc**	**TiO2**	**V**	**Cr**	**MnO**	**Fe2O3**
Hale2	2.0	2.8	9.1	60.2	0.420	0.60	1.97	6.28	14.0	0.51	68	110	0.126	3.61
Hodder1	0.7	1.2	9.6	66.9	0.180	0.50	1.42	4.68	1.0	0.46	59	73	0.141	3.23
Ince Bank1 - 0-5cm	1.1	1.3	4.5	73.7	0.100	0.40	1.51	4.04	0.5	0.29	25	66	0.043	1.55
Ince Bank1 - 10-20cm	2.0	1.7	5.3	68.7	0.150	0.50	1.51	4.59	0.5	0.34	25	71	0.052	1.81
Ince Bank1 - 20-30cm	1.6	1.5	5.0	75.9	0.100	0.30	1.50	4.64	0.5	0.33	27	59	0.046	1.70
Ince Bank1 - 30-50cm	1.9	2.1	6.7	63.0	0.240	0.70	1.65	5.50	0.5	0.38	38	72	0.065	2.13
Ince Bank1 - 50-70cm	2.1	1.9	5.9	71.0	0.170	0.40	1.58	4.87	0.5	0.30	30	68	0.059	1.89
Ince Bank1 - 5-10cm	1.3	1.3	4.2	73.9	0.090	0.50	1.43	4.04	0.5	0.26	19	57	0.038	1.44
Ince Bank2	1.8	1.7	4.9	65.1	0.130	0.60	1.35	4.87	0.5	0.38	27	74	0.049	1.73
Irthing1 - Nr. R.Bank	1.3	2.4	8.8	74.0	0.080	0.20	2.39	1.13	6.0	0.45	42	92	0.084	2.89
Irwell1 - Centre river	0.9	1.2	9.2	68.6	0.690	0.70	1.52	0.81	14.0	0.54	56	124	0.101	5.38
Irwell2 (central)	0.9	1.1	9.7	68.2	0.330	0.50	1.35	1.12	1.0	0.57	53	100	0.114	6.04
LiddellWater1 - R.Bank	1.1	2.2	10.1	68.4	0.090	0.40	2.63	0.82	4.0	0.66	43	113	0.068	3.03
LiddellWater1-R.Bank	1.5	2.4	8.8	70.3	0.130	0.40	1.77	0.47	0.5	0.45	47	85	0.063	4.22
LiddellWater2 - L.Bank	1.1	2.3	10.5	66.6	0.130	0.40	2.71	0.94	4.0	0.66	54	82	0.088	3.44
M/O	2.9	3.1	10.3	56.8	0.250	0.90	2.08	6.47	9.0	0.59	71	124	0.092	3.97
M/U	2.2	2.2	6.9	64.5	0.200	0.50	1.65	5.74	0.5	0.59	49	106	0.097	2.81
Mersey1	1.3	1.2	6.8	58.7	0.570	1.00	1.48	1.44	0.5	0.68	55	185	0.052	6.57
Mersey1	0.8	0.6	3.8	81.9	0.390	0.50	0.94	0.43	0.5	0.18	21	45	0.023	2.71
MickerBrook1	0.5	1.2	5.9	75.5	0.080	0.50	1.55	1.32	4.0	0.47	34	69	0.107	2.82
NBright1 - 0-5cm	1.5	1.1	3.0	82.0	0.020	0.30	1.15	4.03	0.5	0.16	19	44	0.029	1.15
NBright1 - 10-20cm	1.9	1.2	3.3	73.3	0.050	0.50	1.16	4.29	0.5	0.16	12	33	0.029	1.18
NBright1 - 5-10cm	1.7	1.2	3.0	80.3	0.020	0.40	1.12	3.83	0.5	0.17	21	42	0.028	1.17
New Brighton1	2.2	1.7	4.1	62.1	0.090	0.60	1.23	6.73	0.5	0.68	50	160	0.066	2.69
Nith1	1.8	2.7	11.2	64.2	0.140	0.40	1.75	0.52	4.0	0.69	67	161	0.081	3.99
Nith2	1.5	2.3	9.6	66.3	0.110	0.50	1.97	0.73	3.0	0.50	45	125	0.051	2.66
Nith3 - L.Bank	2.1	2.9	11.8	69.6	0.100	0.10	1.77	0.47	17.0	0.79	84	253	0.086	4.72
Nith4 (Centre bank)	1.9	2.5	11.2	71.1	0.080	0.10	1.69	0.49	10.0	0.76	82	279	0.084	4.45
Nith4 (Centre bank)	1.6	3.2	9.6	70.5	0.110	0.30	1.58	0.33	5.0	0.48	65	101	0.056	3.97
Nith4B	1.7	2.5	8.4	77.9	0.040	0.10	1.45	0.31	7.0	0.44	60	112	0.052	4.11
Nith5	1.7	1.7	6.7	70.4	0.070	0.40	1.90	3.89	0.5	0.31	26	48	0.042	1.79
Nith6	1.6	1.5	6.0	77.1	0.040	0.20	1.89	3.05	0.5	0.28	23	41	0.035	1.51
Nith6B	1.4	1.5	5.9	74.5	0.050	0.30	1.86	3.10	0.5	0.28	21	49	0.035	1.51
Nith7 - L.Bank	1.4	1.7	6.8	71.5	0.090	0.40	1.91	3.33	0.5	0.30	31	42	0.053	1.82
Otterspool1	1.8	1.7	5.1	71.1	0.090	0.30	1.45	5.68	0.5	0.50	32	93	0.064	2.11
Petterel1	0.8	1.1	7.0	71.2	0.090	0.60	1.82	0.69	0.5	0.43	27	96	0.043	1.95
R/O	1.9	2.5	8.5	64.2	0.130	0.40	1.89	7.36	0.5	0.55	57	88	0.068	3.21
Ribble Lower Surface	2.4	2.1	6.8	63.9	0.190	0.40	1.63	7.44	0.5	0.51	40	78	0.090	2.43
Ribble Upper Surface	1.9	2.1	6.8	64.8	0.190	0.50	1.70	6.65	0.5	0.39	32	66	0.080	2.21
Ribble1	0.4	0.9	4.5	86.5	0.010	0.10	0.74	3.85	10.0	0.28	27	55	0.061	2.97
Ribble1	0.8	0.8	2.9	75.8	0.070	0.40	0.55	5.68	0.5	0.09	14	24	0.048	1.73
Ribble2 - Centre	0.8	1.2	9.2	60.9	0.710	0.60	1.35	3.71	0.5	0.46	41	78	0.167	3.89
Ribble3	1.3	1.4	3.5	71.6	0.060	0.40	1.21	5.63	0.5	0.39	26	98	0.051	1.72
Ribble4 - R.Bank	1.3	2.1	3.4	58.9	0.190	0.50	0.91	9.65	0.5	0.60	43	105	0.074	2.75
Ribble5	2.6	2.5	7.9	59.3	0.300	0.80	1.67	6.15	0.5	0.40	36	64	0.088	2.41
Ribble5 - R.Bank	1.9	2.0	6.7	61.6	0.220	0.60	1.60	6.40	0.5	0.39	35	68	0.074	2.08
Ribble5B	1.9	2.0	6.6	61.8	0.230	0.70	1.57	6.31	0.5	0.37	27	68	0.072	2.04
Ribble6 - L.Bank	1.7	2.0	6.2	60.8	0.200	0.70	1.52	6.15	0.5	0.39	25	86	0.094	1.93
Ribble7 - L.Bank	1.7	1.7	5.2	61.9	0.200	0.70	1.37	6.16	0.5	0.29	18	65	0.055	1.57
Ribble8 - R.Bank	1.3	1.7	6.2	68.0	0.210	0.40	1.58	5.87	0.5	0.32	29	50	0.066	1.94
Richmond Bank1 - 0-5cm	1.4	2.0	6.9	66.1	0.380	0.50	1.68	7.49	0.5	0.35	42	74	0.086	2.54
Richmond Bank1 - 10-20cm	1.3	1.9	6.4	64.7	0.420	0.60	1.63	8.09	0.5	0.31	34	68	0.078	2.31
Richmond Bank1 - 20-30cm	1.0	1.6	5.1	57.8	0.540	0.70	1.52	8.46	0.5	0.25	32	56	0.069	2.14
Richmond Bank1 - 30-50cm	1.4	1.6	5.4	59.4	0.420	0.70	1.57	8.20	0.5	0.28	27	61	0.068	2.10
Richmond Bank1 - 50-75cm	1.3	1.8	6.3	58.3	0.380	0.70	1.59	7.69	0.5	0.28	24	57	0.067	1.98
Richmond Bank1 - 5-10cm	1.3	2.1	6.8	56.9	0.500	0.90	1.63	8.12	0.5	0.36	41	79	0.087	2.54
Richmond Bank2	1.2	1.9	6.7	60.5	0.360	0.60	1.63	7.41	0.5	0.36	34	65	0.072	2.22

Appendix 3: ED-XRF Data. 3 of 12

Sample	**Na2O**	**MgO**	**Al2O3**	**SiO2**	**P2O5**	**SO3**	**K2O**	**CaO**	**Sc**	**TiO2**	**V**	**Cr**	**MnO**	**Fe2O3**
Roch1	1.2	1.4	11.8	56.8	0.680	1.30	1.55	1.05	4.0	0.55	62	150	0.134	5.25
Rock Ferry	2.5	2.5	7.8	54.4	0.270	0.90	1.68	6.24	0.5	0.54	43	113	0.090	2.66
Rock FerryB	2.0	2.2	6.9	67.6	0.200	0.50	1.69	5.82	0.5	0.56	47	108	0.088	2.67
RockFerry	2.8	2.7	8.0	54.9	0.330	0.90	1.74	6.42	0.5	0.54	47	122	0.101	2.88
Runcorn Sands1	1.3	1.5	4.6	79.2	0.080	0.20	1.50	4.59	0.5	0.26	25	48	0.042	1.49
Runcorn Sands1	1.6	1.6	5.3	68.6	0.180	0.60	1.51	4.79	0.5	0.25	22	50	0.044	1.57
S.Hale1	1.3	1.4	4.1	75.7	0.060	0.30	1.33	4.41	0.5	0.26	16	44	0.038	1.35
S/O	2.5	2.2	7.3	64.2	0.150	0.60	1.85	4.50	0.5	0.41	29	66	0.047	2.12
Seaforth1	1.9	2.3	7.6	65.6	0.180	1.10	1.76	6.70	0.5	0.57	57	157	0.094	2.94
Seaforth1	2.6	3.0	9.7	59.3	0.260	1.50	1.94	6.16	0.5	0.56	72	119	0.108	3.51
Seaforth1 - 0-5cm	2.5	3.0	10.5	59.9	0.280	1.60	2.10	6.19	0.5	0.61	81	131	0.150	4.05
Seaforth1 - 10-20cm	2.9	3.0	9.2	56.0	0.320	1.70	1.88	6.84	0.5	0.51	51	102	0.116	3.26
Seaforth1 - 20-30cm	2.5	2.8	8.9	57.3	0.330	1.30	1.88	6.58	0.5	0.50	58	103	0.110	3.27
Seaforth1 - 30-50cm	2.2	2.5	8.5	61.3	0.260	1.20	1.85	6.28	0.5	0.55	61	130	0.108	3.32
Seaforth1 - 50-70cm	2.5	2.8	9.3	60.4	0.250	1.40	1.95	5.89	0.5	0.57	74	127	0.130	3.67
Seaforth1 - 5-10cm	3.0	3.2	9.8	57.2	0.320	1.60	2.17	6.24	0.5	0.62	79	134	0.162	4.29
Seaforth1 - 70-100cm	2.4	2.6	8.5	62.1	0.280	1.00	1.87	5.95	0.5	0.55	61	127	0.119	3.20
Solway Lower Surface	2.2	2.0	6.9	73.0	0.150	0.30	1.89	3.55	0.5	0.39	38	57	0.073	2.10
Solway Upper Surface	4.5	2.0	7.2	66.9	0.210	0.30	1.92	3.89	0.5	0.41	38	65	0.094	2.36
Speke1	3.6	2.1	6.6	64.5	0.260	0.40	1.69	6.69	0.5	0.51	51	96	0.083	2.69
Speke1 - 0-5cm	2.4	2.5	8.4	63.4	0.250	0.90	1.82	6.60	0.5	0.53	59	123	0.092	3.20
Speke1 - 10-20cm	2.0	2.6	8.9	62.1	0.330	1.30	1.93	6.76	0.5	0.58	66	136	0.130	3.71
Speke1 - 20-30cm	1.8	3.0	9.8	57.8	0.420	1.40	2.14	6.06	21.0	0.60	78	159	0.169	4.54
Speke1 - 30-46cm	2.4	3.4	10.4	59.7	0.350	1.30	2.12	5.76	0.5	0.58	91	141	0.146	4.32
Speke1 - 5-10cm	2.4	2.5	8.3	61.4	0.300	1.30	1.86	7.03	0.5	0.53	59	111	0.115	3.31
Tame1	0.7	1.4	10.0	65.5	0.460	0.60	1.79	0.86	1.0	0.53	50	92	0.076	4.44
W/O	2.4	2.1	6.3	64.7	0.130	0.50	1.69	6.28	0.5	0.40	32	66	0.077	2.08
Waters1 - 0-5cm	1.9	2.2	6.6	60.2	0.280	0.90	1.61	7.12	0.5	0.35	39	84	0.074	2.27
Waters1 - 10-20cm	2.2	2.5	7.9	60.7	0.270	1.40	1.79	7.03	9.0	0.45	58	105	0.112	4.24
Waters1 - 5-10cm	2.0	2.2	7.0	68.0	0.210	0.60	1.74	6.46	0.5	0.41	45	84	0.090	2.62
Waterside1	1.9	1.8	5.2	72.6	0.150	0.30	1.54	5.90	0.5	0.39	25	65	0.057	1.82
Waterside1B	2.2	1.7	5.1	71.7	0.150	0.30	1.53	5.99	0.5	0.38	26	72	0.058	1.81
Waver1	1.0	1.3	8.5	72.6	0.230	0.40	2.03	0.60	1.0	0.38	32	54	0.095	2.55
Weaver1	1.4	1.2	3.1	14.3	1.010	1.80	0.60	41.16	0.5	0.17	30	69	0.037	1.64
Wyre Lower Surface	2.1	2.1	6.3	67.7	0.130	0.40	1.67	6.36	0.5	0.48	25	87	0.073	2.22
WyreLowerSurfaceB	2.0	2.0	6.3	62.8	0.140	0.50	1.64	6.33	0.5	0.47	40	86	0.070	2.19
Wyre Upper Surface	2.4	2.4	7.9	64.3	0.190	0.40	1.82	7.06	0.5	0.51	48	83	0.102	2.76
Wyre1 - R.Bank	1.9	1.8	5.8	64.8	0.140	0.50	1.62	6.47	0.5	0.31	22	49	0.049	1.69
Wyre10 - R.Bank	2.4	3.3	10.9	57.5	0.300	1.00	2.11	6.07	8.0	0.59	66	92	0.108	3.92
Wyre11	1.8	1.6	4.4	68.8	0.100	0.50	1.42	5.20	0.5	0.27	17	43	0.046	1.40
Wyre11B	1.5	1.6	4.4	66.4	0.100	0.50	1.40	5.58	0.5	0.30	19	56	0.053	1.52
Wyre12 - Sandy muds	1.8	2.0	6.5	59.9	0.120	0.70	1.58	6.43	0.5	0.44	34	85	0.055	2.11
Wyre12B	1.7	2.1	6.7	58.3	0.120	0.80	1.56	6.35	0.5	0.49	32	91	0.055	2.14
Wyre13 - L.Estuary mouth	2.1	2.2	7.2	61.6	0.170	0.60	1.68	6.14	0.5	0.39	36	73	0.078	2.19
Wyre1B	1.6	1.8	5.9	62.0	0.150	0.60	1.60	6.61	0.5	0.32	23	52	0.050	1.74
Wyre2 - Centre river bar	1.0	1.3	4.3	88.5	0.005	0.10	1.45	3.54	9.0	0.32	26	57	0.050	1.84
Wyre3 - L.Bank	1.5	1.4	4.3	73.5	0.050	0.30	1.50	4.84	0.5	0.26	22	51	0.037	1.38
Wyre4 - L.Bank	2.5	2.4	7.1	60.2	0.200	0.70	1.69	6.67	0.5	0.45	34	79	0.075	2.30
Wyre5 - R.Bank	1.7	2.2	7.3	65.8	0.160	0.40	1.77	6.71	0.5	0.48	45	79	0.079	2.47
Wyre5 - R.Bank	2.7	2.5	8.0	62.4	0.230	0.50	1.79	6.76	0.5	0.49	40	84	0.087	2.62
Wyre6	0.9	0.9	5.8	78.3	0.005	0.50	1.14	0.59	0.5	0.42	31	80	0.072	1.90
Wyre6	0.4	0.9	3.5	92.0	0.020	0.10	0.71	0.30	2.0	0.15	18	29	0.052	2.54
Wyre6B	0.6	0.8	3.9	85.6	0.080	0.30	0.76	0.31	0.5	0.15	13	24	0.051	2.46
Wyre7	1.9	1.9	6.0	64.6	0.130	0.50	1.63	6.08	0.5	0.34	39	50	0.072	1.92
Wyre8	1.8	2.0	6.6	66.9	0.120	0.40	1.72	6.71	0.5	0.42	48	73	0.068	2.22
Wyre9	2.5	2.5	8.2	60.6	0.190	0.50	1.76	6.78	0.5	0.58	52	86	0.118	2.83

Appendix 3: ED-XRF Data. 4 of 12

Sample	Ni	Cu	Zn	Ga	Ge	As	Br	Rb	Sr	Y	Zr	Nb	Mo	Sn
Beb1	14	26	185	7	1	9	41	54	172	25	834	11	3	12
Beb1 - 0-5cm	17	31	234	8	1	12	63	62	189	28	843	13	3	11
Beb1 - 10-20cm	39	22	69	13	1	9	15	99	131	21	230	12	2	2
Beb1 - 20-27cm	34	22	101	11	1	7	20	81	139	23	431	12	2	5
Beb1 - 5-10cm	16	27	195	8	1	11	46	55	197	25	831	12	3	11
Bollin1	8	16	86	4	1	5	3	50	63	19	1081	9	4	10
Bollin2	12	17	65	5	1	3	2	54	59	15	508	7	3	8
Calder1	24	37	266	5	1	10	5	34	72	21	701	7	4	25
Calder2	20	35	203	3	2	7	4	26	72	21	784	7	4	33
Calder2	39	39	219	2	1	14	1	21	84	17	93	5	6	103
Caldew1 - R.Bank	19	20	137	7	1	34	9	70	102	21	416	10	2	4
CludenWater1 - R.Bank	36	770	190	4	1	1	9	50	95	17	670	10	3	17
CludenWater2	40	30	110	10	1	3	18	60	101	18	494	10	1	11
CludenWater3	40	18	135	11	1	5	24	69	100	20	410	12	2	5
Crole1 (L.Bank)	44	158	379	7	1	15	15	59	98	24	469	11	5	42
Douglas1 - L.Bank	14	14	74	5	1	5	17	48	146	14	308	7	2	4
Douglas2A	29	69	304	8	1	7	14	61	110	22	446	10	2	13
Douglas2B	38	78	324	13	2	16	34	89	139	25	288	12	2	15
Eden1 - L.Bank	16	14	98	6	1	8	9	66	91	17	357	9	3	5
Eden2 - R.Bank-GRAVEL	17	15	141	6	1	7	7	63	84	14	303	8	2	5
Eden2B - R.Bank (<2mm)	14	10	76	5	2	10	2	45	62	11	94	5	0.5	5
Eden2B - R.Bank-SAND	15	15	112	6	1	8	9	62	86	15	270	8	2	7
Eden3 - L.Bank	14	11	122	5	1	3	11	49	116	18	525	8	4	7
Eden3 - L.Bank	10	7	59	6	1	5	1	45	55	12	100	5	1	2
Eden4 - Centre	13	10	58	4	1	1	6	46	112	17	527	7	2	8
Eden5	11	6	34	6	1	3	2	52	99	9	87	4	1	1
Eden5B	9	6	33	6	1	4	1	51	98	9	91	5	1	1
Eden6 - L.Bank	12	5	27	4	1	3	1	54	90	7	57	4	1	1
Egre1	12	16	120	6	0.5	8	36	51	169	20	563	9	2	6
Egre1 - 0-5cm	21	28	158	8	1	10	71	63	158	16	282	8	1	9
Egre1 - 10-20cm	13	16	119	6	0.5	9	45	49	156	11	165	6	1	6
Egre1 5-10cm	18	26	206	8	1	10	83	67	200	17	244	8	2	10
Ellen1	29	32	109	7	1	11	13	48	76	18	351	8	2	3
Esk 2 - L.Bank	58	23	110	13	2	7	15	72	55	23	288	13	1	2
Esk1	44	25	153	12	1	6	12	69	56	23	314	13	2	6
Esk3	39	20	257	10	1	5	7	67	67	23	669	12	3	5
Esk4 - R.Bank	33	20	94	9	2	4	11	66	74	20	453	11	1	2
Esk5	41	30	177	14	1	6	8	77	90	24	596	14	3	6
Esk5	34	14	71	9	2	4	1	50	59	12	117	7	0.5	1
Esk6 - L.Bank	12	7	37	6	1	4	2	54	113	9	97	5	0.5	1
Etherow1	59	60	337	10	3	6	11	60	79	40	1530	13	11	42
Etherow1	22	28	114	3	1	5	2	25	43	9	130	4	4	22
Eweswater1	51	23	106	13	1	5	7	73	59	24	669	16	1	4
Fiddlers Ferry1 - 0-5cm	9	14	233	5	1	7	5	43	129	10	166	4	1	3
Fiddlers Ferry1 - 10-20cm	9	17	259	5	1	8	6	42	126	11	189	5	1	3
Fiddlers Ferry1 - 20-30cm	12	19	260	5	1	8	8	43	129	10	185	5	1	3
Fiddlers Ferry1 - 30-50cm	8	12	221	4	1	6	4	39	99	11	274	5	1	3
Fiddlers Ferry1 - 50-70cm	11	18	262	5	1	7	7	44	149	11	179	5	1	3
Fiddlers Ferry1 - 5-10cm	11	16	257	4	1	7	7	45	142	11	189	6	1	3
Fiddlers Ferry1 - 70-90cm	13	20	304	4	1	10	9	46	159	10	133	4	0.5	3
Fiddlers Ferry2	30	68	429	9	2	21	54	74	205	23	230	10	1	14
Goyt1 - Centre bar	34	78	260	8	1	12	14	52	92	32	1112	12	7	43
Hale1 - 0-5cm	23	48	378	7	1	18	53	65	177	17	338	8	1	10
Hale1 - 10-20cm	18	35	301	6	1	17	40	55	156	16	368	8	2	8
Hale1 - 20-30cm	11	16	231	5	1	10	22	46	142	12	294	5	1	4
Hale1 - 30-45cm	14	40	428	5	1	20	47	51	179	14	267	7	2	9
Hale1 - 5-10cm	20	46	432	7	2	22	56	61	184	17	275	8	1	11

Appendix 3: ED-XRF Data. 5 of 12

Sample	**Ni**	**Cu**	**Zn**	**Ga**	**Ge**	**As**	**Br**	**Rb**	**Sr**	**Y**	**Zr**	**Nb**	**Mo**	**Sn**
Hale2	28	50	342	9	1	16	69	69	188	23	519	11	3	15
Hodder1	39	27	229	9	1	8	22	56	117	26	624	9	4	2
Ince Bank1 - 0-5cm	9	9	102	4	1	7	11	41	96	13	408	6	2	2
Ince Bank1 - 10-20cm	9	14	139	4	1	7	18	44	108	15	449	7	2	4
Ince Bank1 - 20-30cm	9	11	145	5	1	7	15	44	118	14	404	8	2	4
Ince Bank1 - 30-50cm	16	20	184	5	2	7	23	48	133	16	420	8	1	7
Ince Bank1 - 50-70cm	11	17	156	5	1	8	22	48	126	13	302	6	1	5
Ince Bank1 - 5-10cm	9	8	95	4	1	7	11	39	94	12	364	5	2	4
Ince Bank2	10	10	111	4	2	5	17	38	102	18	665	9	4	4
Irthing1 - Nr. R.Bank	14	11	78	7	1	4	5	67	86	19	688	10	2	3
Irwell1 - Centre river	37	127	409	7	1	5	22	50	77	29	1010	12	6	47
Irwell2 (central)	48	129	401	6	1	16	12	47	80	29	868	12	7	67
LiddellWater1 - R.Bank	24	13	78	7	1	2	6	60	74	20	749	12	3	4
LiddellWater1-R.Bank	30	11	73	7	1	5	1	42	68	15	135	7	1	1
LiddellWater2 - L.Bank	27	17	95	10	1	3	11	69	80	20	478	13	3	3
M/O	29	41	285	11	1	12	111	78	197	26	602	14	3	15
M/U	16	24	200	5	1	10	41	53	155	29	1106	14	4	12
Mersey1	23	67	200	4	0.5	10	6	39	98	56	3838	22	15	113
Mersey1	12	30	94	2	0.5	2	1	23	47	10	221	4	2	17
MickerBrook1	20	30	142	5	1	1	4	44	61	26	1372	14	7	22
NBright1 - 0-5cm	8	4	32	3	1	6	14	33	98	7	190	4	1	1
NBright1 - 10-20cm	3	4	30	3	1	6	14	32	97	7	181	3	1	1
NBright1 - 5-10cm	7	5	30	3	1	7	13	31	92	9	243	4	1	1
New Brighton1	13	6	54	4	1	7	13	34	123	27	1335	14	6	10
Nith1	37	21	213	10	1	1	9	49	101	20	528	12	3	7
Nith2	22	14	144	6	1	1	5	51	87	17	481	9	1	6
Nith3 - L.Bank	45	19	190	8	1	2	8	51	111	25	770	13	3	4
Nith4 (Centre bank)	41	20	199	10	1	1	12	48	111	25	984	14	4	5
Nith4 (Centre bank)	39	16	83	8	1	2	2	38	80	12	130	7	1	1
Nith4B	36	12	84	6	1	2	2	39	79	14	147	8	1	1
Nith5	11	6	43	6	1	4	6	53	119	11	135	6	1	1
Nith6	14	5	31	7	1	4	4	51	99	10	137	5	1	1
Nith6B	11	5	31	5	1	4	4	51	100	10	128	6	1	1
Nith7 - L.Bank	14	5	42	7	1	5	11	55	110	10	135	6	1	1
Otter Pool1	9	15	141	6	1	6	17	44	139	27	1172	12	4	7
Petterel1	12	9	50	4	1	1	6	46	71	16	864	8	3	2
R/O	22	17	114	8	1	8	61	69	210	25	625	12	3	8
Ribble Lower Surface	16	10	94	5	1	6	32	51	186	21	510	10	3	8
Ribble Upper Surface	15	13	106	7	1	6	33	51	172	17	400	8	2	5
Ribble1	18	27	183	4	1	6	8	27	94	21	762	7	4	40
Ribble1	11	7	68	3	1	3	3	14	84	7	74	2	1	4
Ribble2 - Centre	35	42	290	7	1	9	36	50	103	23	502	8	3	9
Ribble3	10	5	42	4	1	5	9	34	109	19	894	9	4	2
Ribble4 - R.Bank	13	5	45	3	2	10	4	26	147	23	726	13	3	2
Ribble5	14	14	101	6	1	6	44	53	162	17	348	8	1	5
Ribble5 - R.Bank	15	13	80	6	1	5	25	48	155	15	408	8	2	3
Ribble5B	11	12	82	5	1	5	24	47	151	16	398	8	2	4
Ribble6 - L.Bank	12	7	71	3	1	5	20	43	134	18	458	8	2	3
Ribble7 - L.Bank	9	8	55	4	1	4	9	38	119	11	192	6	1	2
Ribble8 - R.Bank	12	13	81	6	1	5	13	47	135	13	183	6	1	3
Richmond Bank1 - 0-5cm	16	38	372	6	1	16	23	55	202	15	183	7	1	9
Richmond Bank1 - 10-20cm	17	39	385	7	1	14	18	51	213	14	155	7	1	6
Richmond Bank1 - 20-30cm	14	26	373	4	1	12	7	46	206	12	121	5	1	5
Richmond Bank1 - 30-50cm	13	25	343	3	1	12	11	48	200	13	144	6	1	5
Richmond Bank1 - 50-75cm	16	26	311	5	1	8	10	47	180	12	137	5	1	5
Richmond Bank1 - 5-10cm	18	44	414	7	2	15	25	52	208	14	173	7	1	7
Richmond Bank2	17	31	290	7	1	10	9	49	181	14	187	7	1	6

Appendix 3: ED-XRF Data. 6 of 12

Sample	**Ni**	**Cu**	**Zn**	**Ga**	**Ge**	**As**	**Br**	**Rb**	**Sr**	**Y**	**Zr**	**Nb**	**Mo**	**Sn**
Roch1	52	158	487	7	1	3	82	51	79	24	642	11	7	54
Rock Ferry	18	22	201	5	0.5	9	44	52	155	29	957	12	4	10
Rock FerryB	16	23	193	6	1	10	43	54	158	30	1138	12	4	11
RockFerry	19	29	216	7	1	10	64	55	166	28	939	11	4	11
Runcorn Sands1	8	14	165	5	1	7	8	43	114	11	222	6	1	4
Runcorn Sands1	9	14	188	3	1	8	12	43	114	10	178	5	0.5	3
S.Hale1	9	8	97	4	1	5	5	36	92	11	215	5	1	2
S/O	13	8	50	6	1	5	32	53	125	17	376	8	2	3
Seaforth1	14	31	182	8	1	9	43	55	176	28	955	12	3	12
Seaforth1	27	40	242	9	2	14	69	67	178	24	641	12	2	14
Seaforth1 - 0-5cm	28	45	268	10	2	15	80	77	187	27	622	12	2	16
Seaforth1 - 10-20cm	21	36	230	9	1	11	55	63	189	20	368	10	1	10
Seaforth1 - 20-30cm	21	36	222	8	1	14	57	63	185	22	406	10	1	11
Seaforth1 - 30-50cm	23	43	281	6	1	15	54	63	179	25	751	12	4	14
Seaforth1 - 50-70cm	25	57	357	7	1	18	55	69	176	27	571	12	3	16
Seaforth1 - 5-10cm	33	47	284	12	1	15	90	82	193	24	425	12	3	16
Seaforth1 - 70-100cm	18	53	356	9	1	16	50	63	165	24	589	11	2	13
Solway Lower Surface	15	8	48	6	1	5	35	54	115	15	256	7	1	2
Solway Upper Surface	16	9	59	7	1	7	31	60	130	17	251	9	2	2
Speke1	19	28	222	7	1	11	37	55	178	26	762	11	3	11
Speke1 - 0-5cm	19	41	273	8	1	12	50	63	187	27	704	12	2	13
Speke1 - 10-20cm	24	52	357	9	1	19	55	68	201	27	590	12	3	17
Speke1 - 20-30cm	33	94	497	10	1	30	67	80	190	26	363	13	3	23
Speke1 - 30-46cm	35	91	442	10	2	26	58	81	181	25	346	13	3	19
Speke1 - 5-10cm	23	50	309	9	1	15	52	64	200	24	446	11	2	13
Tame1	31	77	294	6	1	7	11	54	76	32	1169	11	5	42
W/O	15	8	55	7	1	6	31	52	144	17	459	9	2	4
Waters1 - 0-5cm	16	34	319	6	1	13	66	53	195	16	301	8	2	8
Waters1 - 10-20cm	28	63	401	8	1	18	145	67	209	20	365	10	3	14
Waters1 - 5-10cm	15	29	249	7	1	13	56	59	190	18	358	9	2	7
Waterside1	14	15	157	5	1	7	23	46	147	17	450	8	3	4
Waterside1B	11	14	161	5	1	7	23	47	147	16	442	9	2	4
Waver1	17	10	56	7	1	5	5	55	82	13	365	7	1	4
Weaver1	27	54	150	3	2	7	20	23	176	12	79	5	2	3
Wyre Lower Surface	11	8	61	6	2	6	30	50	147	23	660	10	2	4
WyreLowerSurfaceB	13	9	62	6	1	5	30	50	146	24	668	10	3	6
Wyre Upper Surface	19	14	97	8	2	7	53	59	188	22	384	10	1	6
Wyre1 - R.Bank	11	8	52	6	1	4	16	47	151	13	253	6	1	2
Wyre10 - R.Bank	29	26	147	11	1	11	93	75	182	23	246	12	2	10
Wyre11	6	6	34	4	1	5	13	38	107	12	335	5	1	5
Wyre11B	11	6	34	4	1	5	13	38	111	17	465	7	2	2
Wyre12 - Sandy muds	11	8	58	6	1	5	17	46	139	24	768	9	2	4
Wyre12B	11	7	59	4	1	5	16	46	137	23	798	10	3	4
Wyre13 - L.Estuary mouth	12	10	69	6	1	5	36	51	149	17	362	8	1	6
Wyre1B	9	6	52	4	1	4	16	46	151	14	275	6	1	2
Wyre2 - Centre river bar	9	7	62	5	2	5	11	43	113	26	1096	8	4	1
Wyre3 - L.Bank	9	7	38	5	1	4	12	43	105	15	567	7	2	4
Wyre4 - L.Bank	12	12	71	6	1	4	56	53	162	20	384	10	3	5
Wyre5 - R.Bank	16	13	81	7	1	6	34	55	167	22	467	10	2	5
Wyre5 - R.Bank	16	16	93	7	1	6	52	58	170	22	418	10	2	6
Wyre6	13	8	186	4	1	1	4	26	49	48	2852	12	8	7
Wyre6	10	7	54	2	1	4	2	20	40	8	152	4	2	2
Wyre6B	11	8	53	4	1	3	1	21	38	7	103	3	1	3
Wyre7	14	9	52	6	1	6	30	48	138	14	296	7	1	4
Wyre8	17	9	62	6	1	5	22	54	158	19	441	10	2	3
Wyre9	18	14	85	8	2	7	48	57	171	25	476	11	2	7

Appendix 3: ED-XRF Data. 7 of 12

Sample	Sb	I	Cs	Ba	La	Ce	Nd	Hf	W	Pb	Th	U	LAT	LONG
Beb1	0.5	18	4	396	33	54	18	19	1.5	48	6	4	53.3683	-2.9920
Beb1 - 0-5cm	1	31	3	413	29	49	12	19	1.5	64	7	4	53.3683	-2.9920
Beb1 - 10-20cm	0.5	2	5	365	24	44	25	8	1.5	18	7	3	53.3683	-2.9920
Beb1 - 20-27cm	1	7	7	372	27	46	30	12	1.5	30	11	3	53.3683	-2.9920
Beb1 - 5-10cm	1	21	3	371	30	51	20	19	1.5	52	7	4	53.3683	-2.9920
Bollin1	1	0.5	8	389	41	68	38	26	1.5	37	6	2	53.3940	-2.4542
Bollin2	1	0.5	5	382	25	35	10	10	2	32	3	2	53.3201	-2.1772
Calder1	2	4	5	434	35	58	17	15	1.5	94	9	2	53.8229	-2.4163
Calder2	1	4	6	528	32	52	18	19	1.5	94	14	3	53.8220	-2.4148
Calder2	3	0.5	0.5	279	16	24	8	2	2	150	5	2	53.8221	-2.3996
Caldew1 - R.Bank	2	6	10	1097	23	36	15	14	1.5	184	10	3	54.8300	-2.9824
CludenWater1 - R.Bank	0.5	3	4	348	21	26	26	22	1.5	180	7	2	55.0917	-3.6313
CludenWater2	1	5	0.5	369	22	34	5	11	1.5	32	7	3	55.0951	-3.6503
CludenWater3	0.5	7	6	408	23	43	2.5	9	1.5	27	9	3	55.1000	-3.7477
Crole1 (L.Bank)	6	5	6	587	25	45	26	13	2	270	19	3	53.5543	-2.3789
Douglas1 - L.Bank	0.5	7	4	276	15	23	2.5	4	1	24	4	2	53.7263	-2.8413
Douglas2A	0.5	5	5	469	24	39	19	10	2	90	10	2	53.6555	-2.8081
Douglas2B	0.5	21	9	418	29	46	13	6	4	121	21	3	53.6555	-2.8081
Eden1 - L.Bank	1	9	8	880	22	31	2.5	9	1.5	72	5	3	54.9127	-2.9719
Eden2 - R.Bank-GRAVEL	2	8	11	980	20	20	7	8	1.5	65	9	2	54.9118	-2.9813
Eden2B - R.Bank (<2mm)	0.5	1	5	281	14	13	8	3	1	55	2	1	54.9118	-2.9813
Eden2B - R.Bank-SAND	0.5	0.5	11	940	21	25	18	8	1.5	73	5	3	54.9118	-2.9813
Eden3 - L.Bank	0.5	26	26	4121	42	25	2.5	14	1.5	78	6	3	54.8370	-2.7521
Eden3 - L.Bank	0.5	0.5	5	340	15	22	14	4	1	47	4	1	54.8370	-2.7521
Eden4 - Centre	0.5	15	29	4147	38	30	45	12	1	80	3	4	54.8370	-2.7521
Eden5	1	0.5	8	322	10	18	2.5	1	1	15	2	3	54.9455	-3.0320
Eden5B	1	4	7	309	15	18	32	1	1	15	1	2	54.9455	-3.0320
Eden6 - L.Bank	0.5	0.5	6	325	11	9	2.5	1	2	13	1	1	54.9462	-3.0492
Egre1	0.5	12	6	323	21	32	18	11	3	33	5	3	53.4246	-3.0249
Egre1 - 0-5cm	2	27	6	289	21	31	5	3	2	55	9	1	53.4246	-3.0249
Egre1 - 10-20cm	0.5	15	4	253	12	22	15	3	1.5	36	5	2	53.4246	-3.0249
Egre1 5-10cm	2	31	7	319	26	45	2.5	8	1.5	58	10	3	53.4246	-3.0249
Ellen1	0.5	9	9	593	25	43	24	7	1.5	28	4	2	54.7202	-3.4456
Esk 2 - L.Bank	2	5	0.5	242	32	56	15	8	1.5	22	11	3	55.1766	-3.0207
Esk1	0.5	3	5	252	31	49	34	9	1.5	26	8	2	55.1793	-3.0145
Esk3	1	4	6	623	24	43	28	12	2	30	6	4	55.0952	-2.9638
Esk4 - R.Bank	1	3	7	494	21	33	2.5	11	1.5	27	6	3	55.0468	-2.9564
Esk5	0.5	0.5	2	621	25	40	19	13	1.5	39	6	3	55.0477	-2.9564
Esk5	0.5	0.5	0.5	222	13	21	16	2	1	15	3	1	55.0477	-2.9564
Esk6 - L.Bank	0.5	2	5	307	13	25	2.5	1	1	16	4	1	54.9751	-3.0406
Etherow1	1	2	5	403	75	130	39	33	6	116	27	4	53.4236	-2.0361
Etherow1	1	0.5	0.5	172	11	18	2.5	4	4	51	1	2	53.4236	-2.0361
Eweswater1	0.5	0.5	4	293	27	48	23	16	1.5	28	6	2	55.1715	-2.9861
Fiddlers Ferry1 - 0-5cm	1	0.5	4	289	16	21	2.5	1	4	34	4	2	53.3588	-2.6687
Fiddlers Ferry1 - 10-20cm	1	4	5	281	19	21	2.5	3	1.5	34	3	2	53.3588	-2.6687
Fiddlers Ferry1 - 20-30cm	0.5	5	0.5	303	12	25	2.5	1.5	1.5	39	2	1	53.3588	-2.6687
Fiddlers Ferry1 - 30-50cm	1	3	4	268	16	20	2.5	3	1.5	28	1	1	53.3588	-2.6687
Fiddlers Ferry1 - 50-70cm	1	4	0.5	302	15	21	18	1.5	1.5	39	3	2	53.3588	-2.6687
Fiddlers Ferry1 - 5-10cm	0.5	0.5	5	305	13	20	32	1.5	1.5	39	3	2	53.3588	-2.6687
Fiddlers Ferry1 - 70-90cm	0.5	5	0.5	290	13	19	15	1.5	1.5	46	2	0.5	53.3588	-2.6687
Fiddlers Ferry2	2	38	7	434	30	38	6	2	2	107	8	3	53.3588	-2.6687
Goyt1 - Centre bar	3	9	9	1680	49	87	52	30	2	136	14	5	53.3832	-2.0511
Hale1 - 0-5cm	2	27	4	340	22	39	44	4	4	86	7	4	53.3212	-2.7912
Hale1 - 10-20cm	0.5	21	5	308	17	35	11	5	1.5	60	8	3	53.3212	-2.7912
Hale1 - 20-30cm	1	8	5	280	21	28	16	4	1.5	39	5	1	53.3212	-2.7912
Hale1 - 30-45cm	0.5	22	4	321	21	32	13	1.5	2	71	4	3	53.3212	-2.7912
Hale1 - 5-10cm	2	30	3	335	20	33	24	3	3	81	7	3	53.3212	-2.7912

Appendix 3: ED-XRF Data. 8 of 12

Sample	Sb	I	Cs	Ba	La	Ce	Nd	Hf	W	Pb	Th	U	LAT	LONG
Hale2	2	32	5	422	29	52	2.5	12	2	92	12	4	53.3212	-2.7912
Hodder1	1	7	6	323	35	58	32	15	1.5	52	9	5	53.8480	-2.4500
Ince Bank1 - 0-5cm	0.5	4	5	255	16	23	12	6	1.5	23	2	2	53.3093	-2.8300
Ince Bank1 - 10-20cm	0.5	0.5	5	271	19	32	2.5	8	1.5	32	2	3	53.3093	-2.8300
Ince Bank1 - 20-30cm	0.5	7	5	275	22	30	19	10	1.5	30	4	3	53.3093	-2.8300
Ince Bank1 - 30-50cm	1	11	7	313	25	43	17	8	1.5	42	5	2	53.3093	-2.8300
Ince Bank1 - 50-70cm	0.5	11	0.5	287	20	31	26	4	1.5	36	6	2	53.3093	-2.8300
Ince Bank1 - 5-10cm	0.5	0.5	6	240	19	29	31	4	3	20	2	3	53.3093	-2.8300
Ince Bank2	0.5	0.5	4	270	25	40	19	13	1.5	25	4	2	53.3093	-2.8300
Irthing1 - Nr. R.Bank	0.5	0.5	4	443	22	39	13	15	1.5	24	4	3	54.9148	-2.8144
Irwell1 - Centre river	10	0.5	2	571	44	69	26	28	4	163	17	4	53.5507	-2.3774
Irwell2 (central)	5	0.5	2	797	39	72	27	25	2	186	20	6	53.5680	-2.3035
LiddellWater1 - R.Bank	0.5	3	4	458	22	35	11	15	1.5	27	3	4	55.0877	-2.8884
LiddellWater1-R.Bank	1	0.5	0.5	291	15	22	9	2	1.5	16	4	2	55.0877	-2.8884
LiddellWater2 - L.Bank	0.5	0.5	5	453	29	39	36	13	1.5	29	6	4	55.0877	-2.8900
M/O	2	44	6	388	30	52	6	11	4	86	14	5	53.3683	-2.9920
M/U	0.5	18	5	427	37	77	21	27	1.5	51	6	5	53.3237	-2.9459
Mersey1	3	0.5	0.5	1634	143	270	137	100	6	178	30	11	53.4216	-2.2573
Mersey1	0.5	0.5	0.5	340	15	17	10	4	3	50	3	1	53.4216	-2.2573
MickerBrook1	1	3	2	413	47	91	12	28	3	63	8	4	53.3875	-2.2075
NBright1 - 0-5cm	0.5	0.5	5	185	14	20	12	1	1	12	1	1	53.4407	-3.0329
NBright1 - 10-20cm	1	0.5	5	181	15	23	25	2	1	13	0.5	2	53.4407	-3.0329
NBright1 - 5-10cm	0.5	0.5	5	181	13	24	16	3	1	11	1	2	53.4407	-3.0329
New Brighton1	1	1	0.5	273	36	82	43	31	3	17	2	3	53.4407	-3.0329
Nith1	1	3	5	400	26	49	14	13	1.5	128	7	2	55.0579	-3.6033
Nith2	1	0.5	6	381	26	33	2.5	12	1.5	73	5	2	55.0580	-3.6018
Nith3 - L.Bank	0.5	0.5	0.5	421	30	50	15	21	1.5	177	10	4	55.0894	-3.6015
Nith4 (Centre bank)	1	3	0.5	414	31	47	2.5	25	1.5	160	15	4	55.0868	-3.5998
Nith4 (Centre bank)	0.5	1	0.5	260	18	27	2.5	3	1.5	67	4	2	55.0868	-3.5998
Nith4B	0.5	0.5	5	269	21	28	10	4	1.5	73	3	2	55.0868	-3.5998
Nith5	0.5	0.5	5	311	15	17	2.5	4	1	17	2	2	55.0354	-3.6056
Nith6	0.5	0.5	4	291	15	20	2.5	1.5	2	13	2	1	54.9793	-3.5705
Nith6B	0.5	3	6	293	20	20	2.5	2	1	14	2	2	54.9793	-3.5705
Nith7 - L.Bank	0.5	5	0.5	294	19	23	2.5	3	1	19	1	1	55.0035	-3.5730
Otter Pool1	0.5	7	3	364	34	58	27	26	1.5	33	4	4	53.3748	-2.9666
Petterel1	1	3	5	308	28	40	20	20	1	26	3	3	54.8505	-2.8770
R/O	1	32	0.5	307	34	62	35	16	1.5	44	7	3	53.7122	-3.3161
Ribble Lower Surface	0.5	12	3	402	21	47	25	9	1.5	31	9	4	53.7351	-2.9915
Ribble Upper Surface	1	12	4	327	20	35	25	8	1.5	31	4	2	53.7351	-2.8718
Ribble1	1	5	6	755	26	39	20	15	1.5	60	7	3	53.8995	-2.3622
Ribble1	0.5	0.5	3	519	9	14	2.5	1	1	14	2	3	53.8995	-2.3622
Ribble2 - Centre	6	21	7	458	29	47	16	11	2	81	11	4	53.8108	-2.5301
Ribble3	1	0.5	4	227	30	47	2.5	20	1	16	3	3	53.7308	-2.9596
Ribble4 - R.Bank	1	1	3	211	34	57	17	17	1	16	2	2	53.7361	-2.8612
Ribble5	1	12	6	306	25	38	18	8	1.5	34	8	3	53.7361	-2.8612
Ribble5 - R.Bank	0.5	10	3	319	22	38	25	7	1	29	4	2	53.7361	-2.8612
Ribble5B	0.5	7	6	312	22	33	9	8	1.5	27	7	3	53.7361	-2.8612
Ribble6 - L.Bank	0.5	8	3	272	20	36	2.5	11	1	23	2	3	53.7315	-2.8778
Ribble7 - L.Bank	0.5	4	6	246	18	26	2.5	4	1	19	4	2	53.7547	-2.7630
Ribble8 - R.Bank	0.5	7	5	268	12	20	2.5	2	1	26	4	2	53.7576	-2.7327
Richmond Bank1 - 0-5cm	1	18	4	357	21	30	7	1.5	2	70	8	3	53.3743	-2.6434
Richmond Bank1 - 10-20cm	2	13	8	333	19	28	16	1.5	2	65	5	2	53.3743	-2.6434
Richmond Bank1 - 20-30cm	1	6	5	313	15	26	13	1.5	2	53	6	3	53.3743	-2.6434
Richmond Bank1 - 30-50cm	0.5	9	5	338	18	26	15	1.5	2	55	6	2	53.3743	-2.6434
Richmond Bank1 - 50-75cm	0.5	9	0.5	321	16	24	13	1.5	3	53	3	3	53.3743	-2.6434
Richmond Bank1 - 5-10cm	1	19	3	369	16	28	7	1.5	2	73	8	2	53.3743	-2.6434
Richmond Bank2	1	7	5	370	17	26	2.5	3	1.5	52	6	3	53.3743	-2.6434

Appendix 3: ED-XRF Data. 9 of 12

Sample	Sb	I	Cs	Ba	La	Ce	Nd	Hf	W	Pb	Th	U	LAT	LONG
Roch1	32	0.5	6	672	36	63	38	14	2	192	16	5	53.5815	-2.2825
Rock Ferry	0.5	23	6	405	36	61	18	24	6	50	11	4	53.3683	-2.9920
Rock FerryB	1	20	5	404	37	60	26	23	1.5	47	7	3	53.3683	-2.9920
RockFerry	0.5	26	6	389	39	63	50	23	1.5	53	7	4	53.3683	-2.9920
Runcorn Sands1	1	0.5	5	285	13	22	16	3	1.5	28	5	2	53.3514	-2.7107
Runcorn Sands1	1	5	3	276	15	21	18	2	1.5	31	1	1	53.3514	-2.7107
S.Hale1	1	0.5	4	234	15	21	7	2	1	18	2	2	53.3113	-2.7941
S/O	1	13	5	286	20	25	2.5	8	2	22	3	3	54.6120	-3.7080
Seaforth1	1	15	5	419	34	58	28	21	1.5	57	7	5	53.4543	-3.0211
Seaforth1	2	24	4	383	36	59	11	13	1.5	76	12	2	53.4543	-3.0211
Seaforth1 - 0-5cm	2	29	3	390	33	54	46	14	3	93	15	4	53.4543	-3.0211
Seaforth1 - 10-20cm	1	21	3	368	23	36	5	9	1.5	68	11	4	53.4543	-3.0211
Seaforth1 - 20-30cm	2	25	5	350	23	43	35	9	1.5	71	10	3	53.4543	-3.0211
Seaforth1 - 30-50cm	0.5	22	5	397	30	52	32	17	2	86	9	4	53.4543	-3.0211
Seaforth1 - 50-70cm	2	26	2	449	34	52	23	19	3	114	15	3	53.4543	-3.0211
Seaforth1 - 5-10cm	2	31	6	401	32	56	18	9	2	95	14	5	53.4543	-3.0211
Seaforth1 - 70-100cm	0.5	23	5	442	33	51	17	12	2	104	14	4	53.4543	-3.0211
Solway Lower Surface	0.5	14	6	300	22	32	11	6	1	22	4	4	54.8948	-3.3473
Solway Upper Surface	1	12	7	313	19	27	24	5	1	26	7	3	54.9538	-3.1994
Speke1	1	17	4	436	31	45	12	20	1.5	53	8	5	53.3350	-2.8831
Speke1 - 0-5cm	1	25	0.5	430	32	58	30	14	2	72	12	5	53.3350	-2.8831
Speke1 - 10-20cm	2	27	4	487	38	60	14	14	2	94	14	4	53.3350	-2.8831
Speke1 - 20-30cm	2	34	5	550	32	52	32	10	2.5	144	16	4	53.3350	-2.8831
Speke1 - 30-46cm	2	27	7	542	35	50	33	7	2	124	11	5	53.3350	-2.8831
Speke1 - 5-10cm	1	22	4	455	30	46	39	9	2	79	11	4	53.3350	-2.8831
Tame1	5	0.5	3	571	58	102	34	32	2	179	23	5	53.4379	-2.1415
W/O	0.5	11	6	284	24	36	2.5	10	1	22	4	1	53.9880	-3.0000
Waters1 - 0-5cm	1	38	3	310	18	29	2.5	5	2	56	8	2	53.3899	-2.9865
Waters1 - 10-20cm	2	71	5	342	22	41	2.5	8	2	86	8	4	53.3899	-2.9865
Waters1 - 5-10cm	1	25	5	322	23	35	2.5	7	1.5	57	7	3	53.3899	-2.9865
Waterside1	1	9	4	303	22	30	16	8	1.5	32	5	3	53.3899	-2.9865
Waterside1B	1	7	4	300	21	30	2.5	10	1.5	32	4	3	53.3899	-2.9865
Waver1	0.5	0.5	8	389	19	31	2.5	8	1	16	2	1	54.8416	-3.2786
Weaver1	3	4	1	190	2	12	2.5	2.5	2	68	3	6	53.2596	-2.5562
Wyre Lower Surface	0.5	7	7	317	29	47	20	16	1.5	25	5	3	53.9283	-2.9976
WyreLowerSurfaceB	0.5	9	5	316	28	50	5	16	3	25	6	4	0.0000	0.0000
Wyre Upper Surface	0.5	19	5	305	22	38	2.5	10	1.5	35	5	3	53.8782	-2.9675
Wyre1 - R.Bank	0.5	5	5	274	20	23	11	5	1	20	3	1	53.8621	-2.9596
Wyre10 - R.Bank	0.5	31	4	337	22	44	14	7	1.5	56	11	5	53.8960	-2.9893
Wyre11	0.5	3	0.5	258	22	25	2.5	7	1	14	5	3	53.9157	-2.9989
Wyre11B	0.5	2	4	261	26	39	24	9	3	14	1	3	53.9157	-2.9989
Wyre12 - Sandy muds	0.5	9	0.5	298	29	56	28	18	1	24	5	4	53.9156	-3.0034
Wyre12B	0.5	7	5	307	34	52	17	18	1.5	23	6	5	53.9156	-3.0034
Wyre13 - L.Estuary mouth	0.5	14	7	278	25	45	2.5	10	1	26	4	3	53.9273	-3.0052
Wyre1B	0.5	5	5	277	16	25	22	6	1	19	5	2	53.8621	-2.9596
Wyre2 - Centre river bar	0.5	4	4	311	40	61	10	26	1.5	23	7	5	53.8621	-2.9596
Wyre3 - L.Bank	0.5	0.5	5	277	30	45	13	12	1	16	4	3	53.8612	-2.9595
Wyre4 - L.Bank	0.5	10	5	313	23	38	24	9	1	28	3	4	53.8612	-2.9595
Wyre5 - R.Bank	0.5	14	4	307	25	39	20	10	1.5	30	9	4	53.8621	-2.9596
Wyre5 - R.Bank	0.5	19	4	305	23	45	2.5	11	1.5	34	9	4	53.8621	-2.9596
Wyre6	0.5	4	3	585	111	212	96	64	5	25	22	6	53.8622	-2.8166
Wyre6	0.5	0.5	6	212	17	19	8	1	1	13	2	2	53.8622	-2.8166
Wyre6B	0.5	0.5	0.5	183	12	17	6	1	1	11	3	0.5	53.8622	-2.8166
Wyre7	1	9	0.5	269	19	27	2.5	5	2	22	3	3	53.9292	-3.0007
Wyre8	0.5	10	4	302	30	42	2.5	11	1	26	8	3	53.9283	-2.9976
Wyre9	0.5	26	4	372	23	46	12	13	1.5	35	7	4	53.8960	-2.9908

Appendix 3: ED-XRF Data. 10 of 12

Sample	**Description**
Beb1	SIEVED - in plastic bag
Beb1 - 0-5cm	UNSIEVED - in plastic bag
Beb1 - 10-20cm	UNSIEVED - in plastic bag
Beb1 - 20-27cm	UNSIEVED - in plastic bag
Beb1 - 5-10cm	UNSIEVED - in plastic bag
Bollin1	SIEVED - in plastic bag
Bollin2	SIEVED - in plastic bag
Calder1	SIEVED - in plastic bag
Calder2	SIEVED - in plastic bag
Calder2	<2mm in paper bag
Caldew1 - R.Bank	SIEVED - in plastic bag
CludenWater1 - R.Bank	SIEVED - in plastic bag
CludenWater2	SIEVED - in plastic bag
CludenWater3	SIEVED - in plastic bag
Crole1 (L.Bank)	SIEVED - in plastic bag
Douglas1 - L.Bank	SIEVED - in plastic bag
Douglas2A	SIEVED - in plastic bag
Douglas2B	SIEVED - in plastic bag
Eden1 - L.Bank	SIEVED - in plastic bag
Eden2 - R.Bank-GRAVEL	SIEVED - in plastic bag
Eden2B - R.Bank (<2mm)	<2mm in paper bag
Eden2B - R.Bank-SAND	SIEVED - in plastic bag
Eden3 - L.Bank	SIEVED - in plastic bag
Eden3 - L.Bank	<2mm in paper bag
Eden4 - Centre	SIEVED - in plastic bag
Eden5	SIEVED - in plastic bag
Eden5B	SIEVED - in plastic bag
Eden6 - L.Bank	SIEVED - in plastic bag
Egre1	SIEVED - in plastic bag
Egre1 - 0-5cm	UNSIEVED - in plastic bag
Egre1 - 10-20cm	UNSIEVED - in plastic bag
Egre1 5-10cm	UNSIEVED - in plastic bag
Ellen1	SIEVED - in plastic bag
Esk 2 - L.Bank	SIEVED - in plastic bag
Esk1	SIEVED - in plastic bag
Esk3	SIEVED - in plastic bag
Esk4 - R.Bank	SIEVED - in plastic bag
Esk5	SIEVED - in plastic bag
Esk5	<2mm in paper bag
Esk6 - L.Bank	SIEVED - in plastic bag
Etherow1	SIEVED - in plastic bag
Etherow1	<2mm in paper bag
Eweswater1	SIEVED - in plastic bag
Fiddlers Ferry1 - 0-5cm	UNSIEVED - in plastic bag
Fiddlers Ferry1 - 10-20cm	UNSIEVED - in plastic bag
Fiddlers Ferry1 - 20-30cm	UNSIEVED - in plastic bag
Fiddlers Ferry1 - 30-50cm	UNSIEVED - in plastic bag
Fiddlers Ferry1 - 50-70cm	UNSIEVED - in plastic bag
Fiddlers Ferry1 - 5-10cm	UNSIEVED - in plastic bag
Fiddlers Ferry1 - 70-90cm	UNSIEVED - in plastic bag
Fiddlers Ferry2	SIEVED - in plastic bag
Goyt1 - Centre bar	SIEVED - in plastic bag
Hale1 - 0-5cm	UNSIEVED - in plastic bag
Hale1 - 10-20cm	UNSIEVED - in plastic bag
Hale1 - 20-30cm	UNSIEVED - in plastic bag
Hale1 - 30-45cm	UNSIEVED - in plastic bag
Hale1 - 5-10cm	UNSIEVED - in plastic bag

Appendix 3: ED-XRF Data. 11 of 12

Sample	**Description**
Hale2	SIEVED - in plastic bag
Hodder1	SIEVED - in plastic bag
Ince Bank1 - 0-5cm	UNSIEVED - in plastic bag
Ince Bank1 - 10-20cm	UNSIEVED - in plastic bag
Ince Bank1 - 20-30cm	UNSIEVED - in plastic bag
Ince Bank1 - 30-50cm	UNSIEVED - in plastic bag
Ince Bank1 - 50-70cm	UNSIEVED - in plastic bag
Ince Bank1 - 5-10cm	UNSIEVED - in plastic bag
Ince Bank2	SIEVED - in plastic bag
Irthing1 - Nr. R.Bank	SIEVED - in plastic bag
Irwell1 - Centre river	SIEVED - in plastic bag
Irwell2 (central)	SIEVED - in plastic bag
LiddellWater1 - R.Bank	SIEVED - in plastic bag
LiddellWater1-R.Bank	<2mm in paper bag
LiddellWater2 - L.Bank	SIEVED - in plastic bag
M/O	SIEVED - in plastic bag
M/U	SIEVED - in plastic bag
Mersey1	SIEVED - in plastic bag
Mersey1	<2mm in paper bag
MickerBrook1	SIEVED - in plastic bag
NBright1 - 0-5cm	UNSIEVED - in plastic bag
NBright1 - 10-20cm	UNSIEVED - in plastic bag
NBright1 - 5-10cm	UNSIEVED - in plastic bag
New Brighton1	SIEVED - in plastic bag
Nith1	SIEVED - in plastic bag
Nith2	SIEVED - in plastic bag
Nith3 - L.Bank	SIEVED - in plastic bag
Nith4 (Centre bank)	SIEVED - in plastic bag
Nith4 (Centre bank)	<2mm - in plastic bag
Nith4B	<2mm - in plastic bag
Nith5	SIEVED - in plastic bag
Nith6	SIEVED - in plastic bag
Nith6B	SIEVED - in plastic bag
Nith7 - L.Bank	SIEVED - in plastic bag
Otter Pool1	SIEVED - in plastic bag
Petterel1	SIEVED - in plastic bag
R/O	SIEVED - in plastic bag
Ribble Lower Surface	SIEVED - in plastic bag
Ribble Upper Surface	SIEVED - in plastic bag
Ribble1	SIEVED - in plastic bag
Ribble1	<2mm in paper bag
Ribble2 - Centre	SIEVED - in plastic bag
Ribble3	SIEVED - in plastic bag
Ribble4 - R.Bank	SIEVED - in plastic bag
Ribble5	<2mm in paper bag
Ribble5 - R.Bank	SIEVED - in plastic bag
Ribble5B	SIEVED - in plastic bag
Ribble6 - L.Bank	SIEVED - in plastic bag
Ribble7 - L.Bank	SIEVED - in plastic bag
Ribble8 - R.Bank	SIEVED - in plastic bag
Richmond Bank1 - 0-5cm	UNSIEVED - in plastic bag
Richmond Bank1 - 10-20cm	UNSIEVED - in plastic bag
Richmond Bank1 - 20-30cm	UNSIEVED - in plastic bag
Richmond Bank1 - 30-50cm	UNSIEVED - in plastic bag
Richmond Bank1 - 50-75cm	UNSIEVED - in plastic bag
Richmond Bank1 - 5-10cm	UNSIEVED - in plastic bag
Richmond Bank2	SIEVED - in plastic bag

Appendix 3: ED-XRF Data. 12 of 12

Sample	**Description**
Roch1	SIEVED - in plastic bag
Rock Ferry	SIEVED - in plastic bag
Rock FerryB	SIEVED - in plastic bag
RockFerry	<2mm in paper bag
Runcorn Sands1	SIEVED - in plastic bag
Runcorn Sands1	<2mm in paper bag
S.Hale1	SIEVED - in plastic bag
S/O	SIEVED - in plastic bag
Seaforth1	SIEVED - in plastic bag
Seaforth1	<2mm in paper bag
Seaforth1 - 0-5cm	UNSIEVED - in plastic bag
Seaforth1 - 10-20cm	UNSIEVED - in plastic bag
Seaforth1 - 20-30cm	UNSIEVED - in plastic bag
Seaforth1 - 30-50cm	UNSIEVED - in plastic bag
Seaforth1 - 50-70cm	UNSIEVED - in plastic bag
Seaforth1 - 5-10cm	UNSIEVED - in plastic bag
Seaforth1 - 70-100cm	UNSIEVED - in plastic bag
Solway Lower Surface	SIEVED - in plastic bag
Solway Upper Surface	SIEVED - in plastic bag
Speke1	SIEVED - in plastic bag
Speke1 - 0-5cm	UNSIEVED - in plastic bag
Speke1 - 10-20cm	UNSIEVED - in plastic bag
Speke1 - 20-30cm	UNSIEVED - in plastic bag
Speke1 - 30-46cm	UNSIEVED - in plastic bag
Speke1 - 5-10cm	UNSIEVED - in plastic bag
Tame1	SIEVED - in plastic bag
W/O	SIEVED - in plastic bag
Waters1 - 0-5cm	UNSIEVED - in plastic bag
Waters1 - 10-20cm	UNSIEVED - in plastic bag
Waters1 - 5-10cm	UNSIEVED - in plastic bag
Waterside1	SIEVED - in plastic bag
Waterside1B	SIEVED - in plastic bag
Waver1	SIEVED - in plastic bag
Weaver1	SIEVED - in plastic bag
Wyre Lower Surface	SIEVED - in plastic bag
WyreLowerSurfaceB	SIEVED - in plastic bag
Wyre Upper Surface	SIEVED - in plastic bag
Wyre1 - R.Bank	SIEVED - in plastic bag
Wyre10 - R.Bank	SIEVED - in plastic bag
Wyre11	SIEVED - in plastic bag
Wyre11B	SIEVED - in plastic bag
Wyre12 - Sandy muds	SIEVED - in plastic bag
Wyre12B	SIEVED - in plastic bag
Wyre13 - L.Estuary mouth	SIEVED - in plastic bag
Wyre1B	SIEVED - in plastic bag
Wyre2 - Centre river bar	SIEVED - in plastic bag
Wyre3 - L.Bank	SIEVED - in plastic bag
Wyre4 - L.Bank	SIEVED - in plastic bag
Wyre5 - R.Bank	SIEVED - in plastic bag
Wyre5 - R.Bank	<2mm in paper bag
Wyre6	SIEVED - in plastic bag
Wyre6	<2mm - in plastic bag
Wyre6B	<2mm - in plastic bag
Wyre7	SIEVED - in plastic bag
Wyre8	SIEVED - in plastic bag
Wyre9	SIEVED - in plastic bag

Appendix 4: Model Signature Data 1, Catchment geochemistry (GBase DR-OES data)

Catchment	Key River site	Sub-catchments (or Unitary)	Area km2		P2O5%	K2O%		TiO2%	Fe2O3%	Mn	V	Cr	Ni	Cu	Zn	Ga	As	Rb	Sr	Y	Zr	Nb	Sn	Ba	Pb	U
NITH																										
Upper Nith	Nith 3	Unitary	856	2.59	0.15	2.56	0.67	0.98	7.38	3780	100	243	67	26	150	18	12	101	136	31	944	15	4	633	49	3
Old Water	Cluden Water 1, 2	Cluden + Old Water	241	2.66	0.17	2.68	0.68	0.92	7.04	5007	95	248	65	24	149	17	16	106	129	30	859	15	4	652	50	3
Cluden	Cluden Water 3	Unitary	35	2.68	0.17	2.68	0.70	0.92	7.10	5364	94	246	66	25	150	17	16	107	130	30	814	15	4	652	50	3
Middle Nith	Nith 5	Upr Nith + (Cluden)	1124	2.60	0.15	2.59	0.66	0.97	7.26	3882	99	245	66	25	149	18	13	102	134	31	948	15	4	638	49	3
Cargen Pow	Nith 6, 7	(Middle Nith) +Cargen Pow	1218	2.60	0.16	2.60	0.67	0.96	7.25	4016	99	245	66	25	149	18	13	102	134	31	935	15	4	639	49	3
ESK																										
Upper Esk	Esk 2	Unitary	279	2.68	0.17	2.68	0.70	0.92	7.10	5364	94	246	66	25	150	17	16	107	130	30	814	15	4	652	50	3
Ewes Water	Ewes Water 1	Unitary	75	3.02	0.09	3.26	0.49	1.01	7.66	2097	117	218	86	29	155	20	7	132	87	31	661	22	2	592	48	3
Liddell	Liddle 1, 2	Unitary	300	2.47	0.10	3.67	1.19	1.02	7.49	2080	99	195	65	22	188	18	6	127	118	30	1060	22	2	665	52	3
Middle Esk	Esk 3	(Potholm) + Ewes Water + Middle Esk	477	2.72	0.14	3.00	0.73	0.96	7.32	4026	100	231	71	25	158	18	12	117	118	30	820	18	3	641	50	3
Lower Liddell	Esk 4, 5	(Middle Esk) + Liddle + Lower Liddle	822	2.57	0.12	3.23	0.90	0.98	7.32	3180	99	215	67	24	169	18	10	120	118	30	925	19	3	654	50	3
Lower Esk	Esk 6	(Lower Liddle) + Lower Esk	1154	2.34	0.11	3.20	0.95	0.95	6.92	2723	94	203	61	22	167	17	8	116	119	29	992	18	2	652	50	3
WAVER																										
Waver	Waver 1	Unitary	95	1.07	0.05	1.95	1.52	0.77	4.67	1659	74	142	31	20	129	12	5	86	133	29	1173	5	3	609	46	3
ELLEN																										
Ellen	Ellen 1	Unitary	97	1.38	0.05	2.25	2.24	0.91	7.63	5541	92	107	39	29	141	19	5	119	135	36	767	8	4	710	50	3
EDEN																										
Upper Eden	Eden 3, 4	Unitary	1345	1.57	0.05	2.04	3.18	0.83	6.13	5308	81	102	26	19	139	14	4	100	120	33	1054	8	3	706	50	3
Irthing	Irthing 1	Unitary	315	1.12	0.09	2.32	1.41	0.81	6.75	1970	74	137	38	12	139	14	4	94	115	27	1012	13	2	514	51	3
Petteril	Petteril 1	Unitary	128	1.08	0.04	1.77	3.03	0.76	4.67	1950	71	114	28	19	130	12	5	87	149	32	1184	4	3	591	49	3
Caldew	Caldew 1	Unitary	224	1.40	0.05	2.20	2.40	0.90	7.11	4934	89	112	36	27	144	17	5	114	137	36	972	7	4	711	51	3
Middle Eden	Eden 1, 2	Upper Eden + Gelt + Petteril + Caldew+ Middle Eden	2256	1.41	0.06	2.09	2.63	0.82	6.03	4186	80	114	29	18	137	14	4	98	122	32	1063	8	3	667	50	3
Lower Eden	Eden 5, 6	(Middle Eden) + Lower Eden	2309	1.41	0.06	2.10	2.56	0.82	5.98	4091	80	116	29	18	137	14	4	98	122	32	1067	8	3	664	50	3
WYRE																										
Upper Wyre	Wyre 6	Unitary	270	1.19	0.11	1.75	2.92	0.83	6.22	1817	80	118	47	25	180	17	3	89	117	33	1393	16	6	521	53	1
Middle Wyre	Wyre 1-5	Upper Wyre + Mid Wyre	348	1.44	0.14	1.81	2.93	0.82	6.15	1606	79	118	46	30	173	16	3	91	122	32	1279	16	5	538	52	2
Lower Wyre	Wyre 7 etc.	L Wyre, M Wyre, U Wyre	410	1.57	0.15	1.85	2.94	0.81	6.12	1492	78	119	45	33	169	16	4	93	124	32	1217	16	5	548	52	2
RIBBLE																										
Top Ribble	Ribble 1	Unitary	356	0.97	0.08	1.46	5.65	0.78	6.43	2186	81	104	52	20	168	16	3	82	133	36	1215	14	4	547	55	2
Hodder	Hodder 1	Unitary	264	0.93	0.09	1.56	4.40	0.82	6.42	2160	82	106	51	20	180	17	2	85	128	35	1343	15	4	545	53	2
Calder	Calder 1, 2	Unitary	316	1.15	0.16	1.92	0.93	0.86	7.65	2427	86	116	61	80	174	19	3	93	102	33	1264	17	4	578	52	1
Upper Ribble	Ribble 2	Top Ribble + Hodder + Calder + Upper Ribble	1068	1.01	0.11	1.63	3.86	0.81	6.79	2254	83	108	55	38	173	17	3	86	122	35	1268	15	4	558	53	2
Middle Ribble	Ribble 7, 8	(Upper Ribble) + Middle Ribble	1289	1.04	0.11	1.68	3.38	0.82	6.75	2189	82	111	54	39	175	17	3	87	119	34	1296	15	4	551	53	2
Upper Douglas	Douglas 2	Unitary	227	1.40	0.19	1.96	1.26	0.82	7.83	2416	85	122	65	94	156	18	4	95	105	32	1131	18	5	605	51	1
Lower Douglas	Douglas 1	Upper Douglas + Lower Douglas	424	1.50	0.18	1.96	1.48	0.82	7.28	2072	82	123	58	77	160	17	4	95	109	31	1161	18	5	585	51	1
Lower Ribble	Ribble 3-6	(Middle Ribble) + (Lower Douglas)	1817	1.21	0.13	1.76	2.93	0.82	6.81	2097	82	115	54	47	170	17	3	89	117	33	1257	16	5	558	53	1
MERSEY																										
Croal	Croal 1	Unitary	143	1.15	0.16	1.92	0.93	0.86	7.65	2427	86	116	61	80	174	19	3	93	102	33	1264	17	4	578	52	1
Irwell	Irwell 2	Unitary	168	1.12	0.15	1.91	0.90	0.87	7.40	2319	86	116	58	70	180	19	3	93	102	33	1325	16	4	561	53	1
Roch	Roch 1	Unitary	167	1.21	0.17	1.94	0.98	0.84	8.02	2591	87	117	66	95	165	19	3	94	102	33	1174	18	4	604	52	1
Tame	Teme 1	Unitary	144	1.08	0.14	1.88	0.91	0.86	6.95	2108	83	115	52	54	185	18	3	90	100	33	1399	15	4	531	54	2
Etherow	Etherow 1	Unitary	145	1.17	0.21	1.97	0.56	0.79	6.90	3363	97	109	61	40	184	16	12	82	78	32	710	13	6	606	48	4
Goyt	Goyt 1	Unitary	165	1.23	0.21	1.97	0.79	0.81	7.67	3141	93	113	67	75	169	17	8	88	89	32	849	16	5	625	49	2
Upper Bollin	Bollin 2	Unitary	53	1.39	0.27	2.08	0.82	0.71	5.61	2112	82	102	42	36	161	13	13	77	80	29	850	12	8	1069	79	3
Bollin-Dean	Bollin 1	Upper Bollin + Bollin-Dean	272	1.56	0.30	2.13	1.04	0.67	5.11	1539	71	95	35	41	147	11	12	77	82	28	1073	12	7	1014	81	3
Weaver	Weaver 1	Unitary	1237	1.34	0.11	1.97	0.97	0.77	4.94	1383	81	156	37	33	136	13	6	80	117	26	1101	8	3	599	41	3
Micker Brook	Micker Brook 1	Unitary	55	1.46	0.27	2.07	1.12	0.72	6.61	1910	77	103	49	78	145	14	9	84	91	29	1005	15	8	1088	81	2
Lower Irwell	Irwell 1	Roch + Irwell + Lower Roch	368	1.17	0.16	1.92	0.95	0.85	7.78	2485	86	116	63	85	170	19	3	93	102	33	1230	17	4	588	52	1
Mid Mersey	Mersey 1	Tame + Etherow + Goyt + Micker Brook + Mid Mersey	1231	1.18	0.18	1.94	0.89	0.83	7.50	2602	88	114	61	74	172	18	5	90	97	33	1127	16	4	613	53	2
Main Mersey	Richmond Bank	Croal + (L. Irwell) + (Mid Mersey) + (Bollin-Dean) + Main Mersey	2866	1.38	0.19	1.96	1.19	0.81	7.18	2252	83	117	57	73	163	17	5	91	101	32	1135	17	5	635	54	1
Lower Mersey	New Brighton 1	(Main Mersey) + Weaver	4102	1.44	0.20	2.01	1.14	0.76	5.99	1771	79	124	46	54	149	14	7	84	101	29	1080	13	6	757	59	2

Appendix 4: Model Signature Data 2a, Mean GBase geochemical values for major geological lithologies in the study area. Calculations based on samples which include the effects of mining activity. Compare with Model Signature Data 4.

Element	Borrowdale Volcanics	Carb Lst (Cumbria)	Carb Lst' (Irthing&Esk)	Carb Lst (Lancs)	Carb lst'(sst) Borders	Carb Volcs (Scot)	Lias (Carlisle)	Lias (Cheshire)
As	61.4	5.1	3.6	2.8	5.4	3.9	3.9	18.2
Ba	960	654	471	616	689	632	525	1152
CaO%	0.96	6.27	1.5	8.07	1.33	2.19	0.77	2.45
Co	33.6	12.8	23.2	19.7	24.3	16.2	11.9	26
Cr	89.1	105	135	97.2	191	158	203	89
Cu	47.9	21.1	11.4	28.3	20.4	18.1	11.5	30.8
Fe2O3%	11.27	4.87	7.85	6.67	7.58	5.49	4.09	5.6
Ga	24.9	11.5	14.9	14.5	17.7	13.3	9.8	13.3
K2O%	3.1	1.7	2.4	1.26	3.87	2.63	1.78	2.67
La	46.7	29.3	35.8	42.9	37.5	30.9	25	39.2
MgO%	2.41	1.26	1.14	0.93	2.33	2.13	0.99	2.46
Mn	14229	1929	2216	2546	2111	1559	1114	1666
Mo	0.6	0.5	0.1	1.4	2.7	0.1	0	3
Nb	14.9	6.5	15	15.2	23	9.7	5.3	12.2
Ni	34.9	30	42.9	59.3	60.1	44.5	27.3	33.9
Pb	460	58.1	52.8	352	51.5	66.1	33.5	44
P2O5%	0.076	0.04	0.11	0.09	0.11	0.08	0.04	0.45
Rb	162	84	96	79	128	93	68	89
SiO2%	59.38	63.2	72.89	71.2	68.2	68.41	70.8	70.5
Sn	10.1	2.5	1.2	4.3	1.7	3.4	1.1	6
Sr	102	145	107	155	127	115	120	91
TiO2%	1.14	0.77	0.84	0.72	1.03	0.91	0.77	0.7
U	3	2.8	2.7	1.5	3.1	3	2.8	3
V	124	75	75	80	94	87	73	89
Y	44.9	31.5	26.7	36.7	30.3	30.2	21.6	28
Zn	870	196	257	447	199	166	106	137
Zr	416	901	948	1060	1153	1489	1380	598

Element	Permian Volcs(Nith)	Scot Lwr Pal2	Scot Lwr Pal1	Scot Permian sst	Sherwood sst (Cheshire)	Sherwood sst (Cuml	Sherwood ssts (V	Skiddaw Slates
As	7.8	7.6	16.3	7.1	15.7	4.9	0	45.8
Ba	628	581	652	648	1653	667	522	777
CaO%	0.63	0.4	0.7	0.46	1.06	0.65	2.18	0.31
Co	26.4	25.3	26.8	19.6	19.3	12.2	14.9	61.1
Cr	369	221	246	267	88	160	145	109
Cu	33.2	29.8	24.8	16.5	41.1	13.2	39.6	57.4
Fe2O3%	8.51	7.67	7.1	6.39	4.58	4.12	5.86	11.52
Ga	19.4	20.2	17.1	15.7	9.7	11.3	13.9	28.4
K2O%	3.01	3.19	2.68	2.73	2.25	2.29	2	2.82
La	37.8	35.3	45.3	39.7	34.9	27.6	36.4	45.6
MgO%	4.38	3.1	2.68	2.46	1.65	1.1	1.98	1.43
Mn	1030	2095	5364	1168	973	1177	1173	6878
Mo	0.3	0.01	0.4	0.01	2.3	0.02	0.5	0.1
Nb	23.4	21.4	14.6	16.9	11.2	9.1	19.5	10.5
Ni	98.6	89	66	58	26.3	28.4	43.1	63
Pb	33.8	47.9	68.6	46.7	118	74.1	105	364
P2O5%	0.07	0.09	0.17	0.13	0.35	0.05	0.18	0.06
Rb	102	132	107	97	75	89	95	165
SiO2%	68.26	67.87	69.49	70.15	70.5	71.49	79.17	60.36
Sn	2	2.1	4.2	5.6	12	2.4	10.3	7.2
Sr	140	82.6	130	124	79	114	113	125
TiO2%	1.19	1.01	0.92	0.97	0.63	0.76	0.79	1.09
U	3	2.9	3.4	3.3	2.6	2.9	0	2.9
V	147	119	94	102	68	72	74	114
Y	28.4	31.1	30.3	32.3	25.7	25.4	28.7	38.9
Zn	115	222	331	141	139	118	248	382
Zr	1697	606	814	1341	951	1232	1259	406

Appendix 4: Model Signature Data 2b, Mean GBase geochemical values for major geological lithologies in the study area. Calculations based on samples which include the effects of mining activity. Compare with Model Signature Data 4.

Element	Mercia Mdst(Cheshire)	Mercia Mdst(West Lancs)	Mercia Mdst (Carlisle)	Namurian (Cheshire)	Namurian (Cumbria)	Namurian (Lancs)	Permian (Cumbria)	Permian (Lancs)
As	14.4	0	4.1	12.9	4.4	1.9	3.3	4.7
Ba	707	600	558	601	510	473	634	530
CaO%	1.15	2.97	0.83	0.5	2.3	0.72	2.9	1.59
Co	18.9	14.1	12.8	34	11.5	20.5	10	20.5
Cr	86	120	174	108	109	115	125	107
Cu	28.5	48.7	21.1	30.6	17.5	20	14.4	57.7
Fe2O3%	3.93	5.92	4.05	6.71	4.3	6.17	3.68	6.63
Ga	8.5	15.2	11	15.9	13.3	19.4	9.2	12
K2O%	2.2	2.05	1.92	1.97	1.82	1.86	1.71	1.77
La	33.2	41.8	23.3	53.4	28.3	50.5	27.9	31.4
MgO%	1.85	2.3	1.24	1.15	0.99	0.93	1.33	1.36
Mn	1248	861	875	3418	1836	1774	1315	1842
Mo	2.8	0.7	0.2	4.6	0.2	0.5	0.1	3.2
Nb	11.1	16.5	4.1	12.8	3.7	13.9	3.9	14
Ni	25.1	42.7	28.5	59.2	26.9	41.9	18.2	42
Pb	67.8	100.5	37.6	47.5	42	56.2	81.2	132
P2O5%	0.36	0.22	0.05	0.21	0.04	0.09	0.05	0.23
Rb	70	102	76	80	91	90	74	73
SiO2%	70.5	80.47	70.5	70.5	67.8	72.19	68.59	44.03
Sn	9.9	6.6	2.1	5.9	2.5	3.9	4	18.9
Sr	74	138	127	75	170	100	130	90
TiO2%	0.59	0.76	0.76	0.79	0.74	0.91	0.72	0.7
U	2.8	0	2.8	4	3	2.2	3.1	1.4
V	58	74	77	98	70	83	62	71
Y	26.9	28.4	23.8	32.1	32.8	34	29.4	29.4
Zn	130	266	125.8	188	104	209	141	249
Zr	1183	877	1197	675	1020	1626	1883	1165

Element	Slates in Top Ribble	Westphalian (Cheshire)	Westphalian (Cumbria)	Westphalian (LancsCF)	Westphalian in Liddle	Westphalian in Nith
As	5.8	13.9	6	3.4	4.5	4.6
Ba	357	673	649	648	794	572
CaO%	5.87	0.76	1.38	1.07	0.6	0.74
Co	14.1	32.9	19.4	29.1	20.6	25.7
Cr	107	93	121	117	188	187
Cu	19.3	37.5	26.3	120	20.5	32.5
Fe2O3%	5.78	7.87	6.2	8.63	6.9	8.64
Ga	13.6	12.8	14.9	18.5	15.2	22.5
K2O%	1.46	1.88	1.81	1.96	2.35	2.01
La	28.6	42	29.2	44.1	32.6	44.9
MgO%	1.28	0.94	0.82	1.3	1.56	1.97
Mn	1259	2790	2834	2863	1431	1678
Mo	0.9	3.4	0.04	1.4	0	0.1
Nb	4.3	12	3.4	18.8	17.9	11.2
Ni	43.2	44.8	40	74	54.7	70.2
Pb	81.8	90.2	50.7	258	42.1	71.6
P2O5%	0.02	3.19	0.05	0.2	0.11	0.15
Rb	80	72	94	95	89	84
SiO2%	65.72	70.5	69.87	68.45	69.75	67.18
Sn	5.6	11.2	3.7	17.6	2.2	2.4
Sr	101	75	132	103	143	160
TiO2%	0.74	0.73	0.82	0.82	0.95	1.18
U	3.7	2.8	3.4	0.5	3	3.3
V	79	89	79	88	97	106
Y	34	29.6	34	32.5	29.6	31.8
Zn	345	221	153	478	257	165
Zr	913	729	1094	1023	1009	848

Appendix 4: Model Signature Data 3a, Mean GBase geochemical values for major geological lithologies in the study area. Calculations based on samples which exclude the effects of mining activity. Highlighted figures are an estimate of natural background including unworked mineralisation, but excluding mining contamination. These "corrected" values were used to generate model geochemical signatures. Compare with the "uncorrected" data in Model Signature Data 3.

Element	Borrowdale Volcanics	Carb Lst (Cumbria)	Carb Lst' (Irthing&Esk)	Carb Lst (Lancs)	Carb lst'(sst) Borders	Carb Volcs (Scot)	Lias (Carlisle)	Lias (Cheshire)
n =	494	86	544	374	255	146	23	48
As	5	5.1	3.6	2.8	5.4	3.9	3.9	18.2
Ba	960	654	471	616	689	632	525	1152
CaO%	0.96	6.27	1.5	8.07	1.33	2.19	0.77	2.45
Co	33.6	12.8	23.2	19.7	24.3	16.2	11.9	26
Cr	89.1	105	135	97.2	191	158	203	89
Cu	25	21.1	11.4	20	20.4	18.1	11.5	20
Fe2O3%	11.27	4.87	7.85	6.67	7.58	5.49	4.09	5.6
Ga	24.9	11.5	14.9	14.5	17.7	13.3	9.8	13.3
K2O%	3.1	1.7	2.4	1.26	3.87	2.63	1.78	2.67
La	46.7	29.3	35.8	42.9	37.5	30.9	25	39.2
MgO%	2.41	1.26	1.14	0.93	2.33	2.13	0.99	2.46
Mn	14229	1929	2216	2546	2111	1559	1114	1666
Mo	0.6	0.5	0.1	1.4	2.7	0.1	0	3
Nb	14.9	6.5	15	15.2	23	9.7	5.3	12.2
Ni	34.9	30	42.9	59.3	60.1	44.5	27.3	33.9
Pb	50	58.1	52.8	50	51.5	66.1	33.5	44
P2O5%	0.076	0.04	0.11	0.09	0.11	0.08	0.04	0.45
Rb	162	84	96	79	128	93	68	89
SiO2%	59.38	63.2	72.89	71.2	68.2	68.41	70.8	70.5
Sn	4	2.5	1.2	4.3	1.7	3.4	1.1	6
Sr	102	145	107	155	127	115	120	91
TiO2%	1.14	0.77	0.84	0.72	1.03	0.91	0.77	0.7
U	3	2.8	2.7	1.5	3.1	3	2.8	3
V	124	75	75	80	94	87	73	89
Y	44.9	31.5	26.7	36.7	30.3	30.2	21.6	28
Zn	150	150	150	150	199	166	106	137
Zr	416	901	948	1060	1153	1489	1380	598

Element	Permian Volcs(Nith)	Scot Lwr Pal2	Scot Lwr Pal1	Scot Permian sst	Sherwood sst (Cheshire)	Sherwood sst (Cumbria)	Sherwood ssts (West Lancs)	Skiddaw Slates
	6	348	1087	31	76	253	193	319
As	7.8	7.6	16.3	7.1	15.7	4.9	5	5
Ba	628	581	652	648	1653	667	522	777
CaO%	0.63	0.4	0.7	0.46	1.06	0.65	2.18	0.31
Co	26.4	25.3	26.8	19.6	19.3	12.2	14.9	61.1
Cr	369	221	246	267	88	160	145	109
Cu	33.2	29.8	24.8	16.5	41.1	13.2	39.6	57.4
Fe2O3%	8.51	7.67	7.1	6.39	4.58	4.12	5.86	11.52
Ga	19.4	20.2	17.1	15.7	9.7	11.3	13.9	28.4
K2O%	3.01	3.19	2.68	2.73	2.25	2.29	2	2.82
La	37.8	35.3	45.3	39.7	34.9	27.6	36.4	45.6
MgO%	4.38	3.1	2.68	2.46	1.65	1.1	1.98	1.43
Mn	1030	2095	5364	1168	973	1177	1173	6878
Mo	0.3	0.01	0.4	0.01	2.3	0.02	0.5	0.1
Nb	23.4	21.4	14.6	16.9	11.2	9.1	19.5	10.5
Ni	98.6	89	66	58	26.3	28.4	43.1	63
Pb	33.8	47.9	50	46.7	118	50	50	50
P2O5%	0.07	0.09	0.17	0.13	0.35	0.05	0.18	0.06
Rb	102	132	107	97	75	89	95	165
SiO2%	68.26	67.87	69.49	70.15	70.5	71.49	79.17	60.36
Sn	2	2.1	4.2	5.6	12	2.4	10.3	7.2
Sr	140	82.6	130	124	79	114	113	125
TiO2%	1.19	1.01	0.92	0.97	0.63	0.76	0.79	1.09
U	3	2.9	3.4	3.3	2.6	2.9	0	2.9
V	147	119	94	102	68	72	74	114
Y	28.4	31.1	30.3	32.3	25.7	25.4	28.7	38.9
Zn	115	150	150	141	139	118	150	150
Zr	1697	606	814	1341	951	1232	1259	406

Appendix 4: Model Signature Data 3b, Mean GBase geochemical values for major geological lithologies in the study area. Calculations based on samples which exclude the effects of mining activity. Highlighted figures are an estimate of natural background including unworked mineralisation, but excluding mining contamination. These "corrected" values were used to generate model geochemical signatures. Compare with the "uncorrected" data in Model Signature Data 3.

Element	Mercia Mdst(Cheshire)	Mercia Mdst(West Lancs)	Mercia Mdst (Carlisle)	Namurian (Cheshire)	Namurian (Cumbria)	Namurian (Lancs)	Permian (Cumbria)	Permian (Lancs)
	248	121	108	72	27	473	92	10
As	14.4	5	4.1	12.9	4.4	1.9	3.3	4.7
Ba	707	600	558	601	510	473	634	530
CaO%	1.15	2.97	0.83	0.5	2.3	0.72	2.9	1.59
Co	18.9	14.1	12.8	34	11.5	20.5	10	20.5
Cr	86	120	174	108	109	115	125	107
Cu	28.5	48.7	21.1	30.6	17.5	20	14.4	57.7
Fe2O3%	3.93	5.92	4.05	6.71	4.3	6.17	3.68	6.63
Ga	8.5	15.2	11	15.9	13.3	19.4	9.2	12
K2O%	2.2	2.05	1.92	1.97	1.82	1.86	1.71	1.77
La	33.2	41.8	23.3	53.4	28.3	50.5	27.9	31.4
MgO%	1.85	2.3	1.24	1.15	0.99	0.93	1.33	1.36
Mn	1248	861	875	3418	1836	1774	1315	1842
Mo	2.8	0.7	0.2	4.6	0.2	0.5	0.1	3.2
Nb	11.1	16.5	4.1	12.8	3.7	13.9	3.9	14
Ni	25.1	42.7	28.5	59.2	26.9	41.9	18.2	42
Pb	67.8	50	37.6	47.5	42	56.2	50	50
P2O5%	0.36	0.22	0.05	0.21	0.04	0.09	0.05	0.23
Rb	70	102	76	80	91	90	74	73
SiO2%	70.5	80.47	70.5	70.5	67.8	72.19	68.59	70.5
Sn	4	4	2.1	5.9	2.5	3.9	4	4
Sr	74	138	127	75	170	100	130	90
TiO2%	0.59	0.76	0.76	0.79	0.74	0.91	0.72	0.7
U	2.8	0	2.8	4	3	2.2	3.1	1.4
V	58	74	77	98	70	83	62	71
Y	26.9	28.4	23.8	32.1	32.8	34	29.4	29.4
Zn	130	150	125.8	188	104	209	141	150
Zr	1183	877	1197	675	1020	1626	1883	1165

Element	Slates in Top Ribble	Westphalian (Cheshire)	Westphalian (Cumbria)	Westphalian (LancsCF)	Westphalian in Liddle	Westphalian in Nith
	20	54	80	175	12	113
As	5.8	13.9	6	3.4	4.5	4.6
Ba	357	673	649	648	794	572
CaO%	5.87	0.76	1.38	1.07	0.6	0.74
Co	14.1	32.9	19.4	29.1	20.6	25.7
Cr	107	93	121	117	188	187
Cu	19.3	37.5	26.3	120	20.5	32.5
Fe2O3%	5.78	7.87	6.2	8.63	6.9	8.64
Ga	13.6	12.8	14.9	18.5	15.2	22.5
K2O%	1.46	1.88	1.81	1.96	2.35	2.01
La	28.6	42	29.2	44.1	32.6	44.9
MgO%	1.28	0.94	0.82	1.3	1.56	1.97
Mn	1259	2790	2834	2863	1431	1678
Mo	0.9	3.4	0.04	1.4	0	0.1
Nb	4.3	12	3.4	18.8	17.9	11.2
Ni	43.2	44.8	40	74	54.7	70.2
Pb	81.8	50	50.7	50	42.1	50
P2O5%	0.02	3.19	0.05	0.2	0.11	0.15
Rb	80	72	94	95	89	84
SiO2%	65.72	70.5	69.87	68.45	69.75	67.18
Sn	5.6	4	3.7	4	2.2	2.4
Sr	101	75	132	103	143	160
TiO2%	0.74	0.73	0.82	0.82	0.95	1.18
U	3.7	2.8	3.4	0.5	3	3.3
V	79	89	79	88	97	106
Y	34	29.6	34	32.5	29.6	31.8
Zn	150	150	153	150	150	165
Zr	913	729	1094	1023	1009	848

Appendix 5. Additional BIOAVAILABILITY data

Appendix 5.1 Redox data from cores

Depth cm	Ribble Upper	Ribble Lower	Ribble Outer	Mersey Upper	Mersey Lower	Mersey Outer	Wyre Upper	Wyre Lower	Wyre Outer	Solway Upper	Solway Lower	Solway Outer
0												
3	3	54	79	115	145	39	97	77	48	96	47	117
6	14	4	-16	-14	6	-26	33	-46	-51	-25	-37	69
9	-11	-149	-61	30	-21	-52	-57	-123	-81	-131	-50	64
12	-125	24		-31	-161	-104	-149	-163		-177	-72	35
15	-158	-46		-59	-165		-178	-205		-214	-108	24
18	-196	-179		-46	-176			-211		-316		

eH readings were obtained using a portable Russell mV meter equipped with platinum spear electrode, deployed at differing depths down the sediment core. Readings are corrected for hydrogen reference (+198.9mV)

Appendix 5.2 Metals in Irish Sea water samples July 1999

							Filtered	µg/l				
	Date	Salinity	pH	Cd	Co	Cu	Fe	Mn	Ni	Pb	Zn	As
M/O	20/07/99	33.16	7.70	0.084886	0.06	5.49	2.7	14	1.94	1.07	7.13	2.16
M/L	19/07/99	25.66	7.25			8.00	3.05	19			17.00	5.68
M/U	19/07/99	23.13	7.35	0.224189	0.2	10.00	11	20	5.65	1.775	24.58	6.76
R/O	20/07/99	31.44	7.80	0.034987	0.025	3.17	5.3	6	1.00	0.6	3.08	1.44
R/L	19/07/99	22.81	7.50	0.764411	0.055	8.92	0.75	22	3.19	0.995	10.18	4.44
R/U	19/07/99	1.77	7.90	1.788846	0.275	9.47	5.3	50	6.75	1.075	8.13	2.95
W/O	20/07/99	31.29	7.45	0.064047		4.40	6.35	2	0.80	0.485	3.18	1.69
W/L	20/07/99	24.29	7.20	3.087922	0.015	4.24	5.65	20	1.20	0.335	2.83	2.10
W/U	20/07/99	5.89	7.30	0.109984	0.21	8.99	41.8	291	2.62	0.78	1.78	3.45
S/O	20/07/99	31.72	7.80	0.044787	0.025	1.695	2.1	2	0.82	0.52	1.48	1.20
S/L	21/07/99	8.55	7.60	0.699295	0.3	3.82	9.65	345	4.48	0.335	0.78	1.89
S/U	21/07/99	18.50	7.65	0.130777	0.085	3.00	14.55	96	2.11	0.32	0.13	1.64

							Total µg/l					
	Date	Salinity	pH	Cd	Co	Cu	Fe	Mn	Ni	Pb	Zn	As
M/O	20/07/99	33.16	7.70	0.07	0.09	6	110	18	1.45	4.46	8.6	2.32
M/L	19/07/99	25.66	7.25	0.28	3.14	30	6571	896			178.6	14.53
M/U	19/07/99	23.13	7.35	0.19	1.89	13	2399	232			78.4	9.55
R/O	20/07/99	31.44	7.80	0.02	0.12	4	67	12	0.99	1.79	6.3	1.59
R/L	19/07/99	22.81	7.50	0.69	2.18	12	3063	338	5.14		48.9	6.16
R/U	19/07/99	1.77	7.90	0.98	3.54	23	7105	1202	6.69		78.4	7.97
W/O	20/07/99	31.29	7.45	0.03	0.22	5	294	41	0.88	2.69	5.8	1.96
W/L	20/07/99	24.29	7.20	1.35	1.31	6	1916	227	2.56	8.51	24.8	3.18
W/U	20/07/99	5.89	7.30	0.41	4.41	33	12482	1694	5.10		53.8	10.65
S/O	20/07/99	31.72	7.80	0.03	0.02	7	75	23	0.53	0.72	3.2	1.25
S/L	21/07/99	8.55	7.60	0.38	8.89	31	12892	3319			49.4	6.92
S/U	21/07/99	18.50	7.65	0.31	3.26	11	5094	1186	4.87		38.2	4.99

Appendix 5.3. *Scrobicularia plana* and *Nereis diversicolor*: Relationships between metals in sediments and native animals from Irish Sea estuaries, July 1999 (r values which were statistically significant are shaded).

Scrobicularia plana

sediment treatment	Ag	As	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Se
Total (HNO3 digest)	0.9401	0.7036	0.4924	0.8474	0.7630	0.5871	0.1316	0.6103	-0.3803	0.5988	0.7664	0.6816
Total/Fe	0.9325	0.8874	0.4879	0.6955	0.8353	0.5558	na	0.5564	-0.4250	-0.5124	0.7999	0.6858
Total/organics	0.9018	0.8690	0.5480	0.6348	0.9669	0.5332	0.5074	0.6085	0.0902	0.5378	0.8705	0.7884
HCl	-0.1452	0.7235	0.5773	0.9088	0.7874	0.5751	0.1797	na	-0.3326	0.8185	0.7739	na
HCl/Fe	-0.5437	0.7990	0.7240	0.8256	0.8261	0.5222	na	na	-0.2570	0.8128	0.8295	na
1MAmAc	0.5404	na	0.0042	0.9182	0.8143	-0.7559	-0.2468	na	-0.0681	0.5850	0.7650	na

Nereis diversicolor

sediment treatment	Ag	As	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Se
Total (HNO3 digest)	0.4384	0.8319	-0.1977	0.6083	0.3815	0.5869	0.3485	0.5842	-0.0149	0.2502	0.9335	0.9762
Total/Fe	0.5697	0.8965	-0.1530	0.2223	0.4656	0.6152	na	0.6609	0.1701	-0.1936	0.9473	0.9492
Total/organics	0.6600	0.8275	-0.1433	0.7884	0.6280	0.6280	-0.3559	0.6615	0.0361	0.7515	0.9654	0.9096
HCl	0.6269	0.9061	-0.2333	0.8591	0.4405	0.6128	0.2728	na	-0.0161	0.4613	0.9391	na
HCl/Fe	0.7232	0.8587	-0.2350	0.8462	0.5208	0.6628	na	na	0.0895	0.4908	0.9518	na
1MAmAc	0.4185	na	0.0928	0.6378	0.5377	-0.0086	0.6239	na	-0.4401	0.0968	0.9191	na

Marked correlations are significant at $p < .05$

Appendix. 5.4. *Scrobicularia plana.* Irish Sea cores in which metal uptake in clams was statistically significant (P<0.05) following 6 months exposure in the mesocosm. Mersey (M), Ribble (R), Wyre (W) and Solway (S) sediments (/U,/L,- upper and lower estuarine sites).

Ag	Cd	Co	Cu	Cr	Fe	Hg	Mn	Ni	Pb	Se
R/U	none	M/U W/U	none	W/U	W/L	M/L R/U, R/L	W/U	R/U	M/U W/U	none

Appendix 5.5. *Turritella communis.* Irish Sea core locations in which metal uptake in snails was significant (relative to Rame and *outer Solway baselines: P<0.05) following 6 months exposure in the mesocosm. Mersey (M), Ribble (R), Wyre (W) and Solway (S) sediments (/U,/L,/O, - upper, lower and offshore sites).

Ag	Cd	Co	Cu	Cr	Fe	Hg	Mn	Ni	Pb	Se	Zn
none	M/L, M/O R/U, R/L, R/O W/U,WL,W/O S/U,S/L,S/O	M/O S/U	S/U	M/L,M/O* R/O*	M/L,M/O* R/O*	M/U,M/L,M/O R/U, R/L, R/O W/L S/U,S/L,S/O	M/U,M/L,M/O R/L, R/O W/U S/U,S/O	R/U S/U	none	M/L,M/O R/L, R/O W/L S/L	M/L,M/O R/L, R/O W/U S/U,S/L,

Appendix 5.5. *Scrobicularia plana* and *Turritella communis*: Relationships between metals in sediments and animals transplanted to cores from Irish Sea estuaries in the mesocosm (r values which were statistically significant are shaded).

Scrobicularia plana [1]

sediment treatment	Ag	As	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Se
Total (HNO3 digest)	0.2547	na	0.4242	-0.1394	0.5278	0.0462	0.3063	0.1247	-0.0104	-0.4906	0.2940	-0.127
Total/Fe	0.1992	na	0.4720	-0.1851	0.4389	-0.0045	na	0.1195	-0.2092	-0.2818	0.3692	0.0561
Total/organics	0.2057	na	0.4918	-0.1586	0.4518	-0.0226	0.2148	0.1223	-0.1640	-0.3421	0.3600	0.0737
HCl	0.3896	na	0.4073	-0.0783	0.5313	0.0503	0.1725	na	-0.0767	-0.4452	0.2975	na
HCl/Fe	0.2896	na	0.4080	-0.0892	0.5124	0.0368	na	na	-0.2428	-0.4673	0.3197	na
1MAmAc	0.3120	na	0.1855	0.2960	0.0142	-0.0538	0.0236	na	-0.1672	-0.0471	0.0051	na

Turritella communis [2]

sediment treatment	Ag	As	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Se
Total (HNO3 digest)	-0.3953	na	-0.3315	-0.1412	0.5280	-0.0163	0.1197	-0.0162	-0.1501	-0.0954	0.3497	-0.129
Total/Fe	-0.3538	na	-0.3246	-0.0104	0.5609	-0.0872	na	-0.0262	0.2965	0.3304	0.3636	-0.222
Total/organics	-0.3513	na	-0.3158	-0.0403	0.2334	-0.0186	-0.0687	-0.0235	0.3335	0.0809	0.4380	-0.142
HCl	-0.2425	na	-0.3197	-0.0925	0.5909	-0.0166	0.0934	na	-0.0850	-0.1397	0.3580	na
HCl/Fe	-0.1332	na	-0.1791	-0.1129	0.6001	-0.0722	na	na	0.3787	-0.1279	0.3869	na
1MAmAc	-0.1777	na	-0.3617	-0.2868	0.0300	-0.0396	-0.0714	na	0.0768	-0.0799	0.2445	na

Marked correlations are significant at $p < .05$
na - not analysed

[1] *Scrobicularia* originally from Appledore, N.Devon

[2] *Turritella* originally from off rame head, S. Cornwall