The Dispersal, Storage and Remobilisation of Heavy Metals in the River Aire Contaminated by Urban and Industrial Wastes

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The candidate confirms that the work submitted is her own and that appropriate credit has been given where reference has been made to the work of others.

ABSTRACT

Industrial and urban activities in the Leeds catchment of the River Aire have caused the widespread dispersal and contamination by a variety of pollutants, including heavy metals. This contamination is reflected by enhanced metal concentrations in the sediments and soils of the river and floodplain. The cycling of sediment and associated metals in the fluvial environment is highly related to hydrological, geomorphological and chemical phenomena. The main research objective is to investigate quantitatively the dispersal, storage and remobilisation of heavy metals in the Leeds reach of the River Aire.

A wide variety of relevant processes are analysed. Metal pollution studies have often neglected urban and industrial catchments, where sources of pollutants to the river channel are diverse. In the past, heavy metals have entered the river from industrial activities, sewage disposal and coal combustion. The main present source of metals is the disposal of domestic and industrial effluent from sewage treatment works.

The fluvial dispersal of wastes has caused enhanced concentrations of heavy metals in aquatic sediment and floodplain soils. This results in long-term storage of metals in river corridors and poses problems as sediments act as a source of contaminants long after pollution of the fluvial system has been abated. The pollution problem is most severe immediately downstream of sewage treatment works, through the city centre, where traffic and industrial density is greatest and where floodplains are frequently inundated with floodwaters.

Heavy metals are not necessarily permanently fixed by the sediment and can be remobilised through mechanical, chemical and biological processes, affecting surface and groundwater quality and plant animal and human health. However, it is not the total amount of a metal stored in sediment, but how it is actually bound that is important in assessing its environmental impact. Results suggest that a significant proportion of each metal is held in a potentially mobile and bioavailable form, particularly cadmium.

The data collected is used to compile mass budgets of sediments and associated metals for the alluvial area of the River Aire in Leeds.

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CHAPTER 1

INTRODUCTION & AIMS

1.1 Background

Research into heavy metals has increased over the last three decades. Studies have indicated that many areas near urban and industrial complexes (e.g. Attrill and Thomes, 1995; Stigliani et al., 1993), metalliferous mines (e.g. Bradley and Cox, 1987; Lewin and Macklin, 1987) or major road systems (e.g. Flanagan et al., 1980; Page and Ganje, 1970) contain anomalously high concentrations of these elements. In particular, soils and sediments in such regions have been polluted from a wide range of sources with lead, cadmium, mercury and arsenic and other heavy metals. Nriagu (1988), suggested that a 'silent epidemic of environmental poisoning' may be occurring from the increasing amounts of metals wasted into the biosphere. The mining, manufacture and disposal of metals and metal containing materials will inevitably cause environmental pollution. The behaviour of constantly changing natural transport systems such as water and sediment flows, provide the key to understanding the ultimate geographic disposition of the metal, because almost all heavy metals released into the environment are ultimately attached to soil and sediment particles (Graf, 1994).

It is important to realise that soil and sediment act as both a source and a sink for heavy metal contaminants. Sediment and associated heavy metals do not simply enter river systems and move directly to seas, oceans or reservoirs. Instead many of them are stored internally in channel sediments and on floodplains; thereby reducing the amount ouput by the system. Such budgets require information about water and sediment fluxes over large areas, highly detailed and expensive data to obtain, hence attempts to construct mass budgets of heavy metals for river systems have been uncommon.

1.2 Heavy Metals as a Problem in Sediment, Soil & Water

Industrial and urban activities have caused the widespread dispersal of heavy metals in river systems. When sediments and attached heavy metals become incorporated within one of the fluvial storage compartments of the river system, they have not entered a static environment. The subsequent cycling of sediments and associated metals in a fluvial environment is highly related to hydrological, geomorphological and chemical phenomena (Graf, 1985; Salomons and Förstner, 1984). After deposition, sediments and metals may be remobilised through mechanical erosion, from the channel bed or banks (Lewin et al., 1977; Marron, 1989). In addition, within the sediment reservoirs, chemical processes may cause the metals to migrate between the various storage compartments, possibly causing the metal to enter ambient waters and biota (Chester, 1987). Remobilised metals may then be transported as clastic sediments or solutes to be deposited or precipitated in a range of sedimentary environments, both within the floodplain domain and river domain (Lewin et al., 1977). The interaction of these phenomena result in a dynamic spatial distribution of heavy metals within the alluvial area.

The study area covers the catchment of the River Aire in Leeds Metropolitan District. The river has had a long history of industrial and urban pollution and is one of the largest suppliers of pollutants to the Humber Estuary (Robson and Neal, 1997). The fluvial dispersal of wastes has caused enhanced concentrations of heavy metals in aquatic sediments and floodplain soils in the alluvial area of the River Aire. These metals may affect the health of plants and animals that inhabit the riparian areas and are of great importance with regard to both human toxicology and agricultural productivity. Contaminated sediments may be reworked and ultimately discharged into the river, becoming a secondary source of pollution, which implies that contamination of the fluvial system may continue even after the original polluting source is extinguished.

1.3 Research Aims

The main objective of this study is to investigate quantitatively the dispersal, storage and remobilisation of heavy metals in the River Aire in Leeds. An attempt is made to study a wide variety of relevant processes and to analyse their interactions within the complex body of a fluvial system. Eventually, the data collected and knowledge obtained may be used to compile mass budgets of sediment and associated heavy metals in the Leeds reach of the Aire corridor. Within this context, the research aims are outlined below.

(1) To identify the historic and present sources of heavy metal contaminants.
(2) To establish the degree, pattern and storage of metal contamination in the alluvial valley floor in surficial and subsurface soils and in both historical and current sediments.
(3) To analyse the metal associations in floodplain soils and aquatic sediments.
(4) To analyse the hydrological factors that govern the mechanisms of metal transport and quantify transport rates of sediments and sediment-associated and dissolved heavy metals.
(5) To determine the effects of floods on the redistribution of heavy metals, through transport of suspended sediments and the potential for remobilisation from floodplain soils.
(6) To assess the environmental implications for sustainability of enhanced metal levels in the sediments, soils and surface waters of this fluvial system.

The identification of historical and present sources of heavy metals is crucial to characterising a river's past and present water and sediment quality and for predicting future trends. This knowledge may provide insight into the current and potential availability of heavy metals for cycling in this fluvial system. The pollution levels within the alluvial area may provide a quantitative estimate of the total amount of heavy metals in storage. To assess their environmental impact and their potential for remobilisation, it is necessary to know how the metals are stored within the sediment and soil.

1.4 Scope of Thesis

The thesis includes ten chapters. Chapter 1 serves as an introduction to the field of study and outlines the research aims. Before the research aims are addressed, in order to place the contribution of the current work into context, a background to heavy metals in the fluvial environment is provided in Chapter 2. A knowledge of the dynamics of transportation, deposition and remobilisation is essential for the prediction of the fate of sediment-bound heavy metals in the fluvial system, as is, a proper understanding of the interactions between sediment and heavy metals. Chapter 3 surveys heavy metals in the UK environment, including the Leeds atmosphere and discusses detailed aspects of the metals investigated within this research programme. Chapter 4 describes the field area studied, both in specific detail about the River Aire and its catchment characteristics and more generally, with other rivers, as a tributary of the River Ouse. The historical development of Leeds and the River Aire is discussed. In the remainder of Chapter 4, past and present sources of heavy metal pollution are examined. Methods used in field and laboratory investigations are outlined in Chapter 5, concerned with methods of collection and analysing contemporary within channel and river bed sediments, suspended and core sediments and floodplain surface and subsurface soils.

Chapters 6, 7 and 8 present analyses of heavy metal levels in current and historical soil and sediment. Chapter 9 uses all the data collected and knowledge obtained to compile mass balances of sediment and heavy metals in the alluvial area of the River Aire in Leeds.

Chapter 10 concludes the study and addresses the environmental hazards caused by enhanced levels of heavy metals in sediments, soils and surface waters in a sustainability context. Application of the research findings to other river catchments is considered and long-term scenarios for problems of heavy metals in soil and sediment are explored, with respect to future environmental changes. Finally, recommendations for further research are made to address the problems encountered and insights gained from the current study of heavy metal pollution in the River Aire catchment.

The Appendices include additional tables and data not presented in the main body of the text.

1.5 Summary

Information about the geographic distribution and long-term storage of heavy metals in channel and floodplain environments is of paramount importance for safeguarding surface and groundwater quality and for protecting plant, animal and human health. Focusing on sediment-bound metals and contaminant movement and storage, a multiscale approach is used to evaluate the spatial patterns and changes over time of heavy metal pollution in this fluvial environment. Budgets of sediments and heavy metals are compiled and an attempt is made to estimate the environmental implications resulting from enhanced levels of heavy metals in sediments, soils and surface waters.

CHAPTER 2

HEAVY METALS IN THE FLUVIAL ENVIRONMENT

2.1 Introduction

Human activities may directly or indirectly change natural water quality. It is a well known fact that most rivers in the World with highly populated drainage areas are contaminated, partly through the effects of dispersal of wastes, by a variety of pollutants. The most prevalent of all contaminants are heavy metals. This contamination is reflected by elevated levels of metals in the sediments of rivers and floodplains. The importance of sediment in river systems as carriers, long-term stores and secondary sources of metal pollutants is generally well appreciated (Macklin and Klimek, 1992). Soils and sediments are the ultimate sink for metals in the terrestrial environment (Nriagu, 1988) and fluvial processes are the principal mechanism responsible for their transportation and redistribution on the land surface of the Earth (Graf, 1990).

Water quality is the most immediate concern in river systems, because of its use for human consumption. However, river sediment generally contains much higher concentrations of heavy metal pollutants than does water (Graf, 1994). Sediments can reflect the current quality of the system and also the historical development of certain hydrological and chemical parameters (Salomons and Förstner, 1984). Depending on environmental conditions, sediments are a sink or a source for heavy metals in the fluvial system. Heavy metals which are incorporated within the soils and sediments in the floodplain domain have comparatively long environmental residence times which can be of the order of thousands of years (Leopold et al., 1964) or more. This accumulation of contaminants poses problems because the sediments act as a source of pollutants long after pollution of the fluvial system has been abated (Rang et al., 1987). Pollutants entering this slow and complex process of fluvial transport may not only cause immediate damage to aquatic systems, but by being retained in alluvial soils can pose long-term problems. Floodplains therefore act as a geochemical sink in which metals are not necessarily fixed permanently by the sediment, but may be recycled via mechanical, biological and chemical processes, both within the sedimentary compartment and also back into the water column.

The River Aire has long been an industrial river and the gratuitous dumping of waste that started with the Industrial Revolution in the nineteenth century is unacceptable in these environmentally conscious times (Painter, 1994). This contaminant 'legacy' is still present in floodplain sediments (Rang and Schouten, 1989). Particularly since the Second World War, when little was known about the possible deleterious effects of certain waste substances, the use of metals has rapidly grown. Consequently, the extent and severity of metal contamination in the environment has also increased. The scale of the problem has changed from local or regional in the late nineteenth century to continental and global in the 1990s, as shown by heavy metal contamination in remote polar regions (Wolff and Peel, 1985).

The protracted environmental residence time (typically ranging from 100 - 1000 years) of toxic heavy metals in floodplain sediments, frequently results in enduring effects upon the quality of aquatic systems (Macklin, 1992). The possibility of biological, chemical or physical remobilisation, as well as their persistence and bioaccumulation in plants and animals, are some of the most significant effects of metal contamination and engenders them with a greater potential for global distribution and global effect (Macklin, 1992). Studies of the channel and floodplain sediment system therefore assume some considerable importance, not only for quantifying fluxes and storage of sediment-associated metals, but additionally for safeguarding surface and groundwater quality and for protecting plant, animal and human health. Effective environmental protection strategies in river basins affected by metal pollution can only be devised with a knowledge and understanding of short and long-term fluvial sediment transport and storage processes (Macklin, 1996). Therefore, to predict the long-term impact of heavy metals on the fluvial system account must be made of the incorporation of metalliferous sediments into floodplains (Bradley, 1987). Which in many river systems, may now be functioning as a major non-point source of sediment-associated metal contaminants.

2.2 Sources & Background Levels

Both natural and human activities introduce heavy metals into the environment. General factors which influence the extent and degree of such contamination relate to their dispersion. Individual particles may be dispersed on either a wide scale from diffuse sources such as vehicle emissions or on a localised scale from point sources such as a metal works. Dispersion may be in the form of: (a) atmospheric gases and particulate materials; (b) liquid effluents from factories and sewage works; (c) *in situ* site contamination from operational activities and from disposal of waste products. Förstner and Wittmann (1981) identified five sources from which metals may enter the fluvial system:

1. from parent material by geological weathering;
2. release of material during the industrial processing of ores;
3. release during industrial manufacturing which employs metals;
4. metals leached from garbage and solid waste dumps; and
5. from animal and human excretions which contain heavy metals.

With the exception of parent material, all are anthropogenic in nature. Soil parent material is the source of background concentrations. Enrichments on this background occur in zones of mineralisation and from human activity which greatly accelerates the cycling of metals through the environment. It is generally found that human activity is the primary source leading to elevated levels of metals in sediments.

Several factors account for the emergence of heavy metal contamination as an important ecological problem. First and foremost, modern technology requires the use of these elements in much larger quantities than in the past. Contaminated aerosol or particulates may, for example, be released from smelters (Harris, 1981); mine spoil (Davies and White, 1981); automobile exhausts (Ward et al., 1974);

agricultural sources such as fertilisers and pesticides (Wolfenden, 1977); and urban areas (Ellis, 1975; 1986). Inevitably many rivers have been contaminated with heavy metals.

Of particular interest are contaminants released into the fluvial system directly or indirectly from urban, industrial and mining wastes. Sources of these wastes are diverse. For example, mineralised zones when economically viable, are mined to retrieve and process the ore. This in turn leads to disposal of tailings, discharge of effluents and possibly smelting operations which result in atmospheric pollution (Rybicka, 1989).

Urban development, coupled with the presence of industrial activities within urban areas, leads to varying degrees of river and soil contamination with one or more materials (Thornton, 1990). An attempt to produce an inventory of worldwide emissions from industrial and domestic sources suggests that soils are receiving large quantities of metals from a variety of industrial wastes, the disposal of ash residues from coal combustion and the general wastage of commercial products on land (Nriagu and Pacyna, 1988). These authors calculate that if the total metal inputs were disposed uniformly worldwide, annual rates of deposition would vary from 1 g/ha for cadmium and about 50 g for lead, copper and chromium and over 65 g for zinc. Sewer overflows, waste discharge and rubbish dumping introduce many of the characteristics of urban sediments. However, urban runoff is now considered to be a serious pollution problem in itself, due to its ability to pick up pollutants (Pain, 1993). Precipitation over urban catchments washes down particulate matter, gases, etc., produced from residential, commercial and industrial premises and processes. Street surface runoff collects additional metal loadings from animal wastes, leaves, grass clippings, fertilizers, engine oils, detergents, combustion-by products as well as miscellaneous urban litter (Ellis, 1975). Thus producing a runoff which typically contains significant loadings of heavy metals amongst other pollutants. The complex nature of urban and industrial areas and there many uses present problems in assessing the extent and degree of contamination.

2.3 Interactions With Sediments & Soils

Soils and sediments from the perspective of this study refer to specific environmental components. Soils are surface materials whose organic and inorganic components host living organisms. Soils may develop *in situ* as the result of the weathering of bedrock or they may develop on materials that have been transported and deposited in accumulations. In contrast, sediments are unconsolidated surface materials that have been transported and deposited. Soils may receive contaminants from either atmospheric fallout or direct surface additions. Sediments may also receive such inputs, but may additionally contain contaminants collected elsewhere that have been subsequently transported along with the sediments. Sediments also have the property of sorting which occurs during transport.

Metals in rivers may exist in solution, suspension or bedload forms and within each it is likely that several different species exist. For example, a metal may be transported in solution as a simple ion, or it may be complexed with organic matter, or it may exist in crystalline form in the bedload or suspended sediment. The wide variety of metal species, their actions and interactions between chemical, physical and biological factors and the form the metal is transported in will all affect depositional processes.

Interactions between particulates and metals plays an important role in the regulation of dissolved metal concentrations (the most bioavailable). Moreover, adsorption is the first step in the ultimate removal of contaminants from surface water to the particulates (Salomons, 1987). In the aquatic system the biota not only accumulate contaminants, but are additionally involved in the cycling of contaminants.

The solid phases interacting with dissolved constituents in natural waters consist of a variety of components including clay minerals, carbonates, quartz, feldspar and organic solids. These components are usually coated with hydrous iron and manganese oxides and with organic substances which all contribute to the adsorption (removal) of heavy metals from surface waters. These coatings determine to a large extent their adsorption properties. On the other hand, constituents in water such as dissolved organic matter, anions (e.g. chloride, sulphate) may form complexes with the metals and keep them in solution (Salomons, 1987).

A number of sites on the surface of soils and sediments have been shown to be important for the binding of heavy metals. Sorption - desorption processes include surface exchange, diffusion exchange, precipitation and coprecipitation and complexation (Bradley, 1984). Once metals are incorporated in soils and sediments it is important, in order to assess their mobility and bioavailability to know how they are bound (speciation).

According to Leenaers (1989) the following group of metal associations in solid substances are important.

1. **Incorporation in crystalline minerals**

   Heavy metals may be present as the major element in a trace material. The mobility of trace elements in these forms is dependent mainly on simple solubility and solution chemistry or on physical processes transporting the grains (Rose et al., 1979).

2. **Metal precipitation**

   Heavy metals may be incorporated in precipitates of primarily hydroxides, sulphides and carbonates.

3. **Cation exchange and adsorption**

   A number of sediment forming materials with a large surface area - particularly clay minerals, fresh precipitated iron hydroxides, amorphous silicic acids and organic substances - are capable of adsorbing cations and releasing equivalent amounts of other cations by cation exchange.

4. **Sorption onto clay minerals**

   Clay minerals can act as significant conductors and concentrators of heavy metals in solid substances. The major role of clay minerals as metal concentrators is to act as mechanical substrates for the precipitation and flocculation of organic matter and secondary minerals (e.g. hydrous Fe and Mn oxides). In other words the clays are coated with material that actually carries the concentration of heavy metals, rather than the clays themselves (Horowitz, 1985).

5. **Adsorption and coprecipitation on hydrous Fe and Mn oxides**

Hydrous Fe and Mn oxides have long been known to be excellent scavengers of heavy metals from solution (Förstner and Wittmann, 1981). These hydroxides and oxides readily absorb or coprecipitate cations and anions. Under reduced conditions the adsorbed heavy metals are readily mobilized. Accumulation of hydrous Fe and Mn oxides can therefore act as a major source of metals in both soils and natural waters.

6. **Associations with organic substances**

The affinity of heavy metals for organic substances and for the decomposition products is of great importance for the behaviour of trace substances in solid substances. Organic materials may be a significant component of soils but may be entirely absent from sediments. The ability to concentrate various metals appears to be related to a number of factors including large surface area, high cation exchange capacity, high negative surface charge and physical trapping (Horowitz, 1985).

Organic surfaces for metal adsorption could arise in three possible ways, (Hart, 1982):

1. from organisms such as bacteria and algae;
2. by the breakdown of plant and animal material and by the condensation of lower molecular weight organics; and
3. by lower molecular weight organic matter being sorbed onto clay or metal oxide substrates.

The trace metal adsorption capacity of organic matter is generally between that for metal oxides and clays (Guy and Charkabarti, 1976).

A general sequence of decreasing sorptive capacity for metals by fine grained solids has been provided by Guy et al. (1975):

hydrous Mn oxides > humic acids > hydrous Fe oxides > clay

Certain fractions may be enriched in several elements. Bradley and Cox (1990) found that a large proportion of copper was organically bound and much of the zinc was contained in the residual fraction. The exchangeable and surface oxide fractions were important for cadmium. The exchangeable and Fe and Mn oxide forms predominate for lead. Sequential extraction techniques are used to assess which fractions are dominant for a particular metal. This involves partitioning the solid material into specific fractions, to be extracted selectively using appropriate reagents.

2.4 Factors Affecting Geochemical Mobility

Geochemically, an element introduced into the fluvial system may by dissolved in solution or in one of the above forms. The dissolved form and exchangeable form are the mobile forms and are bioavailable; the other forms are immobile and sometimes become mobile and bioavailable with time.

Many chemical and physical factors affect a soil or sediments capacity to collect and concentrate heavy metals. In most aquatic systems concentrations of trace metals in suspended sediments and the top few centimeters of bottom sediment are far greater than concentrations of heavy metals dissolved in the water column (Horowitz, 1985). It is very difficult to predict the fate and behaviour of heavy metals, due to the inherent variability in the biological, chemical and physical properties of soil and sediment. These include:

Grain size distribution:

Grain size exercises a determining influence on the metal concentration of a soil or sediment (Förstner and Wittmann, 1981). Metals are not homogeneously distributed over the various grain size fractions. There is a very strong positive correlation between decreasing grain size and increasing metal concentration. This correlation results from numerous factors that are both physical and mineralogical. Clay sized particles have large surface areas relative to their mass. Thus clay particles provide the main sites for transport and deposition of inorganic constituents through chemical surface reactions. The main mechanism by which this occurs is adsorption. Trace metals therefore tend to be concentrated in the finer grain sizes of soils and both suspended and bottom sediments (Horowitz, 1985). In the silt and fine sand fractions, the metal concentration generally decreases as that fraction is dominated by quartz components with low metal contents. In the coarser fractions the presence of heavy minerals may cause the metal portion to increase once more (Salomons and Förstner, 1984). The fraction smaller than 63 μm is recommended by Förstner and Salomons (1980) for the following reasons:

1. heavy metals have been found to be mainly present in clay / silt particles;
2. this fraction is most nearly equivalent to the material carried in suspension;
3. sieving does not alter metal concentrations; and
4. numerous metal studies have already been performed on this size fraction allowing better comparison of results.

Cation exchange capacity (CEC):

In general, the higher the CEC of a soil or sediment the greater the amount of metal it can accept. The many different materials that are components of soils and sediments and have large surface areas. These include, clay minerals, iron hydroxides, manganese oxides and organic matter, which are capable of sorbing cations and releasing equivalent amounts of other cations. Evidence suggests that as grain size decreases and surface area increases, CEC increases (Horowitz, 1985).

pH:

A lowering of pH leads to the dissolution of carbonate and hydroxide minerals and as a result of hydrogen ion competition - to an increasing desorption of metal cations (Förstner, 1978). In general, the capacity of soil and sediment for binding most trace elements increases with increasing pH. Typically, the adsorption of metals increases from near nil to near 100 % as pH increases through a critical range 1 - 2 units wide (Benjamin and Leckie, 1981). This means that a small shift in pH in soil and surface waters causes a sharp increase or decrease in dissolved metal levels. The onset of the adsorption is characteristic for each metal. In soils and natural waters more than one heavy metal is present and competitive adsorption may take place.

Redox potential:

The water content of soils and sediments influences their capacity for heavy metals through biological or chemical redox reactions. Sulphides of elements such as cadmium, cobalt, nickel, lead, tin and zinc can form under reducing conditions. The sulphides of these elements are quite insoluble so that their mobility and phytoavailability are considerably less than one would expect under well-oxidised sediments. However, Fe and Mn are more soluble under reduced than under oxidised conditions.

Occurrence of synthetic complexing agents:

Significant impacts on remobilisation from polluted soils and sediments may result from the growing use of synthetic complexing agents in detergents which are replacing polyphosphates (Förstner, 1978). The extent of these effects depends on the concentration of the complexing agents, its pH, the mode of occurrence of heavy metals in the soil or sediment and on the competition from other cations.

2.5 Transport & Dispersal

Heavy metal contamination is a direct consequence of technological activities. It follows that the problem is worst where people congregate in towns and industrial areas. Many urban sources of pollution are of low intensity but their concentration makes urban pollution a serious matter (Davies, 1980). Heavy metals produced by industrial processes and urban centres reach land and water by travelling along three general pathways. These were classified into atmospheric, gravitational and mechanical and fluvial transport (Davies 1980).

Metals and their compounds may be released to the atmosphere as gases and particulates or as dusts from smelter stacks, ore stock piles and tailings or during transportation. They are carried by the wind and eventually fall to sink. The greatest proportion of heavy metals added to the atmosphere are from combustion of fossil fuel and the manufacture of metals (Williams et al., 1974). The pattern of ground contamination depends on the nature of the emitting source, the size and density of the particle and wind strength and direction. Ore smelting and refining has always been a notable cause of air pollution. The general conclusion that can be drawn from published reports (Davies, 1983; Little and Martin, 1972; Merry and Tiller, 1978) is that heavy metal contamination is most severe within a 3 km radius of the stack. This decreases exponentially with increasing distance from the smelting complex, until background soil levels are reached between 10 and 15 km. In addition, factories (Hutton and Symon, 1986); chemical plants (Stigliani et al., 1993); power stations (Wadge et al., 1986); and incinerators (Wadge and Hutton, 1987) may emit heavy metals. The pollution pattern conforms to that derived from smelters, i.e. much of the metals accumulated within 10 km of the stack and the spread is controlled by the direction of the prevailing winds.

Hence, land within urban areas is generally contaminated by heavy metals. Lead pollution along roads is a particular problem (Brown, 1992). Almost all the lead in the air comes from the exhaust gases of petrol engines (Page and Ganje, 1970). Maximum contamination is generally observed at 1.5 m from the road and is not usually discernible beyond about 50 m from the road (Ward et al., 1974). The controlling factors appeared to be traffic volume and prevailing wind direction.

The second pathway is through direct mechanical or gravitational effects on the soil. Solid materials such as mine refuse, animal slurries or sewage sludges can be dumped straight on to land or can tumble down from uphill mine waste (Davies, 1980). The most troublesome sources to control are those from agriculture (e.g. animal wastes, fertilisers, pesticides and in particular eroded soil). Soil may become enriched with hazardous heavy metals by the application of plant nutrients and crop protective measures. Sewage sludge is often used as a plant nutrient. The sludge may frequently contain heavy metals with toxic properties. These elements are released and become available for plant uptake when the sludge decomposes.

Finally, the most important and relevant pathway here is the drainage system. Drinking water is usually extracted from natural waters, such as rivers and lakes, which are frequently affected by human activity (e.g. factory effluent, water draining from spoil and rubbish heaps). Hence, heavy metals may derive from a variety of sources within the catchment which may itself vary in the quantity and quality of its output. Metals may then be differentially transported in solution, suspension or bedload forms and deposited to produce patterns of dispersal that can be related directly to floodplain geomorphological processes and channel sedimentation styles (Lewin and Macklin, 1987; Macklin, 1996).

The nature and extent to which any element is present within aqueous and solid phases will depend upon the chemistry of the metal, the type of source area and the range of chemical (e.g. pH, redox potential), physical (e.g. particle size, discharge) and biological (e.g. microorganisms such as bacteria and algae) circumstances prevailing in fluvial systems. Thus the effects of these factors on wastes causes their dispersal downstream to vary in form, distribution and therefore concentration both at a point and spatially. Prediction of the fate of sediment-associated metals in the river environment therefore requires a full understanding of the dynamics of transportation, deposition and remobilisation (Leenaers, 1989).

Transport rates and patterns of dispersal of sediment-bound metals are controlled by four factors (Lewin and Macklin, 1987).

1. Hydraulic sorting according to differential particle density & size

The quantitative significance of suspended sediment in heavy metal transport is well established (Förstner and Wittmann, 1981; Hart, 1982). Data suggests that the suspended load comprises more than 90 % of the particulate load in a majority of rivers (Hadley et al., 1985). The finer particles that are carried in suspension have a greater surface area and the association of adsorbing substances like organic matter and iron hydroxides, with these small grain sizes, are therefore more likely to be associated with pollutants (De Groot et al., 1971) than the coarse particles transported as bedload.

Quantitative relationships between metal concentrations in fluvial sediments and distance downstream have been investigated at a number of sites (Lewin and Macklin, 1987; Wolfenden and Lewin, 1978). In many river systems metal levels tend to decline away from the point of emission and downstream deductions in metal concentration have been successfully approximated using a simple decay model of a linear, exponential or power function. Departures from modelled dispersion patterns have been used to indicate the relative importance of contaminated floodplain sediments as a source of heavy metals. Lewin et al. (1977) in mid-Wales, found that nineteenth century floodplain sediments were possibly the most active source of metals at that time.

In the past the transport and dispersal of sediment-bound heavy metals tended to be studied in relatively small streams with a single, well-defined point source (e.g. Bradley, 1982; Wolfenden and Lewin, 1978) However, in more recent times, larger more complex river systems with multiple metal input sites have been investigated (Leenaers, 1989; Macklin and Klimek, 1992).

2. Chemical sorption-desorption processes related to the formation of Fe / Mn oxides and organic complexes

In the River Tyne (Macklin and Dowsett, 1989) and the River Geul (Leenaers, 1989), fine-grained sediments deposited on floodplains by overbank flooding have shown that only a small proportion (< 10 %) of particulate-bound metals were in the form of original minerals. The majority of heavy metals were present as metal bearing Fe and Mn oxides found either as coatings on sand-size material or as discrete grains. It was generally found that as metal concentration decreased downstream away from the mining area, the proportion of metals in a potentially exchangeable and bioavailable form increased. Downstream dispersal patterns have been found to also reflect an evolutionary sequence in metalliferous mineralogy

(Hudson-Edwards et al., 1996). In which the thermodynamically unstable metal-bearing primary minerals oxidise to form secondary minerals which contain proportionately lower contents of metal than the original source mineral.

3. Mixing processes with additions of sediment from tributaries or from bank erosion, resulting in an increase or decrease of trunk river metal levels

In rivers where heavy metal concentration shows no overall upstream-downstream change and is not related to distance from source by a single exponential function. It has probably been enhanced by the mixing of clean sediment eroding from channel banks or immediately downstream of tributary confluences. In the River Puerco, following the failure of a uranium tailings pond, Graf (1990) found that metal concentrations alternately increased and decreased with metal levels. This was inversely related to unit stream power generated during the peak of the flood wave. Concentrations were also inversely related to the length of time that shear stress exceeded critical values during the passage of the floodwave. Where unit stream power was relatively high in the flood event, most sediments and heavy metals were likely to have been swept downstream and erosion occurs. Whereas when power was relatively low, deposition and high concentrations of heavy metals might prevail.

4. Floodplain deposition & storage

Sediment-associated metals follow the same transport pathways as any other particulate-bound element and therefore their deposition and storage patterns can be related directly to floodplain geomorphological processes and channel sedimentation styles (Lewin and Macklin, 1987; Macklin, 1992). This subject is considered in more detail in the next section.

2.6 Deposition & Storage

During transport, deposition and storage of pollutants takes place in the sediments of river channels and overbank on the floodplain. Alluvial rivers build a range of depositional forms. The most common depositional feature is the floodplain. Formed from a combination of within channel and overbank deposition, although many sedimentary forms are involved (Lewin and Wolfenden, 1978). Alluvial storage patterns relate to floodplain geomorphological processes and their rates of activity.

In British floodplains, patterns of metal storage arising from braided and meandering rivers and from low gradient systems, in which rivers have not changed their courses measurably since the first accurate surveys in the nineteenth century, differ considerably (Lewin et al., 1983). In braided (Lewin et al., 1983; Macklin and Lewin, 1989) and meandering (Davies and Lewin, 1974; Wolfenden and Lewin, 1978) systems, rivers actively migrate across their floodplains causing valley floors to be rapidly reworked. This results in considerable variability of metal concentrations across the floodplain, with metal levels changing abruptly between alluvial units of different age. In contrast, in rivers or reaches with relatively low rates of lateral migration, deposition of metals occurs during overbank floods when fine grained sediment of variable thickness is added across the entire floodplain (Bradley and Cox, 1990; Macklin, 1985). This pattern of dispersal produced metal concentrations, which showed no clear variation in levels across the floodplain, nor vertically in the sediment profile for the River Derwent, Derbyshire. However, in laterally stable reaches of the lower River South Tyne, Macklin (1988) found that with the exception of sites immediately adjacent to the present channel, metal values decrease with increasing distance from the river bank. These lateral variations in surface floodplain sediment metal concentrations in both rivers appear to relate primarily to the particular grain-size fractions with which metals are associated.

Fluctuating inputs of heavy metals to river systems, together with changes in inundation frequency and deposition rate, are commonly reflected in floodplain sequences by varying amounts of metals in vertical sediment profiles (Macklin et al., 1992; Rang and Schouten, 1989). Floodplains in general, and overbank sediments in particular, can contain an invaluable record of both natural geochemical patterns and those showing the influence of human activity (Macklin et al., 1994; Ridgway et al., 1995). By acting as a focus for deposition, particulate-bound contaminants can remain stored in these alluvial environments for periods of decades to centuries. Particularly in floodplains that are characterised by low rates of channel migration or those experiencing aggradation (Macklin, 1996). Marron (1987), found that at least a third of mine tailings discharged into the Belle Fourche River system, South Dakota, were stored in the floodplains.

Floodplains in many river basins of the World that have been affected by mining or industrial activity are now functioning as a major non-point source of sediment-associated metal contaminants. In the historically polluted River Vistula, Poland, (Macklin and Klimek, 1992) it was found that overbank sediments contaminated by past and present mining and industrial activities constituted the most important secondary source of metal pollutants. Similarly, Lewin et al. (1977) in mid-Wales concluded that nineteenth century floodplain sediments formed sources of metals (possibly the most active source at present), in addition to the still remaining waste tips, so that a continued input of metals is assured. Although since the early 1970s more stringent controls of effluent discharges to rivers in North America and Europe have resulted in reduced metal loads (Graf, 1994), none of these measures will have any effect on metals currently stored in alluvial sediments on valley floors. Yet, it can be anticipated, that in these and other historically polluted river systems the importance of contaminated floodplain sediments as a source of heavy metals is likely to increase significantly in coming years.

2.7 Remobilisation

Once a metal has become incorporated into a sediment or soil, it has not entered a static environment and particulate-bound metals can be remobilised if contaminated soil or sediment is disturbed, or if environmental conditions change. A metal may be considered to be 'potentially mobile' if it is stored in the non-residual fraction of a sediment.

Metals are slowly depleted from these environmental compartments by leaching and plant uptake (Macklin, 1992), natural processes (e.g. surface and bank erosion) and human induced changes in external parameters. These pollutants are then transported further downstream where they may leave the fluvial system or re-enter one of the storage compartments (Leenaers, 1989). The capacity of the soil to act as a geochemical sink implies that river pollution may continue long after the original polluting source is extinguished. Indeed, the fact that many historically metal contaminated floodplains are now themselves functioning as sources of river pollution is the most clear indication that they are rather 'leaky' sedimentary sinks (Macklin, 1996). Any increase in the rate at which metals are remobilised from polluted river sediments, could have serious environmental consequences.

The cycling of heavy metals in floodplains is controlled by both chemical and physical processes. Changes in the chemical environment, particularly pH and redox conditions, may frequently result in the alteration of element forms which can dramatically increase the solubility, mobility and bioavailability of sediment-based metals. For example, a rise or fall in floodplain watertable levels or acidification of soils, either through weathering or pedogenic processes or as a result of atmospheric pollution (Hudson-Edwards et al., *in press*).

Selective chemical extraction techniques in which operationally defined metal-associated sediment fractions are identified (Tessier et al., 1979) have provided very useful basic information in this context. Most notably the manner in which metals are stored in river sediments and how their mobility may change in respect to variations in the ambient physico-chemical environment (Chester, 1987). Despite the well documented analytical and interpretive problems (Guy et al., 1975; Rendell et al., 1980) that exist with selective chemical extraction techniques they do appear to mimic a general environmental mobility sequence of sediment-bound metals and give a reasonable indication of how they might behave should chemical conditions change. Information on the chemical partitioning of metals in floodplains may therefore be of considerable value in developing assessment and long-term containment strategies in polluted river basins.

The second principal mechanism whereby metals are reintroduced into rivers is by erosion of their beds and banks. In a dynamic fluvial environment, where the river channel rapidly migrates across its floodplain and during floods, contaminated streambank deposits are rapidly reworked resulting in high metal levels in suspended sediments. This may not only effect water quality but also be deposited on and contaminate floodplains further downstream. Significant river bed and bank erosion could result in large scale reworking of metal contaminated alluvium presently stored in floodplains and may have long lasting effects upon the quality of the aquatic system (Bradley and Cox, 1987; Lewin and Macklin, 1987; Marron, 1987).

2.8 Bioavailability

Since essential elements are only used by organisms in trace amounts and generally only occur in the environment in small concentrations, their occurrence in the organism does not exceed the level which allows the enzyme system to function without interference. This means that the concentration of essential trace elements are generally higher in the organism than in the water (Förstner and Wittmann, 1981). If there is too great an abundance of heavy metals, the metal content in the organism can be regulated by homeostatic control mechanisms. However, if the heavy metal concentration at the source of supply (e.g. water, food) is too high, the homeostatic mechanisms cease to function and the heavy metals act in an either acutely or chronically toxic manner. Thus, in the event of a resulting extended bioaccumulation of heavy metals, the organism may be damaged.

Because many biological systems exist naturally on the margins of metal toxicity, the physical and geochemical redistribution of toxic metals in aquatic environments by human activities has a strong potential to disrupt aquatic ecosystems. A number of environmental and biological processes may influence the accessibility of metals to organisms, affecting metal bioavailability. Our poor understanding of the processes controlling the biological availability of metals is a major impediment to defining, proving or predicting metal impacts in nature (Luoma, 1983).

The principles which control transport of most substances into biological tissues also apply to metal transport. The characteristics of the interface between the environment and an organism greatly influence the metal form that is accumulated. The concentration of free metal ions appears to be the most important control on metal uptake from solution of at least cadmium, copper, iron, manganese and zinc, by algae, invertebrates and fish (Luoma, 1983). The high concentration of metals in the food of most organisms, relative to water, suggests food should be an important vector of metal uptake. However, establishing the importance of metal uptake from food has proven to be difficult (Luoma, 1983). Differences in metal availability appear to occur among foods and also with prey species.

Sediments represent the most concentrated physical pool of metals in aquatic environments and are ingested by many types of aquatic organisms. The amounts of heavy metals concentrated here present a particular danger to organisms, especially to those living in the sediment and which enter the food chain (Luoma and Bryan, 1979). Although sediments are able to detoxify surface waters by adsorption / precipitation processes causing a decrease in the dissolved metal concentration, part of the metals in the sediments is bioavailable (Salomons, 1987). In studies with deposit-feeding clams, Luoma and Jenne (1977), found the differences in metal availability were related to the strength of metal binding to the particulates. More weakly bound metals were more available and more strongly bound metals were less available.

However, to assess the bioavailability of metals in sediments is difficult due to the complexity of the system. Geochemical and physiological processes are both important in determining metal availability. Exposure occurs in both food (particulate) and solution. Within each phase, the organism is exposed to a variety of physicochemical forms of each metal and each form may differ in its accessibility to the organism (Luoma, 1983).

A multitude of environmental processes may affect metal availability to aquatic organisms. Separating the relative importance of these processes could be the most important key to predicting metal availability in nature. The most important of these appear to be:

1. metal concentration in solution;
2. solute speciation of the metal;
3. metal concentration in food;
4. metal partitioning among ligands within food;
5. the influence of other cations;
6. temperature; and
7. pH and redox potential.

The impacts of heavy metals in aquatic environments cannot be assessed realistically without a greater understanding of the processes controlling biological availability.

The uptake of metals in plants and animals is well documented (Adriano, 1986; Alloway, 1995; Koeppe, 1977). Other than occupational exposure and inhalation, the primary route of entry of heavy metals is via ingestion of foods of plant and animal origin (figure 2.1). Thus it is important to understand the soil-plant-animal interrelationships (Nriagu, 1984). Plants can be considered as intermediate reservoirs through which metals from primary sources are transferred to other organisms. Livestock such as cattle and sheep ingest soil particles at a rate equal to 2 % and 14 % of their diet (Adriano, 1986). Also ingested are whatever foreign materials are present on foliage surfaces.

The factors affecting the amounts of metal absorbed by a plant are those controlling:

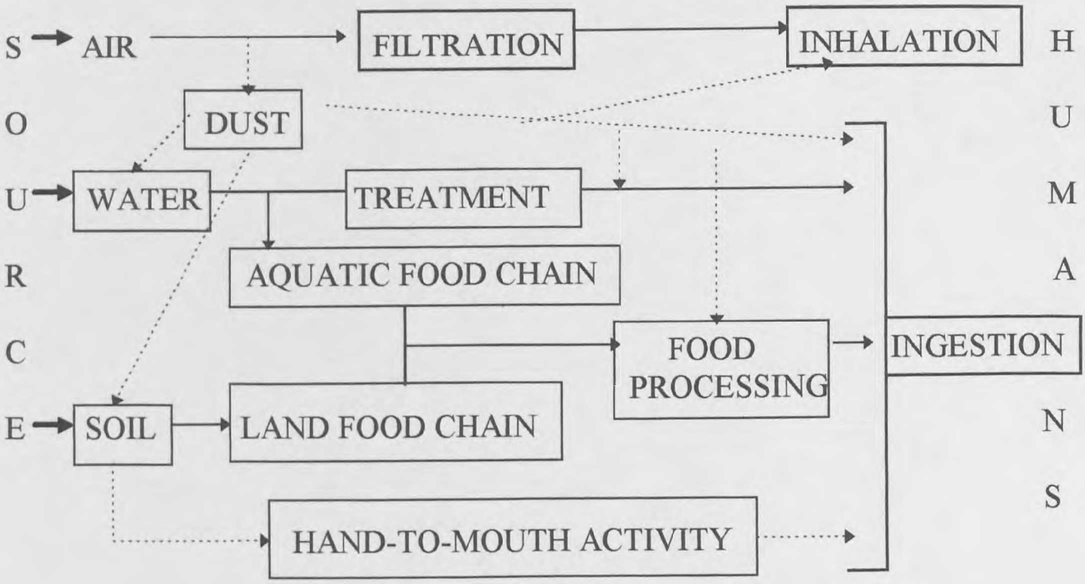
- the concentration and speciation of the metal in the soil solution;
- the movement of the metal from the bulk soil to the root surface;
- the transport of the metal from the root surface and into the root; and
- its translocation from the root to the shoot (Alloway, 1995).

Plant uptake of mobile ions present in the soil solution is largely determined by the total quantity of this ion in the soil. Absorption mechanisms vary for different metal ions, but ions which are absorbed into the root by the same mechanisms are likely to compete with each other. Relative differences in the uptake of metal ions between plant species and cultivars is genetically controlled and can be due to various factors, including:

- surface area of the root;
- root CEC;
- root exudates; and
- rate of evapotranspiration.

The last factor affects the mass flow of the soil solution in the vicinity of the root and thus the movement of ions to the root absorbing surface. Following root absorption, the extent to which elements are translocated within plants decreases in the order cadmium > zinc > copper > lead (Alloway, 1995).

Figure 2.1 - Pathways of trace elements to humans (*after Nriagu, 1984*)



In addition to root absorption plants can also derive significant amounts of some metals through foliar absorption. Foliar absorption of solutes depends on the plant species, its nutrient status, the thickness of its cuticle, the age of the leaf, the presence of stomata guard cells, the humidity at the leaf surface and the nature of the solutes.

Excessive concentrations of both essential and non-essential metals result in phytotoxicity. The relative toxicity of different metals to plants can vary with plant genotype and environmental conditions. The metals which, when present in excessive amounts are the most toxic to higher plants and microorganisms are mercury, copper, lead and cadmium. Food plants which tolerate relatively high concentrations of these potentially hazardous metals will probably be a greater health risk than those which are more sensitive and show definite symptoms of toxicity.

2.9 Past Research

Sediments and attached heavy metals that originate from the erosion of hillslopes or waste sites or waste discharges do not simply enter river systems and move directly to seas, oceans or reservoirs. Instead many of them are stored internally in channel sediments and on floodplains, thereby reducing the amount output by the system. However, attempts to construct mass budgets of heavy metals for entire river systems have been rare. Such budgets require detailed information about the water and sediment fluxes over large areas. There are, however, at least five regional budget studies of heavy metals.

2.9.1 Regional mass balance budget studies for heavy metals

Imhoff et al. (1980) constructed a heavy metal budget in a densely populated region for the large Ruhr River, which has a catchment area of 4488 km^2 and is a tributary to the Rhine. The Ruhr River is the main source of drinking and process water for a population of about 6 million and for industry. Among other industry, about 300 plating plants have settled in the Ruhr basin and these plants discharge a considerable amount of heavy metals, affecting metal concentration in the river water up to critical levels. 55 % of heavy metals (lead, copper, zinc, nickel, chromium and cadmium) in the Ruhr River are discharged from municipal and industrial waste water treatment plants; 45 % are of geochemical origin.

Graf (1985) constructed a mass balance for mercury in the Upper Colorado River basin. To explain the origins and transportation of 2200 kg of mercury that is annually deposited in lake Powell. Almost all the mercury in the lake is derived from weathering of natural source rocks in the lake's 279,000 km^2 drainage area and delivered in fluvial sediments. The mercury budget showed a definite spatial structure. Streams contributing large amounts of mercury to the lake either discharge large quantities of sediment or have extensive outcrops of particular geologic formations in the drainage areas. 40 % of the mean annual mercury input to the lakes, comes from a single tributary, the Green River. The Colorado River contributes 40 % of the water to the lake, but only 6 % of the mercury. Local Canyon Lands streams contribute only 9 % of the lake's water but 36 % of the mercury and 40 % of the sediment.

Sediment and soil sampling were used to investigate quantitatively the dispersal of metal mining wastes in the catchment of the River Geul, a 350 km^2 watershed, through Belgium and the Netherlands (Leenaers, 1989). A multiscale approach was used to evaluate the spatial patterns of metal pollution and to construct mass balances of sediments and heavy metals (cadmium, copper, lead and zinc) in this fluvial environment.

An investigation into floodplain storage of arsenic in a 121 km study reach of the Belle Fourche River in South Dakota, was derived using a sediment budget approach (Marron, 1992). Arsenic contaminated mine tailings were discharged into Whitewood Creek from 1876 - 1978 and deposited along its floodplains. About 13% of the discharged mine tailings were deposited in overbank sediments and filled abandoned meanders. About 29 % of the mine tailings were deposited along the Belle Fourche River, approximately 60 % of this material in overbank sediments. The remaining 40 % in point-bar sediments.

In northern New Mexico, Graf (1994), derived a regional budget for plutonium in the 71,700 km^2 drainage area of the Rio Grande system based on the construction of water and sediment budgets. Untreated plutonium waste was discharged into Los Alamos Canyon between 1945 and 1952. And through the processes of erosion and fluvial transport the plutonium moved into the Rio Grande.

Research into heavy metal contamination specifically from urban and industrial activity is lacking far behind that from metal mining. However, there are a number of studies concerned with these sources of metal pollutants. The major industrial uses of various heavy metals have been compiled by Dean et al. (1972), and are shown in table 2.1.

Table 2.1 - Heavy metals employed in major industries *(after Dean et al., 1972)*

	Cd	Cr	Cu	Hg	Pb	Ni	Zn
Pulp, paper mills, paperboard, building paper, board mills		*	*	*	*	*	*
Organic chemicals, petrochemicals	*	*		*	*		*
Alkalis, chlorine, inorganic chemicals	*	*		*	*		*
Fertilisers	*	*	*	*	*	*	*
Petroleum refining	*	*	*		*	*	*
Basic steel works foundries	*	*	*	*	*	*	*
Basic nonferrous metal works	*	*	*	*	*		*
Motor vehicles, aircraft-plating, finishing	*	*	*	*		*	
Flat glass, cement, asbestos products, etc.		*					
Textile mill products		*					
Leather tanning, finishing		*					
Steam generation power plants		*					

Helz (1976) in the northern half of Chesapeake Bay, Maryland, evaluated the relative importance of various human and natural sources of certain heavy metals. The principal source for chromium and copper was found to be direct industrial discharge. For cadmium it was municipal wastewater and atmospheric dust and rain for lead. There are many more sources of metal pollution resulting from industry which generally receive very little attention. Nevertheless they are still important. Klein et al. (1974), in an investigation conducted by the New York City wastewater authorities revealed 13 industrial activities discharging wastes rich in heavy metals (table 2.2).

Table 2.2 - Metals in industrial wastewaters (*after Klein et al., 1974*)

Industry	Average concentrations in µg/l				
	Cu	Cr	Ni	Zn	Cd
Meat processing	150	150	70	460	11
Fat rendering	220	210	280	3890	6
Fish processing	240	230	140	1590	14
Bakery	150	330	430	280	2
Miscellaneous foods	350	150	110	1100	6
Brewery	410	60	40	470	5
Soft drinks and flavourings	2040	180	220	2990	3
Ice cream	2700	50	110	780	31
Textile dyeing	37	820	250	500	30
Fur dressing and dyeing	7040	20,140	740	1730	115
Miscellaneous chemicals	160	280	100	800	27
Laundry	1700	1220	100	1750	134
Car wash	180	140	190	920	18

The River Rhine is a good example of a river into which large quantities of metals are discharged. Stigliani et al. (1993), studied heavy metal pollution from industrial and urban sources between 1950 and 1990 in the Rhine basin. The basin area has a very high density of industrial activity and is also an important for agriculture. Emissions to air of cadmium, lead and zinc in the basin peaked in the mid-to late 1960s and have declined substantially since. The reduction is due to the decreasing concentration of lead in petrol, the decline of iron and steel production and most important, the implementation of technologies for reducing atmospheric emissions. Significant declines have also been reported of aqueous emissions. Emissions from point sources, opposed to diffuse sources have declined more. Reasons include the installation of water pollution control equipment for compliance with increasingly stringent regulations and structural changes in the major polluting industry, i.e.

cleaner industrial processes replaced older technologies. Diffuse sources of emissions in the basin are dominated by storm runoff from urban and agricultural areas. Storm runoff discharges from impermeable surfaces may have a significant impact upon receiving rivers within urban catchments. There is now clear evidence (Ellis, 1986) to suggest this sediment derived from stormwater runoff constitutes a major source of river pollution within urban rivers and solids can be regarded as being of 'sewage quality' (Ellis, 1986). The main inputs of heavy metals on urban surfaces in the Rhine Basin originate from vehicle exhausts, tyre wear, corrosion of building materials and atmospheric deposition. In agricultural areas storm water runoff and erosion and seepage from natural geochemical deposits are the major sources of diffuse emissions. Concentrations of metals in wet deposition and storm runoff from agricultural areas have declined. In contrast, metal levels in eroded soil have increased despite the reductions in annual inputs of heavy metals to agricultural soils, because the absolute concentrations of the metals in the soils are still increasing.

Similarly, changes to the industrial structure or the implementation of pollution control technologies is evident in the floodplain sediments of the Rhine. Samples from the floodplain have high concentrations of copper, zinc, lead, cadmium and mercury (Salomons and De Groot, 1978). All heavy metals concentrations studied in the sediments from the Rhine have increased between 1920 and 1958. This rise in concentration continued for cadmium, copper and chromium between 1958 and 1975. However, the concentrations of lead, zinc and mercury, decreased and the concentrations of copper remained constant. The decline in sediment arsenic concentrations was noticeable and was probably caused by a ban on the use of arsenic containing pesticides.

Hutton and Symon (1986) estimated the quantities of cadmium, lead, mercury and arsenic entering the UK environment from human activity. Cadmium is mainly used in the UK as a protective plating for steel, in nickel-cadmium batteries and in certain pigments and stabilisers used in plastics. Electroplating and pigment manufacture account for the majority of the estimated 34 tyr^{-1} cadmium discharged to the UK sewage system. The disposal of pigmented plastics and electroplated items were also estimated to be important sources of cadmium to the municipal waste and steel scrap pathways with total inputs of 606 tyr^{-1} and 116 tyr^{-1} respectively. Lead is consumed for a variety of purposes but the use of alkyl lead compounds in petrol and the manufacture and disposal of lead-acid batteries are considered to result in the largest environmental discharges. An estimated 6790 tyr^{-1} alkyl lead was emitted to the atmosphere each year. The chlor-alkali industry is the principal user of mercury in the UK and estimated losses to the environment from this sector totalled 58 t in 1982. Primary battery manufacture accounts for the second largest quantity of mercury consumed. Other important uses of mercury include pesticides and dentistry. In 1982 12 t of mercury was applied to agricultural land in the form of pesticides. Of the 21 tyr^{-1} metallic mercury consumed by dentistry. It has been estimated that about 6 tyr^{-1} is lost to the UK sewage system from the 21 tyr^{-1}. About 5000 tyr^{-1} arsenic as arsenic trioxide is imported to the UK for conversion to other arsenic compounds. These processes result in an estimated discharge of 87 tyr^{-1} arsenic in manufacturing sludges. There are two major uses of arsenic in the UK: the manufacture of copper/chromium/arsenic (CCA) wood preservatives and the production of certain types of glass. Most of the remaining arsenic is re-exported. About 500 tyr^{-1} arsenic is consumed in the CCA treatment of timber of which at most 5 tyr^{-1} is retained in sludges. The disposal of treated timber after use results in an environmental discharge of about 13 t arsenic yr^{-1}.

The direction for future research and the major policy issues needing to be addressed relate to ensuring compatibility between environmental goals and important socioeconomic activities. Two major issues arise: the increasing importance of diffuse source emissions and how to reduce them and the environmental implications of large-scale changes in landuse and management strategies for mitigating potential impacts on soil and river water quality.

2.10 Conclusions

Metals which are released into the aquatic environment both from natural and anthropogenic sources enter the major physical and biogeochemical cycles which operate on the Earth's surface. In most cases, observed concentrations are higher (in some cases orders of magnitude) than background concentrations.

Thus, metals are derived from a variety of sources within certain catchments which may themselves vary in the quantity and quality of their output; metals may then be differentially transported in solution, suspension or bedload form and deposited to produce patterns of dispersal that have been controlled by a variety of chemical (e.g. pH), physical (e.g. discharge) and biological (e.g. bacteria) factors (Wolfenden and Lewin, 1978) and can be directly related to floodplain geomorphological processes and channel sedimentation styles (Lewin and Macklin, 1987; Macklin, 1992).

Sediments and soils are an important storage compartment for metals released into river systems. However, it is not the total amount of a metal which is present in a sediment or soil that is important in assessing its environmental impact. It also involves how it is stored within a specific component of the soil or sediment. Once a metal has become incorporated into a solid substance it has not entered a static environment and particulate-bound metals can be remobilised, causing migration between the various storage compartments within the reservoir or into surrounding waters and biota. This degree of mobility depends to a large extent on how a particular metal is stored within the various compartments which comprise the sediment. This in turn depends on complex, often inter-related factors. These sediment bound heavy metals can dissolve into the water column and may enter the food chain thus creating a significant environmental impact. Several relatively inert metals can degrade or react with others to form soluble and potentially toxic forms (e.g. conversion of elemental mercury to toxic methyl-mercury).

Hence, it is the protracted environmental residence time of heavy metals in sediments and soils that is one of the most significant aspects of metal contamination in river environments. To predict the long-term impact of heavy metals on the fluvial system account must be made of this incorporation of metalliferous sediments into floodplains (Bradley, 1987). Indeed, in many river systems the floodplain may now be functioning as a major non-point source of sediment-associated metal contaminants.

CHAPTER 3

HEAVY METALS IN THE UK ENVIRONMENT

3.1 Definitions & Toxicity

Davies (1980) defined heavy metals as metallic elements with a density greater than or equal to 6 g/cm^3. This is a rather arbitrary chosen parameter and therefore includes elements with widely different chemical properties. The significance of this definition is that all heavy metals behave similarly from the perspective of their physical transport in rivers (Graf, 1994). Although the metals may exhibit various characteristics of chemical mobility, they all adsorb onto sedimentary particles and these particles are likely to be distributed by physical processes.

There is growing interest and concern for these heavy metals in air, soil and water and their effects on humans. However, no organic life can develop and survive without the participation of metal ions (Förstner and Wittmann, 1981). Heavy metals become toxic if levels exceed those required for correct nutritional response (Venugopal and Luckey, 1975). The toxicity of heavy metals follow the general trend of: an undersupply leading to a deficiency; sufficient supply results in optimum conditions; and oversupply results in toxic effects and lethality in the end (Förstner and Wittmann, 1981). There is no doubt that all metals are potentially hazardous to living organisms and not necessarily at large exposure levels.

The heavy metals investigated in this study include arsenic, cadmium, copper, chromium, lead, mercury and zinc. Cadmium and arsenic are extremely poisonous, mercury, lead and chromium are moderately so and copper and zinc are relatively lower in toxicity (Brady, 1984). All these metals, according to Förstner and Wittmann's (1981) classification of metal toxicity, using the criteria of solubility and abundance, fit into the 'very toxic and relatively accessible' category.

Arsenic is a semi-metal element which has been described as having a ubiquitous distribution in nature (Dickerson, 1980). It is readily taken into animals and seafood, especially crustaceans, via food and water and can accumulate abnormal levels if their environment is contaminated. Copper and zinc fill essential roles in life processes, but only when present in small amounts. Lead and cadmium in plants and animals are, however, regarded with more suspicion, as they are generally believed to constitute cumulative poisons. Toxicity in man from the latter may result from inhalation of metal particulates or ingestion of foodstuffs (Shukla and Leland, 1973). Chromium is a relevant trace element of toxicological interest due to its potential role as an environmental pollutant. It has a wide range of industrial uses and originates in the environment from manufacturing industry effluents and drainage from mining activities. Evidence suggests that chromium compounds may be carcinogenic. Mercury in any form is toxic to humans and other living organisms. Methylmercury, the most toxic form, is many times more toxic and several times more available to man than its metallic or organic form (Crounse et al., 1983). Methylmercury is formed mainly by the methylation of mercury by the methanogenic bacteria which are widely distributed in the sediments of rivers. Humans absorb from ingested food practically all of the methylmercury present.

In an earlier era, uncontrolled industrial wastes were either deposited into or stored at a variety of land and water based disposal sites. There was a general feeling that nature could effectively treat or otherwise handle hazardous substances. By the end of the 1970s most industrialised nations were attempting to develop comprehensive rules and regulations regarding the use, storage and disposal of these wastes to protect air, soil and water quality and plant, animal and human health.

3.2 Heavy Metals in the UK Atmosphere

Metals in varying concentrations are a ubiquitous component of the lower atmosphere, occurring mainly in association with particulate matter. At sufficiently high concentrations in the atmosphere metals can be damaging to human health. Effects can result directly through inhalation, or indirectly, due to wet or dry deposition of metals to the ground and subsequent entry into drinking water and the food chain. The principal anthropogenic sources in the UK are fossil fuel combustion, metallurgical industries, vehicle emission, waste incineration and the cement and fertiliser industries (DOE, 1993). These source materials are volatilised at high temperatures and recondense on particulate matter before emission to the atmosphere. Mercury is an exception, it is emitted as a vapour and remains in the atmosphere principally in elemental form. The form of metals in particulate matter is varied and can be complex. They may occur in their elemental form or as organic and inorganic compounds. They may be present in different valancy states each with variable levels of reactivity and toxicity. Some species are readily soluble and others are not.

At present there is not a systematic and regularly maintained source inventory for heavy metals in the UK. However, estimates of atmospheric emissions in the UK have been analysed by Warren Spring Laboratory (McInnes, 1992). Data from this analysis are summarised in table 3.1.

Table 3.1 - UK emissions of heavy metals *(after DOE, 1993)*

	As		**Cd**		**Cr**		**Cu**		**Pb**		**Hg**		**Zn**		**Total**
	T	**%**	**T**	**%**	**T**	**%**	**T**	**%**	**T**	**%**	**T**	**%**	**T**	**%**	**T**
Non-ferrous metals	82	34	19	40	-	-	147	25	630	7	2	5	1620	47	2510
Fossil fuel combustion	130	54	12	26	222	20	246	42	150	2	16	43	230	7	1870
Iron/steel production	9	4	4	9	870	77	97	17	490	6	2	5	480	14	1971
Cement production	8	3	1	2	26	2	-	-	30	0.3	3	8	140	4	208
Waste incineration	1	0.4	11	23	16	1	88	15	170	2	5	14	970	28	1263
Petrol consumption	-	-	-	-	-	-	-	-	6800	83	-	-	-	-	6800
Chlor-alkali production	-	-	-	-	-	-	-	-	-	-	9	24	-	-	9
Miscellaneous	9	4	0.5	-	-	-	2	0.3	12	0.1	0.5	-	2	0.1	28
Total	9	4	0.5	-	-	-	2	0.3	12	0.1	0.5	-	2	0.1	28

(Reference years 1979, 1982, 1983) (Tonnes /annum)

Emissions of arsenic occur mainly from the combustion of fuels and the smelting of metals, particularly in the production of copper and nickel. It is present in the atmosphere in particulate form, mainly as inorganic arsenic. The largest single source of cadmium is the smelting of metals principally, copper, nickel and zinc.

Fossil fuel combustion also produces a significant proportion as does waste incineration. A smaller proportion arises from the production of iron and steel, solid waste disposal, battery manufacture and cement production. Chromium enters the atmosphere mainly from processes involved in the production of iron and steel, with a smaller proportion from the combustion of fossil fuels, mainly coal. Chromium occurs most commonly in its trivalent form which is insoluble and not highly toxic. However, the hexavalent form is often soluble, very toxic and carcinogenic (DOE, 1993). Copper and zinc originate mainly from smelting processes with smaller but not insignificant emissions arising from the burning of fossil fuels. Tyre wear is also a source of zinc. The dominant source of lead is petrol combustion. In January 1986 the permitted lead content of petrol was reduced from 0.40 g/l - 0.15 g/l and there has been the introduction of lead free petrol. As a result lead emissions have reduced substantially and it has been estimated that between 1984 and 1990 annual vehicle emissions in the UK decreased from 7.2 kt to 2.2 kt (Coleman et al., 1991). On the assumption that emissions from other sources have remained constant during that period, this still leaves petrol combustion as the major source, but other sources are now becoming more important. The main sources of mercury in the atmosphere are fossil fuel combustion, chlor-alkali processes and waste combustion. Of the metals discussed only lead has an Air Quality Standard, which is 2 $\mu g/m^3$ (annual mean value) for aerosol lead (DOE, 1993).

Long-term temporal variations in atmospheric metal concentrations are clearly illustrated by the Warren Spring Laboratory 'Multi-element Survey' data (McInnes, 1992) and will be discussed in the next section with particular reference to Leeds.

3.3 Heavy Metals in the Leeds Atmosphere

Warren Spring Laboratory operated a Multi-element Survey on the behalf of the Department of the Environment, beginning in 1976 with measurements at twenty monitoring sites at a range of UK urban locations. After two years the programme was reduced to cover five stations which had produced relatively high concentrations of the elements monitored during the first two years. Leeds was one of these sites. The objective of the survey was to provide data on concentrations and trends of a range of metals at urban locations. It covers the period 1976/7 to 1988/9 and is the longest time series of urban trace element concentration available in the UK.

The atmospheric concentration of a number of metals were routinely monitored at Market Buildings, Vicar Lane, near the centre of Leeds. The time series is incomplete since two sites operated during 1976 to 1978, one at Bramley from 1978 to 1981 and the station at Market Buildings only from 1981. The results are illustrated in table 3.2 and in figure 3.1.

Airborne concentrations of arsenic were generally found at concentrations below the limits of detection of the analytical method used. Over this period lead produced a statistically downward trend of 9.9 % per year. The other elements also produced statistically significant downward trends over the thirteen year period, with the exception of copper. This was due to its marked rise in annual concentration during 1986/7.

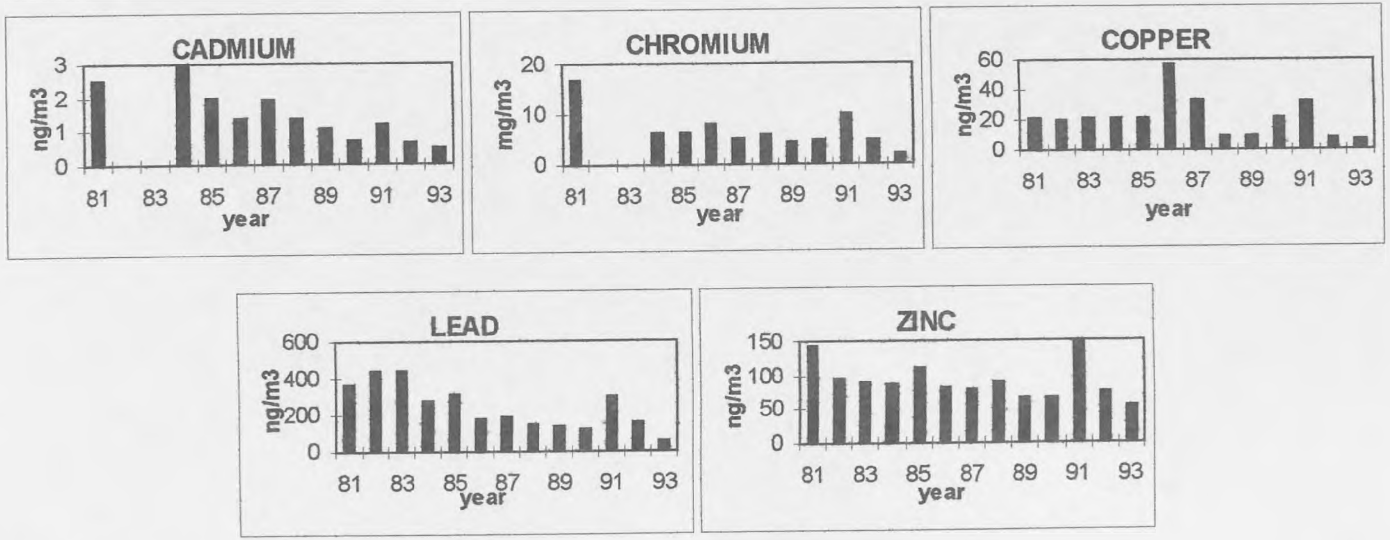
Over the five Warren Spring Laboratory 'Multi-element Survey' sites the key trends to emerge for metals other than lead, is one of a steady year by year fall between 1977 and the early to mid-1980s. This was followed by a levelling out. Lead however, is quite a different matter. Overall lead concentrations for all the five urban sites have reduced by 77 % over the years 1976/7 - 1988/9. Such reductions reflect initiatives on the reduction of the lead content of petrol, which is evident from the decline in atmospheric lead after 1985 (figure 3.1).

Emissions of some pollutants from many sources have decreased greatly for a variety of reasons, including the widespread use of natural gas for domestic heating, the introduction of less polluting industrial processes and the installation of abatement equipment on existing ones. However, at this stage it is difficult to determine whether the overall decline in metal levels is due to improvements in control technology / working practices or whether it is linked to the decline of

Table 3.2 - Multi-element survey, Leeds 1976/7 - 1988/9 *(after McInnes, 1992)*

Metal	Annual Averages, ng m^3													Overall % reduction
	1976/7	1977/8	1978/9	1979/80	1980/1	1981/2	1982/3	1983/4	1984/5	1985/6	1986/7	1987/8	1988/9	
As	6.5	7.1	6.1	-	-	7.0	12	-	-	-	-	-	-	-
Cd	7.1	4.9	4.4	4.5	2.7	2.5	1.7	2.8	2.6	2.6	1.5	3.2	3.5	51
Cr	18	19	9.5	-	-	16	12	16	5.6	6.4	7.8	7.1	6.9	62
Cu	54	42	38	28	26	23	21	20	22	24	47	35	18	67
Pb	820	610	650	620	480	500	430	380	370	350	220	200	190	77
Zn	860	820	440	270	200	200	120	110	100	130	120	160	170	80

Figure 3.1 - Multi-element survey, Leeds *(after Leeds Environment Department, 1994)*



(Monthly values averaged for the year)

manufacturing industry in the UK. However, the growth of road traffic has led to large increases in emissions from motor fuel combustion, despite continuing progress in reducing emission levels from individual vehicles (Brown, 1992).

3.4 Metals to be Investigated

The metals considered in the present study are discussed in relation to their general properties, production and uses, sources and affect on environmental media, in a context arising from either industrial or urban pollution. For arsenic, cadmium and mercury incidents of large scale human poisoning have occurred from industrial and other sources and these are discussed in the relevant sections.

3.4.1 Arsenic

Arsenic is considered in the study as it is a metalloid, i.e. it behaves similarly to other heavy metals, has similar sources and is of environmental concern.

3.4.1.1 General properties

Arsenic has a ubiquitous distribution in the environment and is found in detectable concentrations in all soils and nearly all other environmental matrices. It has been used in both homicidal and medicinal preparation for centuries. In nature arsenic occurs usually as a sulphide ore, an arsenate of a metal or as a natural occurring sulphide of arsenic (Dickerson, 1980). Elemental speciation of arsenic is of critical importance; inorganic arsenicals are far more toxic than organic forms. Arsenite (III) is the form that primarily causes industrial contamination of soils, water, air, plants, foods and animals.

3.4.1.2 Production & uses

Consumption of arsenic in the UK is estimated at < 1000 t/yr (Mance et al., 1984) although an additional 5000 t/yr is imported to the UK for conversion to other arsenic compounds, which are mainly re-exported (Hutton and Symon, 1986). There are two major uses of arsenic in the UK: the manufacture of copper/chromium/arsenic (CCA) wood preservatives and the production of certain types of glass. More recently certain arsenic compounds, for example, gallium arsenide have found applications in the semi-conductor industry. Arsenic pesticides, once a major use of arsenic, are now no longer used (Hutton and Symon, 1986).

3.4.1.3 Arsenic in environmental media, its sources & affects

Arsenic levels in uncontaminated non-treated soils seldom exceed 10 ppm (Adriano, 1986). However, soils are usually contaminated through the repeated use of arsenic pesticides. Arsenic is a labile element and can exist in several forms and oxidation states. Under moderately reducing conditions, such as flooded soils, arsenite (III) may be the dominant form. Arsenite is a common commercial form of arsenic and one of the most toxic. The reduced state of arsenic (III) has been reported to be 4 - 10 times more soluble in soils than the oxidised (V) state (Adriano, 1986). There is no evidence that arsenic is essential for plant growth. Crops have differing degrees of tolerance to soil arsenic. Members of the bean family, rice and most of the legumes are fairly sensitive to arsenic (Adriano, 1986). It is unlikely that arsenic can contribute to human toxicity through the plant-food chain as plants growing in soils with high arsenic, show reductions in growth and crop failure as the main consequences (Dickerson, 1980). Most arsenic pollution in water occurs by agricultural and industrial contamination. Air is contaminated primarily by smelting of metals, burning of coal, mixing and spraying of arsenical pesticides. Arsenic because of its widespread existence is taken into animals readily via food and water. All animals have some normal level of arsenic but can accumulate abnormal levels if their environment is contaminated. However, there is little if any evidence of concentration upward through the food chain. Seafood, especially crustaceans, can have high concentrations of arsenic if the aquatic environment is contaminated. However, marine invertebrate concentrate organic forms that are apparently non-toxic to man (Thornton, 1983). Chronic exposure to arsenic in drinking water is related not only to skin cancer but also to an increase in cancer deaths of many types (Thornton, 1983). Chronic arsenic poisoning occurs over many weeks and months. It is difficult to diagnose and therefore a favourite of poisoners.

3.4.1.4 Episodes of arsenic poisoning

A mass outbreak of arsenic poisoning in young children occurred in Japan in 1955. Intoxication stemmed from the consumption of dry milk powder which arsenic contaminated sodium phosphate had been added as a stabiliser. About 12,000 cases broke out, 130 of them fatal (Förstner and Wittmann, 1981). Medical follow-up fourteen years later showed persistent changes in the central nervous system including mental disturbances. Health problems related to the intake of drinking water containing high concentrations of arsenic have been encountered in some regions in Taiwan, Argentina and Chile. In Taiwan, peripheral vascular disorders with gangrene, skin changes and skin cancer have been reported (Moore and Ramamoorthy, 1984). Epidemiological studies on children living in the vicinity of a coal power plant in former Czechoslovakia, where coal used contained 1000 - 1500 g/t arsenic, showed respiratory symptoms and hearing loss (Förstner and Wittmann, 1981).

3.4.2 Cadmium

3.4.2.1 General properties

Cadmium is known as one of the most toxic metals (Förstner, 1978). There is no substantial evidence indicating its essentiality to humans and it has no known biological functions. For the general population exposure to cadmium is derived mainly from food, although relatively minor amounts can be taken up from drinking, smoking and through inhalation. Cadmium is generally toxic to both aquatic and terrestrial biota.

3.4.2.2 Production & uses

Cadmium is produced commercially as a by-product of the zinc industry. From the smelting and refining of zinc, cadmium is recovered at a rate of about 3.5 - 3.9 kg/t of primary zinc (Förstner, 1983). No ores are mined and processed exclusively to provide cadmium. Zinc refining and the smelting of iron and steel can lead to losses of cadmium to air, land and water. The use of cadmium has greatly increased since the mid-1940s and UK consumption fluctuated in the late 1980s between 1,100 and 1,400 t/yr. Several of cadmium's properties, for example, ductility, resistance to corrosion, gold solderability and ease and high rate of electrodeposition have resulted in one of its major uses being in electroplating on ferrous metals. Other electrical properties have resulted in applications in batteries and photoelectric cells (Fasset, 1980). Currently cadmium is mainly used in the UK as a protective plating for steel, in nickel-cadmium batteries and in certain pigments and stabilisers used in plastics (Hutton and Symon, 1986).

3.4.2.3 Sources

Because of its many uses significant amounts of cadmium may be released to the environment, dispersed from industrial processes, domestic activities, agricultural practices, the use and wear of cadmium containing goods and disposal of wastes (e.g. discarded manufactured articles, scrap metals, sewage sludge and incinerated rubbish) (DOE, 1980). Water, sewage and industrial effluents are an important route of entry of cadmium into rivers. Principle human-made sources to the atmosphere result from emissions from smelters; processing of various cadmium-containing metals; burning of plastics; and power generation from coal. The importance of atmospheric cadmium in relation to potential effects on humans, lies not so much on its direct inhalation as in the possible contribution to soil, water and vegetation through dry or wet deposition and ultimately to food (Fasset, 1980).

3.4.2.4 Cadmium in environmental media & its affects

A survey of soils in England and Wales revealed a median value of < 1.0 ppm cadmium, with a range of 0.08 - 10 ppm, (Archer, 1980). Cadmium is thought to be relatively immobile in soil, almost all cadmium remains in the surface layers (Thornton, 1983). The mobility and phytoavailability of cadmium largely depends on its chemical form and speciation in soil. Cadmium is not only available to plants from soil and other substrates, but is also known to be toxic to them at much lower concentrations than other metals like copper, lead and zinc (Adriano, 1986). Cadmium is a non-essential element in plant nutrition. In contaminated soil cadmium is readily taken up by roots and distributed throughout the plant.

Numerous studies add credentials to plants tendency to accumulate cadmium (Chaudri et al., 1995; MAFF, 1983). Radish tops can accumulate 5 ppm of cadmium when grown on soil containing 0.6 ppm cadmium (Lagerwerff, 1971). Soil pH appears to be the most important single soil property that determines cadmium availability to plants. In general, cadmium uptake by plants almost always increases with decreasing pH, possibly due to an increase in solubility and / or mobility of cadmium in the soil (Moore and Ramamoorthy, 1984). In spite of the availability of cadmium in soil to plants, only a small fraction of the cadmium pool is recovered by plants. One reason is that cadmium is phytotoxic up to certain levels which can drastically reduce plant yield (Fasset, 1980). The association of cadmium and zinc in geological deposits and the chemical similarity of the two elements carry over into biological systems (Leenaers, 1989). Cadmium and zinc appear to compete for certain organic ligands, accounting in part for the toxic effects of cadmium and the ameliorative effects of zinc on cadmium toxicity (Adriano, 1986). For this reason the ratio between these two elements within plant tissue is thought to be biologically important. Plant species exert marked differences with regard to cadmium uptake, accumulation and tolerance by plants. Sensitive crops include spinach, soy bean and field beans. Among edible parts, highest cadmium levels were found in lettuce and spinach leaves, followed by radish and carrots (Adriano, 1986). The main sources of cadmium in the diet are from atmospheric deposition, the use of fertilisers and sewage sludge on agricultural land and consumption of large quantities of contaminated shellfish. Cadmium appears to accumulate with age, especially in the kidney and liver (Förstner, 1980) and it is a suspect in the aetiology of cancer and cardiovascular diseases. Both of which are age related (Thornton, 1983). Cadmium in cigarettes is suspect in contributing to cigarette smoking related disorders (Fasset, 1980). Kidney-filter mechanisms may be affected. The high toxicity of cadmium may lead to hyper tension, disturbances of the metabolism of bones, damage to the central nervous system and it affects reproduction (Leenaers, 1989).

3.4.2.5 Episodes of cadmium poisoning

Chronic toxic effects from cadmium as normally encountered in food, water and air are largely unknown at present. The only report of such effects comes from Japan (Thornton, 1983). Medical interest in cadmium was sparked by reports of Itai-Itai disease (translates Ouch-Ouch). Itai-Itai disease was noted as a syndrome in Toyama, Japan, in 1947, characterised by bone pain, multiple bone fractures and renal loss of protein and large amounts of calcium which is presumed to be the result of bone resorption. Death resulted from kidney failure, autopsies showed high cadmium tissue concentrations. The cadmium was traced to rice and soy beans grown in local soils that were contaminated from a lead / zinc mining operation, 40 km upstream from the farming area. Those persons most affected were those who lived where soil cadmium levels were the highest and who had been the most stressed from malnutrition, multiple pregnancies or the menopause. Wastewater from floatation processes periodically entered the Jintsu River in the Toyama Prefacture, causing it to become turbid from metal contamination and the metals in the water were deposited in the soil, either through irrigation or flooding. It is estimated that approximately 100 deaths occurred due to the disease until the end of 1965 (Fasset, 1980).

3.4.3 Chromium

3.4.3.1 General properties

Chromium is omnipresent in the environment, found in varying concentrations in air, soil, water and all biological matter. Chromium can occur in any of the oxidation states from II to VI but it is not commonly found in oxidation states other than 0, III, VI, the III being the most stable. Of the two forms found in nature, Cr (III) and Cr (VI), the trivalent form is relatively benign and the hexavalent form is relatively toxic (Mance et al., 1984).

3.4.3.2 Production & uses

World production of chromium has been increasing since the mid-1960s. The only important chromium ore is chromite. UK consumption of chromite in 1980 was

91,000 t and with 59,000 t from ferrochrome gives a total gross consumption of 700,000 t chromium (Mance et al., 1984). Chromium is used in the manufacture of stainless steel and refractory steel, but has a wide range of other industrial uses and is therefore frequently found in industrial effluents and sewages. The most important chromium compound in industry is sodium dichromate from which virtually all other chromium compounds are produced (Adriano, 1986).

3.4.3.3 Sources

Important sources of chromium (VI) discharge are metal-plating and finishing industries, pigment production and cooling tower blow downs (Adriano, 1986). The major industrial discharges of chromium (III) arise from textile colouring, lithographic and photographic applications, glass manufacture, ceramics production and leather tanning. Various other industries including paper, fertiliser, steel manufacture, petroleum refining and wood preserving may also be sources of chromium in the environment (Mallett et al., 1992). It is very resistant to ordinary corrosive agents and is thus used extensively in the electroplating industry and in corrosion resistant steels (Moore and Ramamoorthy, 1984). The main sources in rivers is from effluents originating from manufacture industry and drainage from mining activities and also municipal wastes. Industrial effluents may contain chromium in both the trivalent and hexavalent form and both of these oxidation states are found in surface waters (Mallett et al., 1992).

3.4.3.4 Chromium in environmental media & its affects

The fate of chromium in the environment is more complex than that of other metals partly because of its more variable oxidation state. Berrow and Reaves (1984) reported a mean value of 50 ppm chromium for world soils. Most chromium in soils occurs probably as chromium III. If chromium VI is added it can be expected to rapidly reduce to chromium III. Sorption by organic matter and iron oxides was the most likely explanation for immobilisation of chromium III in some soils, since humic acids have a high affinity for chromium (Adriano, 1986). Chromium is not a significant contaminant of plant tissues except at site specific discharge points (Moore and Ramamoorthy, 1984). Toxicity to plants varies between species. It is also dependant on the pH of the media, which affects the solubility of the chromium forms and therefore its sorption by soil and its availability to plants. Oxidation state is very important in relation to its mobility and role in plant and human nutrition. The hexavalent form being more toxic and mobile in the soil environment than the trivalent form (Adriano, 1986). Chromium is not acutely toxic to humans. Chromium VI is more toxic because of its high rate of adsorption through intestinal tracts. Chromium VI has mutagenic properties (Moore and Ramamoorthy, 1984). Epidemiological studies have shown a positive relationship between occupational exposure to chromates and cancer incidence (Sittig, 1975). Risk of lung cancer appears greatest among ferrochromium, chromate and chrome pigment works. In water, chromium VI is generally more toxic to aquatic life than chromium III in short-term tests (Mallett et al., 1992). The mode of acutely lethal toxic action in fish has been suggested as disruption of the gill tissue at low pH values and disruption of the kidney tissue was noted at higher pH values. There is a clear tendency for toxicity to be increased under acidic conditions. The major contributors to airborne chromium are: ferrochrome production and handling; coal combustion; and chromium-steel production. Installation of fly ash removal devices on stack emissions have led to slight decreases in chromium concentrations in sediments and soils since 1968 (Adriano,1986).

3.4.4 Copper

3.4.4.1 General properties

Copper is one of the most important metals to humans. It is malleable, ductile and a good conductor of heat electricity, qualities which have been utilised for thousands of years. Copper occurs in the I and II oxidation states, but copper toxicity is thought to be largely attributable to the Cu^{2+} ion. (Adriano, 1986).

3.4.4.2 Production & uses

Copper production is mainly from low grade sulphide ores containing 2 % or less of the metal (Mance et al., 1984). Major world producers of copper are USA, Chile, Canada, USSR and Zambia. There are no primary copper mines in the UK.

In 1981, 186,000 t was produced in small amounts in the UK as by-products from other mining operations (Mance et al., 1984). In the UK, copper metal is widely used in the manufacture of various alloys with zinc, nickel and tin, in metal plating and in the production of copper wire and piping. Compounds of copper are used in a variety of manufacturing industries, for example, copper nitrate in plating and textile dyeing processes, copper chloride in the manufacture of glass and ceramics. Various copper compounds including cuprous oxide, cupric sulphate and cupric acetate are used as fungicides and in the manufacture of wood preserving agents, rayon and paint pigments.

3.4.4.3 Sources

Of these industries, foundries and metal plating operations are the major sources of copper bearing wastewaters. Non-point sources such as runoff from agricultural lands and urban areas can also make significant contributions to input of copper to surface waters (Nriagu, 1979).

3.4.4.4 Copper in environmental media & its affects

The average total content of British surface soils has been reported as 20 ppm (Swaine and Mitchell, 1960). Applied or deposited copper will persist in soil because it is strongly fixed by organic matter, oxides of Fe, Mn and Al and clay minerals. Thus it is one of the least mobile of the metals, thereby rendering it uniformly distributed in many soil profiles (Moore and Ramamoorthy, 1984). Copper tends to accumulate in the litter overlying the soil profile or within the top few cm of the soil profile. Organically-bound copper accounts for about 20 - 50 % of the total soil copper (Tessier et al., 1980). Copper is essential for normal plant nutrition. Plants require copper in very small amounts: 5 - 20 ppm in plant tissue is adequate for normal growth (Nriagu, 1979), while less than 4 ppm is considered deficient and in excess of 20 ppm is considered toxic (Adriano, 1986). The most common copper toxicity symptoms include reduced leaf growth, poorly developed and discoloured root system and leaf chlorosis (Robson and Reuter, 1981). The solubility, mobility and availability of copper to plants is largely dependent on soil pH. Copper availability is drastically reduced at soil pH above 7 and is most readily available below pH 6 and especially at pH's below 5 (Adriano, 1986). Copper solubility also dramatically decreases under reducing conditions (Nriagu, 1979). Copper is not acutely toxic to humans unless it is contained in high concentrations in drinking water. However, copper in water is exceedingly toxic to aquatic biota, only mercury is consistently more toxic (Moore and Ramamoorthy, 1984). Concentrations as low as 5 - 25 µg/l are lethal to some invertebrate and fish species (Mance et al., 1984). In contrast, copper has a much lower toxicity to mammalian consumers of water.

3.4.5 Lead

3.4.5.1 General properties

Lead is naturally present in small amounts in almost all environmental matrices (Thornton, 1983). Since it is used as a petrol additive, lead concentrations in the atmosphere have increased. Thus even remote terrestrial ecosystems are subject to lead enrichment. Industrialisation, therefore, has remarkably intensified human exposure to lead. Lead is non-essential but is present in all tissues and organs of mammals. In the industrial world lead enters the human body through food, water and air. Most of the absorbed lead is retained in the skeleton where it can remain immobilised and undetected for years (Leenaers, 1989). Lead is undeniably toxic at high levels of exposure (Thornton, 1983). The human health implications of lower levels of exposure are only now being defined (Nriagu, 1978). Lead has been known for centuries to be a cumulative metabolic poison (Förstner and Wittmann, 1981). Although occasional episodes of classical lead poisoning still occur, particularly in young children, acute exposure is a rare event. Of greater concern is the possibility that continuous exposure to lower levels of lead as a result of widespread environmental contamination may result in adverse health effects (Nriagu, 1978).

3.4.5.2 Production & uses

There is a long history of human production and use of lead. The widespread and general use of lead, due especially to its exceptional properties such as a high degree of ductility and low corrosiveness, has resulted in lead being concentrated in the environment. The automobile and construction industries are the primary users of lead, consuming lead for use of alkyl lead compounds in petrol and the manufacture of lead-acid batteries. About 63,000 t of lead was used in alkyl lead production in the UK in 1980 of which only 20 % was consumed in the UK (Hutton and Symon, 1986).

3.4.5.3 Sources

Lead is widely distributed in the environment, primarily because of its emission from combustion of lead-containing fuel. Until the early part of this century, lead smelting and refining were the major sources of lead emitted to the atmosphere, but with the more rigid methods of control and the emergence of other sources, it is now a minor contributor. The single most important source of lead in the atmosphere is leaded petrol, which, in general, accounts for 90 % or more of the total amount present (Waldron, 1980). Fallout from automobile exhaust has been shown to increase lead levels in areas near highways (Warren and Delavault, 1960). Numerous studies have been conducted on environmental contamination by lead from automobile emission. Studies almost invariably showed that most of the impacted area lies within 50 m from roadways; that most of the lead on the surfaces of vegetation is suspendible particulates; and that lead in soil is primarily concentrated in the surface 0 - 5 cm (Page and Ganje, 1970; Ward et al., 1974). A second major source includes the manufacture and disposal of lead-acid batteries. Other contributions come from the production of metals, thermal power plants and other coal combustion plants. Smaller contributions come from mining, cement production, refuse incineration and wood combustion (Leeds Environment Department, 1994).

3.4.5.4 Lead in environmental media & its affects

In England and Wales the median lead content was 42 ppm with a range of 5 - 1200 ppm (Archer, 1980). In soil, lead accumulates at the surface and does not penetrate to any great extent (Brady, 1984). Butler (1954) suggested that the formation of fairly insoluble lead sulphide may partially explain the immobility of lead in the soil profile. Lead remains largely as a superficial deposition on plant surfaces (Adriano, 1986). If lead is deposited in a soluble form or is rendered soluble after impact, it is probably taken into the plant through stomata and other openings. Plants with a large leaf area such as lettuce or spinach, or vegetables with an extensively dissected foliage such as parsley may accumulate relatively higher quantities of lead when grown near major roads (Adriano, 1986). The phytotoxicity of lead is relatively low compared with other trace elements (Nriagu, 1978). Excess lead in plants can alter several physiological and biochemical processes within the plants. The concentration of total lead found in rainwater can be high, because large quantities of lead are released to the atmosphere. As a result of relatively high concentrations in rainwater and the flashing of street dusts high in lead, concentrations of total lead as high as 4 mg/l can occur in stormwater, most in particulate form (DOE, 1993). Lead is absorbed by aquatic organisms from both water and food. Lead forms highly toxic organo-lead compounds and these accumulate in the tissues of fish, in the bones, scales, gills, liver, and kidney. With decreasing pH, more lead should exist as the readily assimilated Pb^{2+} and therefore be more bioavailable to fish (Mallett et al., 1992). Lead is a dangerous air pollutant which can act as a neuro-toxin. In humans the major source of lead is through the respiratory tract. This reflects the strong association of lead with urban airborne particulates (Moore and Ramamoorthy, 1984). Lead may affect membrane permeability of kidney, liver and brain cells, resulting in either reduced functioning or complete breakdown of these tissues since lead is a cumulative poison (Förstner and Wittmann, 1981). It can be accumulated in the body and affect the central nervous system. It may lead to damage to nerve cells in the young. Recent research has shown that even at low levels of exposure, there may be effects on intelligence levels (Leeds Environment Department, 1994).

3.4.6 Mercury

3.4.6.1 General properties

Mercury is a widespread toxic element, its toxicity being highly dependent upon chemical form. It is not known to be essential in anyway to humans or animals, yet it is capable of entering the human food chain in many ways (Thornton, 1983). Inorganic mercury is poorly absorbed, organic mercury compounds are rapidly absorbed and are much more toxic, especially methylmercury.

3.4.6.2 Production & uses

Since the 1960s world production of mercury has more than doubled. It is used in the chemical industry, in the production of chlorine, in catalysts and paints, in agriculture and related areas and in pharmaceuticals, dentistry and the electrical industry. About 9000 t annually are used world-wide and Hutton and Symon (1986) estimated the consumption of mercury in the UK to be between 527 - 542 t/yr. The chlor-alkali industry is the principal user of mercury in the UK (211 t/yr). Primary battery manufacture accounts for the second largest quantity of mercury consumed in the UK. A proportion of mercury in these is recycled after use but the majority will be eventually disposed of to municipal waste. The combination of physico-chemical properties, such as liquidity at room temperature, uniform volume expansion over a wide temperature range, high surface tension and non-wettability to glass surfaces, makes mercury uniquely useful for measuring devices such as thermometers and barometers (Moore and Ramamoorthy, 1984). The low electrical resistivity and high thermal conductivity make mercury an excellent electrical conductor and coolant respectively (Mitra, 1986). Mercurials have also found widespread use in insecticides, fungicides, bactericides and pharmaceuticals.

3.4.6.3 Sources

There are several sources of mercury in the environment, both natural and anthropogenic. Mercury released in this century through human activities is almost ten times the calculated release due to natural weathering (Moore and Ramamoorthy, 1984). Agricultural and industrial uses of mercury and its compounds have caused a widespread occurrence of this metal in the environment and the presence of mercury residues in foods. The consumption and discarding of mercury containing goods is the largest source of mercury through human activities (Moore and Ramamoorthy, 1984). Fossil fuel burning and materials processing will keep discharge to air-land at relatively high levels. Mercury also may enter soil via disposal of sewage sludge, dry atmospheric fallout, rainfall and agricultural use of mercury-based pesticides. Significant quantities of mercury are discharged to waterways from sources such as chloride manufacture, pulp and paper treatment, laboratories, hospitals, dental clinics, the manufacture and use of paints and use of catalysts, mining and refining of ores, disposal of used mercury containers, sewage treatment and use of mercury-based pesticides (D'Itri, 1993).

3.4.6.4 Mercury in environmental media & its affects

Mercury is present naturally in soils at background concentrations ranging from a few ppb to a few hundred ppb (Adriano, 1986). Berrow and Reaves (1984) reported that the typical concentration of mercury for world soils is about 60 ppb. Mercury is strongly absorbed by soils and sediments and is desorbed very slowly. In general the availability of soil mercury to plants is low and there is a tendency for mercury to accumulate in the roots, i.e. the roots serve as a barrier to mercury uptake (Adriano, 1986). Mercury, because it exchanges slowly, accumulates in organisms more efficiently than do other elements which exchange rapidly (Luoma, 1983). Fish are important in relation to mercury intake because natural processes occurring in sediments can convert all forms of mercury to methylmercury which are water soluble, highly toxic, readily transported and accumulate through the aquatic food chain to edible fish. Water hardness and pH influence the rate of uptake and availability of mercury to aquatic biota and accumulation is greater in acidified waters. Fish take in mercury predominantly through their diet and through their gills and nearly all (95 - 99 %) is present as methylmercury. Man absorbs from ingested food practically all the methyl mercury present. Methylmercury is relatively stable and has a propensity for the human nervous system and about 10 % of total body burden is in the brain.

3.4.6.5 Episodes of mercury poisoning

The outbreak of an unknown, non-infectious, neurologic illness amongst inhabitants especially fishermen and their families living around Minamata Bay, Japan, was recognised in 1953 (Förstner and Wittmann, 1981). Patients who had consumed fish and shellfish from that region progressively suffered from a weakening of muscles, loss of vision, impairment of cerebal functions and eventual paralysis which in many cases resulted in coma and death. The disease, called Minamata Disease, was caused by the consumption of fish and other foodstuffs contaminated with methylmercury. The source of contamination was traced to effluents from various plants of the chemical firm Chisso, manufacturers of plastics. For several years before 1953, the plants had discharged methylmercury into the bay. The disease affected at least 111 persons, causing 41 deaths (Adriano, 1986). A second outbreak of Minamata Disease occurred in Japan in 1964 - 65. The most severe incident of human mercury poisoning occurred during 1972 in Iraq. Farmers had received wheat seed treated with mercurial fungicides from Mexico and ate the seed instead of planting it. When local government authorities began to note this, it was announced that any farmer possessing treated seed was liable to prosecution involving the death sentence. Subsequently the farmers disposed of these hazardous seeds into nearby rivers and lakes. The combined effect of this blunder caused the loss of an estimated 5,000 - 50,000 lives and the permanent disability of more than 100,000 people (Förstner and Wittmann, 1981).

3.4.7 Zinc

3.4.7.1 General properties

Zinc is one of the most abundant essential trace elements in the human body (Leenaers, 1989). It's a constituent of all cells and is involved in the healing process of tissues in the body. The wide industrial application of zinc stems from its chemical and metallurgical properties. The oxidation state of zinc in a natural environment, like soils, is exclusively Zn^{2+} .

3.4.7.2 Production & uses

Most of the zinc produced in the world comes from ores containing zinc sulphide minerals. Canada is the world's largest producer. In 1981 the EC produced 422,000 t of which the UK produced 11,000 t (Mance and Yates, 1984). Approximately 41 % of EC consumption is used in the manufacture of various alloys, including bronze and brass and about 32 % is used in galvanising and electroplating processes (Mance and Yates, 1984). Major industrial discharges may arise from these uses and from the manufacture of rayon textiles and production of paper. Zinc is also used in a variety of other industries including the production of fungicides, rubber, paint, ceramics, glass, reprographic materials which are all potential sources of contamination of the environment during both manufacture and use. Zinc and its compounds are ingredients of many household items including utensils, cosmetic and pharmaceutical powders, ointments, antiseptics, glues, porcelain products, varnishes, oil colours, car tyres and dry cell batteries (Moore and Ramamoorthy, 1984).

3.4.7.3 Sources

Zinc has many uses, consequently a high potential exists for environmental contamination. Large quantities of zinc are transported and deposited by precipitation. Aerial fallout from large industrial - urban complexes is also a major source of metal transfer to the soil. Airborne zinc from automobile emissions is also another pathway of plant contamination with zinc. Zinc originates from tyre wear, fuel additives, brake linings and motor oils. (Flanagan et al., 1980). Zinc from municipal refuse can also be markedly available to plants. Other sources include animal wastes, pesticides, coal combustion, mining and smelting, fertilisers and sewage sludges.

3.4.7.4 Zinc in environmental media & its affects

In England and Wales from a survey that involved 748 randomly selected samples, Archer (1980) gave the median value of 77 ppm zinc with a range of 5 - 816 ppm. However about 63 % of the samples had zinc concentrations between 40 - 99 ppm. At pH values of 6.5 + zinc tends to be only slowly available to plants. Soil ties up large quantities of the element if soil pH is high and drainage is good. Zinc is most soluble and hence phytoavailable under acidic conditions (Brady, 1984). Zinc is one of the essential nutrients for plant growth and is required in only minute amounts. Even at relatively low levels of zinc in the soil toxicity for plants may occur due to accumulation. When concentrations of zinc in the soil exceed 100 - 200 ppm, a negative impact on the yield of agriculture crops may be expected

(Leenaers, 1989). Evidence suggests that zinc is absorbed nearly exclusively by the small intestine (Nriagu, 1980). Once absorbed zinc is deposited in both soft tissues and bone and a large portion is found also in the liver and intestine. Zinc has a high toxicity to fish, which accumulates in the kidneys and skeletal tissue, but acute toxicity to freshwater invertebrates is relatively low.

3.5 Standards for Heavy Metals in Soil & Sediment

Whilst there are strict limits for the heavy metal content of food, drinking and surface waters, the UK's Department of the Environment has not developed statutory limits for determining contamination in soils and sediments. Furthermore, there is at present no systematic and regularly maintained source inventory in the UK for atmospheric heavy metal pollution (DOE, 1993). The only metal for which there is EC air quality legislation is lead (limit value of 2 $\mu g/m^3$). There are also WHO air quality guidelines for cadmium and lead (cadmium in urban areas 0.01 - 0.02 $\mu g/m^3$; lead 0.5 - 1.0 $\mu g/m^3$). The WHO have identified arsenic and chromium as being carcinogenic and give no safe threshold for atmospheric concentration. This section sets out the UK's policy on land quality and in direct contrast to this, the Dutch system, which is often used in metal contamination studies (Leenaers, 1989; Macklin, 1988; 1992).

3.5.1 The UK's Policy

The UK government's view on land quality objectives is that land must be fit for the present or immediate future use and that clean-up should not aim to restore the land for all possible future uses ('fitness for purpose' principle (DOE, 1990)).

Current guidelines on levels of contamination are given in publications of the Interdepartmental Committee on the Redevelopment of Contaminated Land (ICRCL 1983; 1987; 1990). Two important features of the guidelines and the way they have been used in the UK are particularly important according to Smith (1993):

(1) they have frequently been used by those without any formal training in relevant disciplines and this has caused difficulties in interpretation and implementation; and

(2) their limited scope and the fact that they remained essentially unchanged for about 10 years have hindered their proper application and may have also hindered the development of a proper understanding of the problems posed by contamination and the development of a risk assessment based approach.

Contamination was recognised as an issue because of the constraints it could pose on new development rather than because it might pose a threat to the health of an existing population or to the environment. Guidance on assessment and remediation of polluted sites is based on 'trigger concentrations' for certain contaminants and intended 'end uses'. In each case there are two values: a threshold value and an action value (ICRCL, 1987). However, for heavy metals these action concentrations are still to be specified. For most contaminants, it is very difficult at present to set upper values at which the concentration would automatically be considered undesirable or unacceptable (ICRCL, 1987). The action values are expected to be set in the next ICRCL edition. Trigger concentrations are defined as those values below which a site could be regarded as uncontaminated, that is, it would present no additional risk to the critical group (ICRCL, 1983):

- where all concentrations are below the threshold values, no remedial action is needed for the proposed land use;
- where some or all concentrations lie between the threshold and action values, there is a need to consider whether remedial action is required for the proposed use or whether the planned use should be changed; and
- where some or all concentrations equal or exceed the action value, action of some kind, ranging from minor remedial treatment to changing the proposed use of the site entirely is then unavoidable.

The ICRCL stress that the trigger concentrations do not apply to sites already in use and they may have to be modified where development has already begun before contamination was discovered. Trigger concentrations are intended only as guidance prior to development. The values do not define sites where remedial action is essential, nor should they be interpreted as the maximum permissible concentration. The decision whether to take remedial action, has to depend on the particular end use proposed for the site and the extent of the contamination (ICRCL, 1987). The guidance levels are partitioned into two groups (figure 3.3). Since not all site uses are at equal risk from the hazards, it follows that the threshold trigger value varies with the actual or proposed use of the site. The first group includes toxic metals (arsenic, cadmium, chromium, lead and mercury) where trigger concentrations are given for domestic gardens and allotments, where vegetables may be contaminated, and for amenity soils such as parks, playing fields and open spaces where human exposure is likely to be reduced. The second group includes metals which are phytotoxic but which are not normally hazardous to health (copper and zinc).

The principle of 'fitness for purpose' together with considerations on environmental protection are used as concepts for setting remediation or clean-up objectives. Any value will be site specific and based on professional judgement. Phytotoxicity and chemical attack on building materials are taken into account. The guidelines, however, suffer from a number of deficiencies, including:

- the limited range of contaminants covered;
- the lack of 'action values' for heavy metals;
- the failure to take certain risks to human health into account when setting the values;
- environmental hazards are generally not considered;
- potential to affect ground or surface waters is not covered;
- there are no guidelines for groundwater; and
- the analytical methods to be employed are not specified.

Table 3.3 - Tentative trigger concentrations for selected metal contaminants
(after ICRCL, 1987)

	Planned Uses	Threshold Trigger Conc/. (mg/kg air dried soil)
GROUP A: contaminants which may pose hazards to health		
Arsenic	Domestic gardens, allotments	10
	Parks, playing fields, open spaces	40
Cadmium	Domestic gardens, allotments	3
	Parks, playing fields, open spaces	15
Chromium(hexavalent)	Domestic gardens, allotments	25
	Parks, playing fields, open spaces	
Chromium (total)	Domestic gardens, allotments	600
	Parks, playing fields, open spaces	1000
Lead	Domestic gardens, allotments	500
	Parks, playing fields, open spaces	2000
Mercury	Domestic gardens, allotments	1
	Parks, playing fields, open spaces	20
GROUP B: contaminants which are phytotoxic but not normally hazardous to health		
Copper	Any uses where plants are to be grown	130
Zinc	Any uses where plants are to be grown	300

Trigger values are available for a limited range of contaminants and have no statutory or formal administrative backing (Smith, 1993). There are currently no proposals for statutory quality objectives for soil (DOE, 1990). The DOE (1991) stated that it would extend the list of contaminants covered by the trigger values (Smith, 1993). No new guidance has yet been issued, but the DOE has embarked on a number of developments likely to contribute to correction of some of the deficiencies, or otherwise seriously impact the way that contaminated land problems are approached in the UK.

3.5.2 Dutch Policy

By contrast to the UK, the Netherlands have had a long history of soil protection policy, dating back to 1962. The guiding principle in Dutch soil protection policy (which includes the protection of soil, sediment, groundwater and biota) is the maintenance or the restoration of soils 'multifunctionality' (Visser, 1994). Important functions of the soil in relation to human landuse are the possibility to build on it, to extract groundwater, to provide raw materials and to produce crops. Ecological, hydrological and cultural functions also have to be protected in the Dutch concept of multifunctionality. The Dutch approach to soil protection therefore aims at preservation and protection of the soil as a valuable resource for the future. Human activities may only have temporary effects on soil quality, irreversible effects on the quality of the soil should be avoided.

The Soil Clean-up Guideline was published in 1983 to deal with contaminated sites (Visser, 1994) formulated by the Ministry of Environment. This guideline describes general procedures for investigation and remediation of polluted sites. In this, A-, B- and C- values were formulated as tools for investigation and decision making. These values were to be used in conjunction with site specific information on the geohydrological conditions, which control the transport of pollutants to surrounding areas and on landuse which determines exposure and risks involved, before a final decision on the necessity of a clean-up could be made.

After ten years a major revision of the guideline was considered necessary. The Soil Clean-up Guideline for investigation and restoration of polluted sites is now part of a more general Soil Protection Act which deals with prevention as well. The new soil quality standards were based on ecotoxicolgical and human toxicological criteria. The revision involved the following changes:

- The A- values have been reformulated using ecotoxicological methods
- The B- values have been omitted
- New C- values to be based explicitly on (eco)toxicological data and all potential human exposure routes.

Within the Dutch concept, two major soil quality standards are defined: 'target values' the upper limit for a multifunctional soil quality and 'intervention values' representing the lower limit of an unacceptable soil quality. According to these principles various risk levels have been established. For man the risk is based on the affects of an exposure to individual people. For ecosystems the basic principle is safeguarding of all important processes in the soil ecosystem (Eleveld, 1995). The distinction is made between the necessity and the urgency of a clean-up. The new C- values are developed to describe this situation. The latest proposals for the new C- values are in table 3.4, with A- values (target values) and current C- values. The values in the table are valid for a 'standard' soil (25 % clay < 2 μm and 10 % organic matter) and refer to average concentrations of substances in soil over an area of 50 m^2 and a depth of 0.5 m.

Table 3.4 - Latest proposals for C- values (intervention values); A- values (trigger values) & current C- values (mg/kg) *(after Visser, 1994)*

METAL	NEW C- VALUE	A- VALUE	CURRENT C- VALUE
Arsenic	55	29	50
Cadmium	12	0.8	20
Chromium	380	100	800
Copper	190	36	500
Lead	530	85	600
Mercury	10	0.3	10
Zinc	720	140	3000

If concentrations do not exceed the A- value the site is considered clean. If concentrations exceed the value (A+C/2) further investigations are necessary. The value (A+C/2) is a temporary trigger value which replaces the former B- value. If C- values are exceeded at stage one, clean-up is considered necessary. In the second stage the timetable for clean-up is set, depending on the urgency of the remediation. Actual human exposure, mobility of pollution and ecological effects determine the urgency of the clean-up. The third step is the determination of the clean-up objective (Visser, 1994).

There is a very clear disparity between the guidelines issued by the British and Dutch governments, particularly considering the new (proposed) C- values in the Dutch system. The British government setting considerably less stringent guidelines. The UK system is slow to adapt and does not properly address the urgency of the situation. The issue of any new guidance still seems many years away.

CHAPTER 4

THE STUDY AREA

4.1 The River Aire Catchment

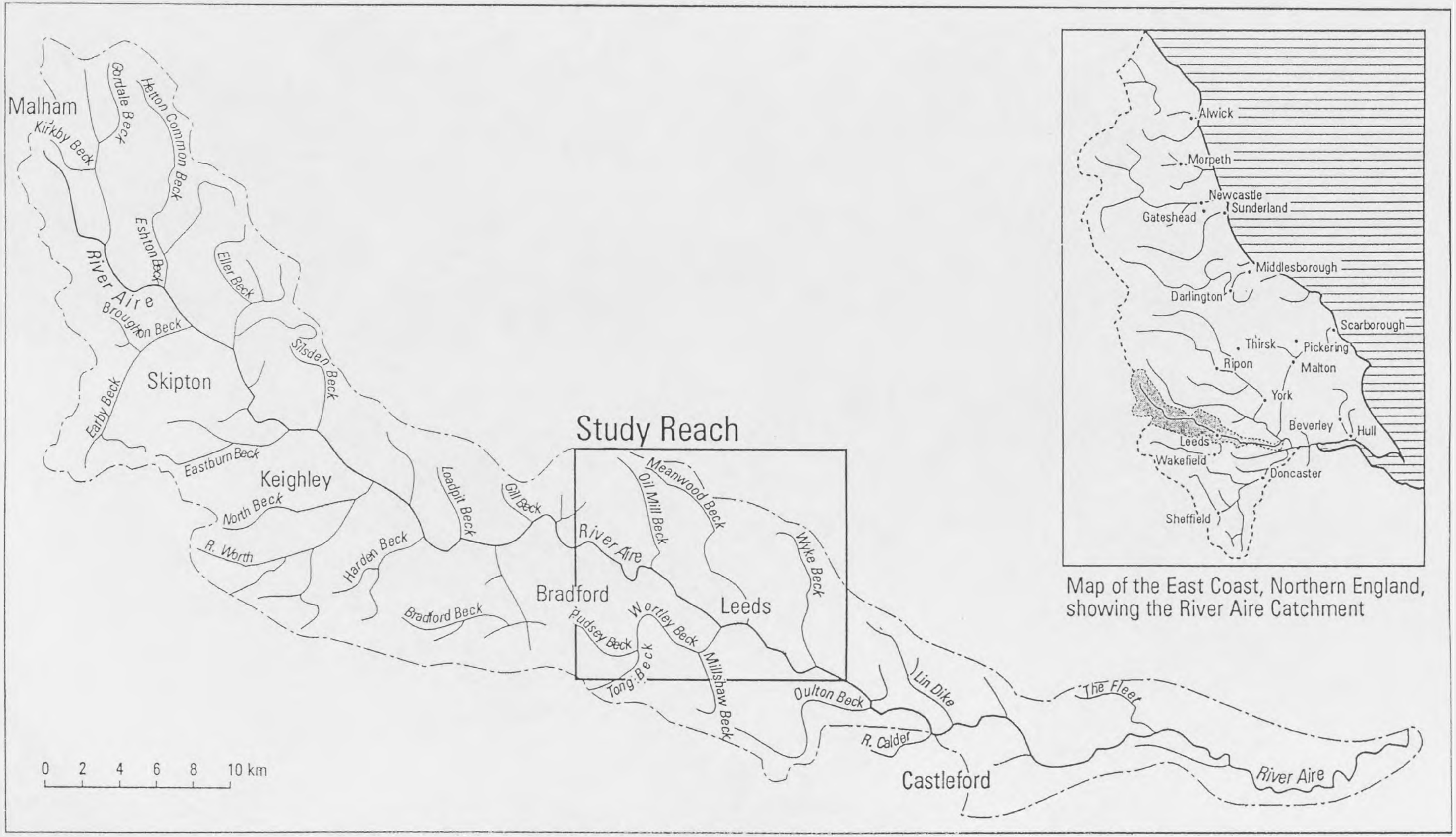
4.1.1 General characteristics

The source of the River Aire rises on the limestone moorlands around Malham in the Yorkshire Dales. The River flows 148 km to its confluence with the Ouse, near Goole, the last 26 km of the Aire being tidal. The River Aire has a catchment of 1100 km^2 (figure 4.1) with a total population of about 1,110,000 (NRA, 1993). The principal towns and cities are Skipton, Keighley, Bingley, Bradford, Leeds and Castleford. The Aire catchment is also home to the many industries and urban populations of these towns and cities and in the past, the river has been used as a convenient means of disposal of effluents from sewage works and industries. The Aire is joined by the River Calder at Castleford, 13 km below Knostrop sewage treatment works in Leeds, which means the lower reaches of the River Aire carry sewage effluent from a population of 1,900,000 and approximately 80 % of Yorkshires industrial effluent (NRA, 1993).

The river does not provide sufficient water to meet the needs of the Aire catchment. Consequently much of the water is imported from reservoirs and rivers in the Derwent, Nidd, Ouse, Ure and Wharfe catchments. Most of this water is then returned to the environment, via sewage treatment works discharging to the Aire and its tributaries. The result is, in the dry summer weather over 70 % of the river flow derives from effluent discharge from sewage treatment works (Edwards et al., 1997). In the upper catchments of the Aire the main water abstractions made by YWS Ltd (Yorkshire Water Services Ltd) are for public water supply. In the lower reaches the principal abstractions are for industrial cooling and power generation.

The disposal of domestic and industrial effluents has a major influence on the quality of the river system. The effects of the largest sewage treatment works in the

Figure 4.1 - The River Aire catchment



Map of the East Coast, Northern England, showing the River Aire Catchment

catchment, especially Marley (Keighley), Esholt (Bradford) and Knostrop (Leeds) dominate the river quality. There is a large chemical manufacturing industry in West Yorkshire and the principal problems from chemical wastes in the study reach of the River Aire, occur currently, from Esholt sewage treatment works. There is a large quantity of a wide range of wastes generated within the Aire catchment, many of which are disposed of in the immediate locality and have been so for many years.

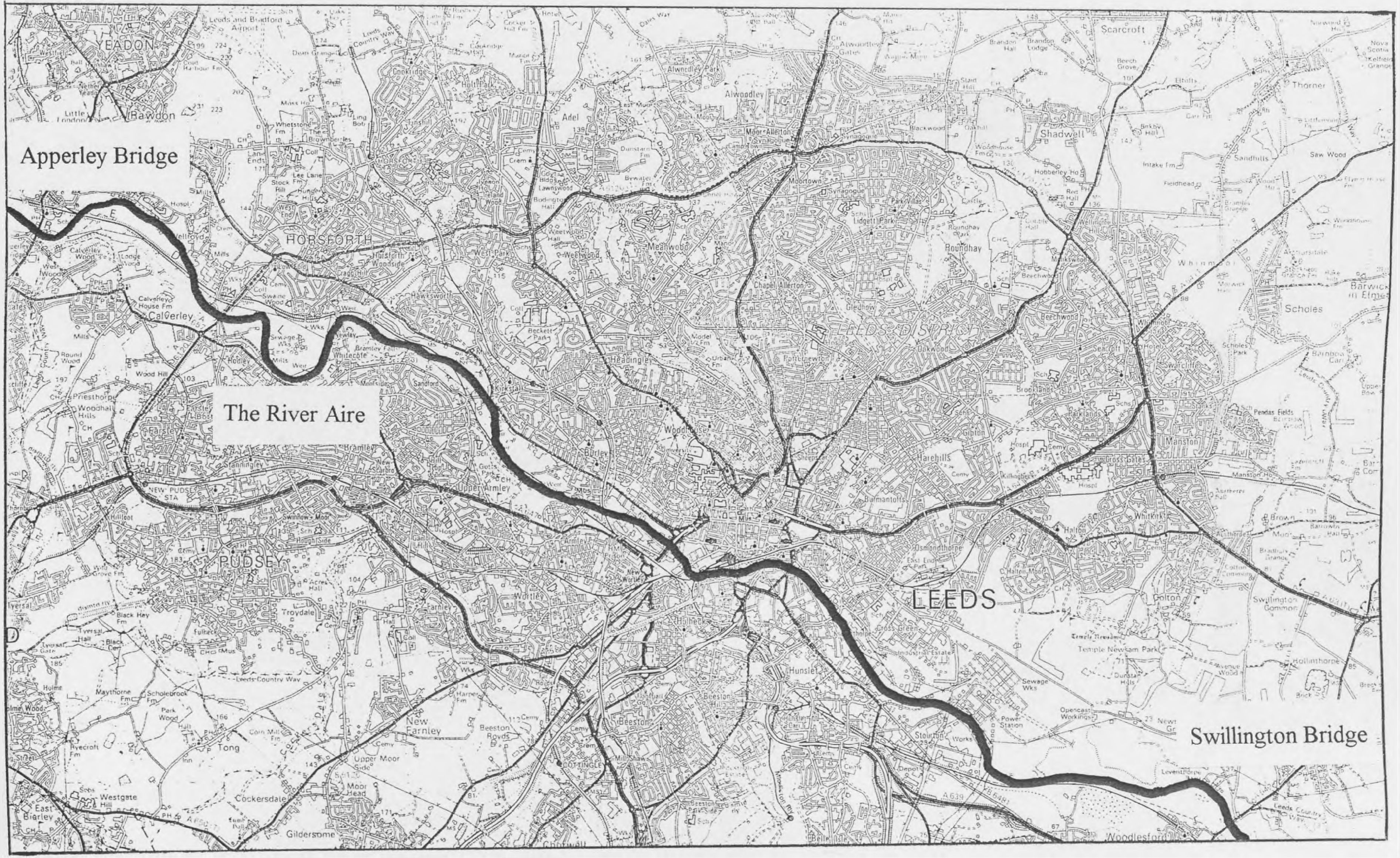
In the past there has been considerable gravel extraction and opencast coal mining in the middle and lower section of the Aire valley. Today, opencast mining still takes place at Skelton (south Leeds) and further east outside Leeds. There has also been considerable deep mining on the lower Aire downstream of Leeds which has resulted in subsidence of the river banks.

The present study is concerned with the River Aire in Leeds Metropolitan District, from Apperley Bridge (NGR SE 19500 37900) (0 km, upstream) through the city centre to Swillington Bridge (NGR SE 37200 29400) (26 km, downstream) (figure 4.2). Throughout this reach the landuse changes considerably providing a catchment that varies greatly both in its potential sources, storage and likely impacts of heavy metal pollution (4.3.2). From Apperley Bridge, the landuse is predominantly agricultural, becoming more residential, industrial and urbanised with increasing distance downstream towards the city centre. South of Leeds city centre, heavy industry prevails, gradually becoming more agricultural towards Swillington Bridge.

4.1.2 Geology

The headwaters of the River Aire at Malham is predominantly limestone. The area from Skipton to Bradford is covered by Millstone Grit, a sequence of shales and grits, which form the higher moorland areas, such as those around Keighley. The coal measures, comprising shales, grit and coal seams of Carboniferous age cover much of the Bradford and Leeds area. Coal mining has now largely moved eastwards and become centred in the coalfield east of Castleford. Magnesium

Figure 4.2 - The study reach



limestone overlying the coal measures, forms a low north - south ridge. These rocks dip gently eastwards and are overlain by Sherwood Sandstone that increases in thickness towards Goole. This soft sandstone forms the Vale of York and is extensively covered both by glacial and alluvial material (Versey, 1948).

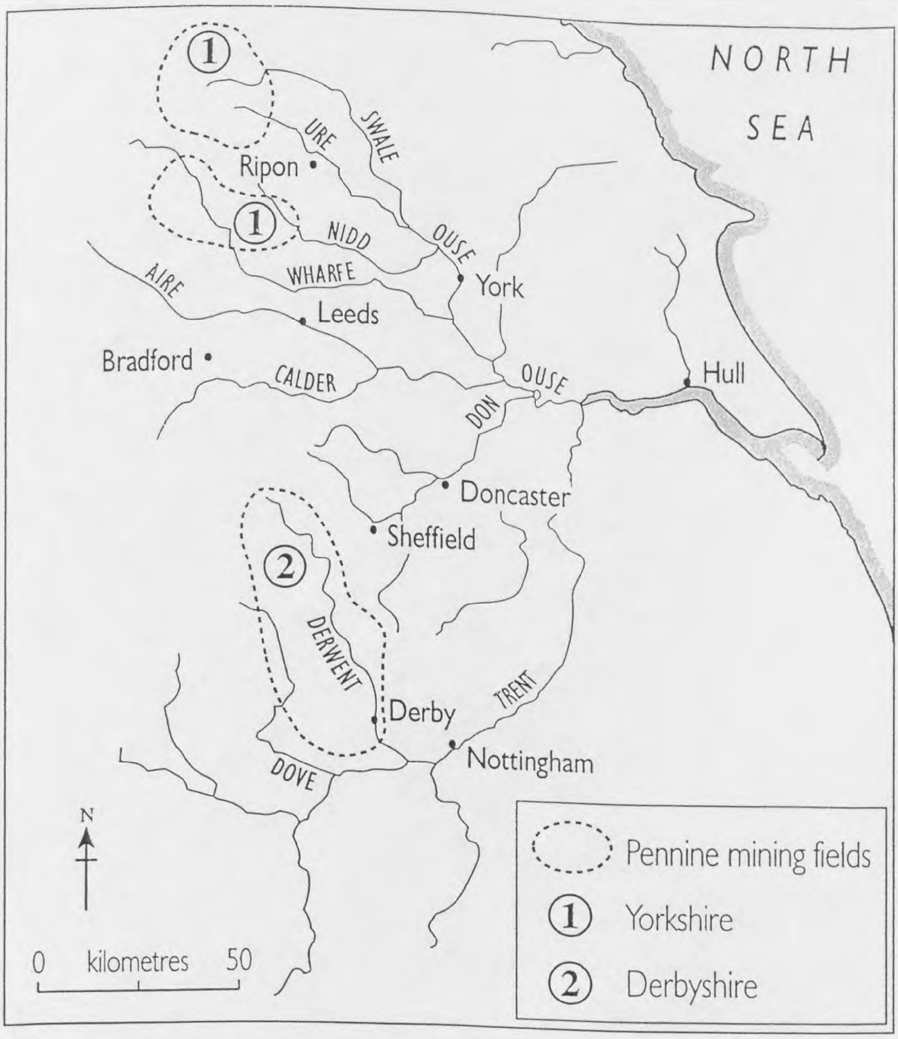
4.1.3 The Ouse tributaries

The River Aire, along with Rivers Derwent, Don, Nidd, Swale, Ure and Wharfe all join the River Ouse, which passes through to the Humber Estuary and out into the North Sea. The Humber is the largest contributor of freshwater to the North Sea in England. Improved environmental awareness has led to concern over discharges of pollutants to the oceans. The North Sea is of particular concern because of its small size and because several of the European industrialised nations discharge into it (Neal et al., 1997). For many substances, around 60 - 80 % of the total riverine load to the North Sea is derived from the Humber Rivers, even though this region supplies only a half of the river water flow (Robson and Neal, 1997). The Aire and Don in particular, contribute high loads relative to their catchment area.

Variations in water quality and chemical loads for UK rivers draining to the North Sea are related to regional differences in geology, climate, landuse and population distribution. In sampling and analysing suspended sediment from each of the Ouse tributaries (5.1.4) these differences may be evident, as found by other workers (Macklin et al., 1997; Neal et al., 1997; Robson and Neal, 1997). In general, a broad separation exists between the rivers discharging into the Humber Estuary, the southern rivers (e.g. Aire, Don) draining urban and industrial areas and the northern rivers (e.g. Nidd, Swale) draining predominantly rural and mineralised catchments, or in the case of the Derwent, an almost unpolluted catchment.

The orefields of the North Pennines, Yorkshire Dales and Peak District were among the most productive lead and zinc mining areas of Britain. Studies (Bradley and Cox, 1987; Macklin, 1992; Macklin et al., 1994) indicate that historic metal mining continues to severely impact river water and sediment quality. Mine waste

Figure 4.3 - The Ouse tributaries



derived from old spoil heaps and floodplains contaminated by mining presently constitutes the primary source of contaminant trace metals.

Of all the rivers that flow to the Ouse, the two that have made the biggest contribution historically as a transportation system, assisting the development of trade and commerce of West Yorkshire, and are now the most successful of this country's commercial inland waterways, are the rivers, Aire and Calder (Smith, 1987). For centuries these waterways have enabled Leeds to develop and prosper as England's northern capital. The River Aire powering its mills, bringing in coal and raw materials and exporting manufactured goods to Europe and the Leeds-Liverpool Canal carrying Leeds' products across the Pennines, for export across the Atlantic. As Leeds rose to become one of the great workshops of the world, its factories produced vast amounts of smoke and effluent. Then as heavy industry and commercial use of the waterways went in to decline, it left behind dereliction and decay. This was very evident in the 1960s and 1970s, but since then a major transformation has taken place, as the potential of the river for recreation and tourism slowly began to emerge. Since then there have been many notable improvements to the Leeds waterfront. New building and bridges have been erected, old buildings have been cleaned restored and converted to new uses and areas of dereliction sensitively landscaped. To promote the public use, enjoyment and appreciation of the riverside, the Leeds Waterfront Tourist Development Action Programme was established in 1990. Over the past five years its partners, Leeds City Council, British Waterways, Leeds Development Corporation and the English and Yorkshire Tourist Boards have made considerable progress (Brears, 1993).

4.2 Historical Development of Leeds & the River Aire

The historical development of Leeds owes much to the raw materials the region possessed. Leeds on the lower coal measures series, yielded not only coal for furnaces and steam engines, but also building stone and clay, which gave rise to an important brickmaking and earthenware industry. The local measures also contained bands and nodules of ironstone which had given birth to a local iron industry at a very early date, for example, Kirkstall forge, which dates back to the thirteenth century (Ward, 1972).

Two commodities played an important part in the economic growth of Leeds: wool, the basic raw material of the woollen industry and coal, the standard fuel for domestic and industrial purposes. Most importantly, however, the Leeds area had a river valley ideal for exploiting water power, but also a uniquely advantageous position for transport and future trade. Leeds acted as a market centre, promoting industrial growth and encouraging the development of transport and commercial facilities.

Communications and urban development in Leeds were funnelled along the Aire and Meanwood valleys and later to the south. In an age dependent upon steam power, water was used to raise steam in boilers and thus to convert mineral energy into motive power. Water was used for washing and cooling purposes, particularly in the dyeing and textile trades, but also in tanneries, foundries and brickworks. In some manufacturing industries water constituted an important ingredient, for example, the brewing trade. Water, therefore, was used to raise steam, to wash, to cool, to carry away wastes and as a raw material. Only a handful of firms did not consume it in quite extensive quantities. It was, as a result a factor of prime importance in the location of manufacturing industry, to most industries of nineteenth century Leeds, the most important factor.

As the town grew, new factories began to line the river banks; iron forges, engineering factories, textile mills, chemical works, dyehouses, oil mills, grinding mills, saw mills, corn mills, tanneries, etc., many of which used the waterways both as a means of transport and as a convenient drain and sewer. Founding and engineering became major Leeds industries during the first half of the nineteenth century and Leeds became a metal working district second only to the Black country in importance. Originally the basic raw material for the engineering trades was supplied by an important local iron industry. Production of wrought iron fell towards the end of the nineteenth century as local ores were exhausted and steel replaced iron, but the engineering industry continued to prosper, using material brought from Cleveland and Sheffield among other sources. From Kirkstall forge to Thwaitegate both banks of the Aire were lined with engineering works, with rarely more than four or five firms in exactly the same line of business. Leeds developed as one of the World's great centres of engineering, virtually the whole town, south of the river being devoted to the industry. Growth in textiles gave impetus to other trades besides that of machine making, some of which emerged as industries of national importance. The modern leather industry in Leeds began with the erection of a tannery in Kirkstall Road. The chemical industry served not only the woollen industry and other textiles but also the glass makers of Hunslet and later the leather industry.

Purity of the water was important and of great significance to the dyeing and leather trade. The surface water courses remained fairly pure until the beginning of the nineteenth century and still had fish in abundance (Brears, 1993). Contamination increased as time passed. By 1838 Gipton Beck was said to be the only unpolluted stream left in Leeds. The fish were soon to disappear, poisoned by the dyes, chemicals and other effluent which poured into the Aire. Leeds developed an unenviable reputation as one of the most polluted towns in Europe. The construction of the first sewerage system in Leeds from the early 1850s slightly improved the situation in the town centre, by collecting the raw effluent and dumping it in the river a couple of miles downstream near Knostrop.

In the second half of the nineteenth and early twentieth century commercial and distributive activities regained their pre-eminent position. By 1914 manufacturing was of diminished importance relative to commercial activities. The number of jobs in commerce rose extremely rapidly and the tertiary sector grew more rapidly than manufacturing had. The most noticeable feature was the decline in textiles. Fortunately the decline of this staple trade was more than compensated by the growth in other industries, notably engineering, leather and chemicals, by the emergence of four new industries - clothing, footwear and printing and also the service industry. Since the first world war there was a gradual decline in

Yorkshire's importance in the national economy as the old manufacturing industry contracted in face of international competition. However, industry was still markedly concentrated along the Aire and Meanwood valleys, even by 1914 and whilst these locations also provided good communications and suitable land, more often than not, it was access to water that was the critical factor.

To summarise, in a period throughout which the dominant source of power was the stream engine and in a town noted for its textile industry, the key consideration in intra-urban location of manufacturing was frequently the provision of water and sites alongside the River Aire and its tributaries were favoured alike for workshops and factories. This choice was reinforced by the general orientation of transportation facilities along these valley corridors and by the nature of the land available. Also significant were the distribution of the working population and the close degree of inter-dependence between the firms and industries which sometimes produced marked areal association of firms. Access to raw materials, fuel and markets though important in attracting industry to Leeds in the first place was not a critical factor in the siting of factories within the intownship of Leeds (Ward, 1972).

4.3 Sources of Heavy Metal Contamination

4.3.1 Past sources

Effluent disposal was a problem faced by all industries and one made easier if an open water course ran conveniently nearby. The culverts which led water from river or beck to factory well, were matched by an equal number of drains returning polluted water and other wastes to the water courses. Water was a factor of prime importance in location of industry, to raise steam, to wash, to cool, to carry away wastes and as a raw material. Industry therefore was markedly concentrated along the Aire and Meanwood valleys in the early 1900s and these are considered to be the main historic sources of heavy metal pollutants.

A belt of riverside industry (figure 4.4) virtually traverses the city continuously from Armley to Hunslet. Almost all the industries turned their backs on to the river using them for process water and as a sewer. Westwards and eastwards industrial development begins to peter out to a much more rural Aire Valley, which even today remains relatively open. To the north and south of this lie vast residential areas. Textile manufacture was prominent throughout, mixed with engineering, dye, leather and chemical works. The leather and tanning industry were located largely in two areas, along Kirkstall Road and Meanwood Valley. Holbeck and New Wortley were characterised by a huge complex of railways, goods yards and stations. South of the river, particularly in Hunslet, heavy engineering was prominent, dominated by the working of iron and steel and engineering products. Many Hunslet industries, foundries, forges, glass and chemical manufacture used coal in quantity from local pits or from the Yorkshire coalfield, to provide the heat needed in processing as well as a general source of steam power. Small collieries were plentiful locally, at Knosthorpe, Parkside and Middleton.

Two non-point sources of river and soil pollution associated with the concentration of population and industry, were important at these times: sewage and coal combustion. During the rapid and largely unplanned expansion of early nineteenth century Leeds, virtually no provision was made for the disposal of human and animal waste. Heavy metals found in human and animal excretions include cadmium, copper, lead and zinc. In 1850 - 1855 a scheme promoted by an improvement act of 1842 saw the construction of the first public sewers in Leeds, collecting the raw effluent and discharging it into the river a few miles downstream at Knostrop (figure 4.4, No. 79). In 1869 a chancery injunction prevented the discharge of raw sewage directly into the river. The first Knostrop sewage treatment works were built in 1874. However, further expansion of Leeds and its sewers rapidly outgrew this facility and in 1907 the city was able to purchase 600 acres at Knostrop for the development of a new and efficient sewage works.

In general, fossil fuel combustion results in the dispersion of a wide range of heavy metals including arsenic, cadmium, chromium, copper, lead, mercury and zinc over a large area, although not all these elements are present in significant concentrations in all types of coal and petroleum. Average concentrations of metals found in coal are shown in table 4.1.

Table 4.1 - Average concentration (ppm) of heavy metals in coal *(after Adriano, 1986)*

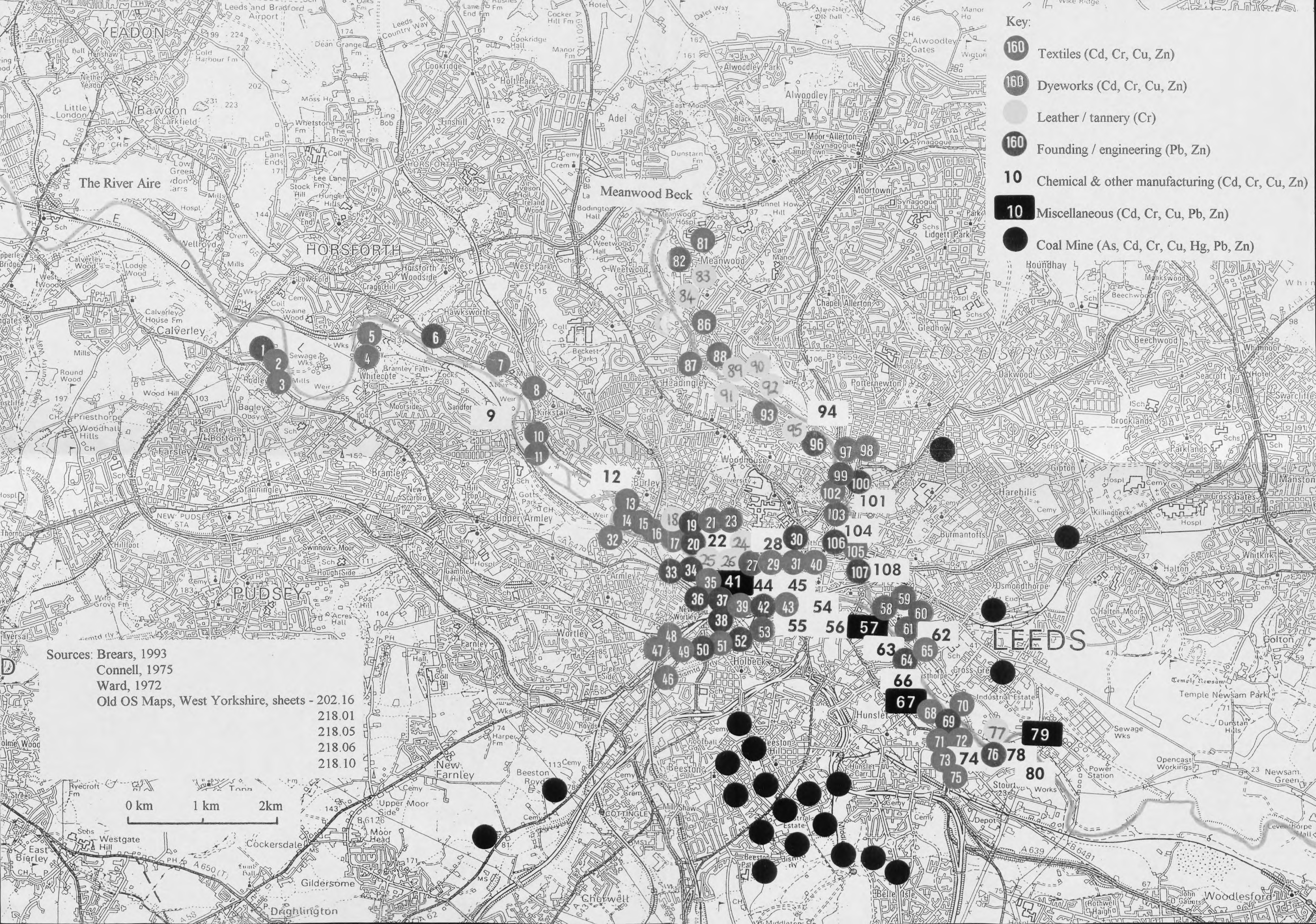
Arsenic	Cadmium	Chromium	Copper	Lead	Mercury	Zinc
15	1.3	15	19	16	0.18	39

Coal was the standard fuel for both domestic and industrial purposes and used in vast quantities by all the industries mentioned. The metals are either emitted into the environment as airborne particles during combustion to be deposited at a later date on soil or surface waters, or they accumulate in the ash residues, which may themselves be disposed of in rivers or on floodplains.

Point sources of heavy metal contaminants include iron and steel forges and foundries (lead and zinc) textile and leather works (cadmium, chromium, copper and zinc), chemical and other manufacturing industries (cadmium, chromium, copper and zinc). Metallurgical industries can contribute to river and soil pollution in several ways: by the emission of aerosols and dusts which are transported in the atmosphere and eventually deposited; by liquid effluents discharged directly into the river; and by the creation of waste dumps on which metals become corroded and leached into the underlying soil. Many heavy metals are involved, cadmium, chromium, copper, lead and zinc, among others. Hence both the manufacture of these materials, their fabrication into products such as machines and vehicles and their disposal or recycling in scrap metal can lead to environmental pollution by a wide range of metals. The manufacture of iron and steel from iron ore produces large amounts of dust (50 kg/t of steel produced) containing large quantities of lead and zinc (Pacyna, 1986). Significant quantities of cadmium, chromium and copper are also released from steel production. In the leather industry, chromium was widely used, especially after 1850 when tanning by chrome became very popular (Ward, 1972). The textile and dyeing trades also used large amounts of chromium (Förstner and Wittmann, 1981) but their effluents are likely to have also contained quantities of cadmium, copper and zinc. Other significant sources of heavy metal pollution of rivers and floodplains include breweries (cadmium, chromium, copper and zinc) and the printing / paper industry (cadmium, chromium, lead and zinc).

Figure 4.4 - List of past industries / sources

1 Rodley Crane Works (Pb, Zn)
2 Airedale Mills (Cd, Cr, Cu, Zn)
3 Ross Mills (Cd, Cr, Cu, Zn)
4 Airedale Vale Dyeworks (Cd, Cr, Cu, Zn)
5 High Mill (Cd, Cr, Cu, Zn)
6 Kirkstall Forge (Pb, Zn)
7 Abbey Mill (Cd, Cr, Cu, Zn)
8 Abbey Mills (Cd, Cr, Cu, Zn)
9 Kirkstall Brewery (Cd, Cr, Cu, Zn)
10 Savins Mills (Cd, Cr, Cu, Zn)
11 St Ann's Mills (Cd, Cr, Cu, Zn)
12 Cardigan Boot Factory (Cd, Cr, Cu, Zn)
13 Burley Mills (Cd, Cr, Cu, Zn)
14 Cardigan Mills (Cd, Cr, Cu, Zn)
15 Milford Place Works (Cd, Cr, Cu, Zn)
16 Burley Vale Mills (Cd, Cr, Cu, Zn)
17 Burley Bridge Mills (Cd, Cr, Cu, Zn)
18 Viaduct Tanneries (Cr)
19 Corporation Yard (Pb, Zn)
20 Screw Manufacture (Pb, Zn)
21 Wellington Dyeworks (Cd, Cr, Cu, Zn)
22 Oil works (Cd, Cr, Cu, Zn)
23 Dyeworks (Cd, Cr, Cu, Zn)
24 Valley Leather Works (Cr)
25 Oak Tannery (Cr)
26 Joppa Tannery (Cr)
27 Dyeworks (Cd, Cr, Cu, Zn)
28 Yorkshire Chemicals (Cd, Cr, Cu, Zn)
29 Perserverance Mills (Cd, Cr, Cu, Zn)
30 Wellington Foundry (Pb, Zn)
31 Victoria Mills (Cd, Cr, Cu, Zn)
32 Armely Mills (Cd, Cr, Cu, Zn)
33 Leeds Forge (Pb, Zn)
34 Albion Works (Pb, Zn)
35 Queen Mills (Cd, Cr, Cu, Zn)
36 Albion Works (Pb, Zn)
37 Iron Works (Pb, Zn)
38 Wheel & Axle Works (Pb, Zn)
39 Canal Mills (Cd, Cr, Cu, Zn)
40 Bean Ing Mills (Cd, Cr, Cu, Zn)
41 Goods Sheds (Cd, Cr, Pb, Zn)
42 Monk Bridge Iron & Steel Works (Pb, Zn)
43 Whitehall Mills (Cd, Cr, Cu, Zn)
44 Whitehall Soap Works (Cd, Cr, Cu, Zn)
45 Electric Lighting Works (Cd, Cr, Cu, Zn)
46 Ingram Works (Cd, Cr, Cu, Zn)
47 Holbeck Mills (Cd, Cr, Cu, Zn)
48 Victoria Mills (Cd, Cr, Cu, Zn)
49 Low Hall Mills (Cd, Cr, Cu, Zn)
50 Globe Foundry (Pb, Zn)
51 Holbeck Clothing Works (Cd, Cr, Cu, Zn)
52 Midland Junction Foundry (Pb, Zn)
53 Tower Works (Cd, Cr, Cu, Zn)
54 Printing Works (Cd, Cr, Pb, Zn)
55 Drug Mills (Cd, Cr, Cu, Zn)
56 Victoria Ware Mills (Cd, Cr, Cu, Zn)
57 Electric Power Station (Cr, Pb, Zn)
58 Bowman Lane Dyeworks (Cd, Cr, Cu, Zn)
59 Crown Point Dyeworks (Cd, Cr, Cu, Zn)
60 Nether Mills (Cd, Cr, Cu, Zn)
61 Fearn's Island Dyeworks (Cd, Cr, Cu, Zn)
62 Bank Paper Mills (Cd, Cr, Pb, Zn)
63 Victoria Chemical Works (Cd, Cr, Cu, Zn)
64 Clarence Iron & Steel Works (Pb, Zn)
65 Low Fold Mills (Cd, Cr, Cu, Zn)
66 Airedale Chemical Manure Works (Cd, Pb, Zn)
67 Aire Bank Saw Mills (Cr, Pb, Zn)
68 Aire Bank Mills (Cd, Cr, Cu, Zn)
69 Hunslet Nail Works (Pb, Zn)
70 Hunslet Mills (Cd, Cr, Cu, Zn)
71 Victoria Mills (Cd, Cr, Cu, Zn)
72 Hunslet Linen Works (Cd, Cr, Cu, Zn)
73 Hunlet Old Mills (Cd, Cr, Cu, Zn)
74 Hunslet Paper Mills (Cd, Cr, Pb, Zn)
75 Lowgate Mills (Cd, Cr, Cu, Zn)
76 Hunslet Forge (Pb, Zn)
77 Gibralter Leather Works (Cr)
78 Soap Factory (Cd, Cr, Cu, Zn)
79 Knostrop STW (As, Cd, Cr, Cu, Hg, Pb, Zn)
80 Thwaite Mills (Cd, Cr, Cu, Zn)
81 Grove Mill (Cd, Cr, Cu, Zn)
82 Valley Dyeworks (Cd, Cr, Cu, Zn)
83 Cliff Tannery (Cr)
84 Valley Mills (Cr)
85 Valley Leather Works (Cr)
86 Ridge Mills (Cd, Cr, Cu, Zn)
87 Carr Mills (Cd, Cr, Cu, Zn)
88 Scott Hall Mills (Cd, Cr, Cu, Zn)
89 Spring Well Leather Works (Cr)
90 Hill Top Tannery (Cr)
91 Buslingthorpe Tannery (Cr)
92 Sheepscar Leather Works (Cr)
93 Oatlands Mill (Cd, Cr, Cu, Zn)
94 Watson's Chemical Works (Cd, Cr, Cu, Zn)
95 Sheepscar Mills (Cr)
96 Sheepscar Foundry (Pb, Zn)
97 Sheepscar Dyeworks (Cd, Cr, Cu, Zn)
98 Low Close Mills (Cd, Cr, Cu, Zn)
99 Skinner Lane Dyeworks (Cd, Cr, Cu, Zn)
100 Hope Foundry (Pb, Zn)
101 Melbourne Brewery (Cd, Cr, Cu, Zn)
102 Melbourne Street Mills (Cd, Cr, Cu, Zn)
103 Watson's Dyeworks (Cd, Cr, Cu, Zn)
104 Lady Bridge Mills (Cd, Cr, Cu, Zn)
105 Millgarth Street Mills (Cd, Cr, Cu, Zn)
106 Union Foundry (Pb, Zn)
107 Albert Nail Works (Pb, Zn)
108 Trumble's Paper factory (Cd, Cr, Pb, Zn)



Sources: Brears, 1993
Connell, 1975
Ward, 1972
Old OS Maps, West Yorkshire, sheets - 202.16
218.01
218.05
218.06
218.10

Figure 4.4 - Past sources of heavy metal pollution

4.3.2 Present sources

The River Aire through Leeds Metropolitan District supports a mass of industrial and urban population. Demands from the community on the river catchment are wide ranging, whether it be for water supply, effluent disposal, fisheries, conservation, recreation or protection from flooding. Abstraction from surface waters in this reach of the Aire are largely for water supply and cooling, whilst the main abstractors of groundwater are for cooling waters and manufacturing industry. Water quality of the River Aire declines in Leeds due to the impacts of industry and urbanisation. Every discharge to the river requires a consent. The multipurpose usage of numerous heavy metals may lead to difficulties in tracing the source of origin of water pollution conclusively. Sources of heavy metals include: sewage effluent; industrial effluent; agriculture; waste disposal; atmospheric deposition; and urban runoff.

4.3.2.1 Sewage effluent

The discharge of sewage and sewage effluent is one of the most important influences on water quality. The River Aire receives discharges of sewage effluent from sewage treatment works, combined sewer overflows and sewer dykes. The effects of the largest sewage treatment works at Esholt and Knostrop dominate the river quality. Waste is extracted as 'sewage sludge' the resultant treated effluent (essentially wastewater) is discharged into water courses. About 95 % of the polluting load of sewage is removed by treatment before being discharged (NRA, 1993). It is a fact that total effluent discharges represent a very significant proportion of most urban flows, which, for the River Aire, can be as much as 70 % in dry weather. Locations where final effluent is discharged from sewage treatment works in to the river are marked on figure 4.5.

Generally wastewaters from domestic effluents probably constitute the largest single source of elevated metal levels in rivers (Yorkshire Water, 1994). Solid wastewater particulates may cause appreciable metal enrichment of the suspended load in waters (Novotny et al., 1993). Sources of these metals include urban runoff (section 4.3.2.6), corrosion of metal plumbing fittings, excretion of metals in the human diet, cosmetics, health care products and other domestic products, such as household cleaning items and detergents (Yorkshire Water, 1994). Other smaller sewage treatment works may also be a cause or have caused pollution in the past, for example, Rodley and Smalewell sewage treatment works.

Sewer systems in times of heavy rain also carry stormwater. Sewers are not of unlimited capacity and in periods of heavy rain the excess stormwater is discharged to water courses through combined sewer overflows (CSO's). These overflows should only operate in times of heavy rain so that the wastewaters are well diluted and the water courses have a higher flow than normal to dilute the waste further. One of the principal causes of poor water quality in many urban rivers are CSO's. Untreated sewage is highly polluting and requires effective treatment before the effluent produced can be discharged safely to a water course. In regarding the location of stormwater outlets, Michelbach and Wöhrle (1994) observed a high level of contaminants in river water and a major accumulation of contaminants in the sediments near the overflow outlets. Sediments were highly contaminated and poor water quality could be observed up to 250 m downstream from CSO's. The concentration of heavy metals were found to be 10 - 15 times higher than those measured upstream. Such overflows presently have the greatest effect on water quality of the River Aire. Obviously the discharge of poorly diluted sewage to a river is not desirable but is an unfortunate necessity. Pollution emanating from the premature operation of CSO's is widespread throughout the catchment and a particular problem in Tyersal, Pudsey, Milshaw, Low and Meanwood Becks (figure 4.5).

4.3.2.2 Industrial effluent

Industrial effluents which discharge either via sewage works or direct to the river are major sources of heavy metals. There is a large chemical manufacturing industry in West Yorkshire and traces of some of their raw materials, intermediates and by-products pass through sewage treatment and into the river. These industries are situated on the River Aire itself. Residues from chemical manufacturing occur in low concentrations in sewage and to a lesser extent in cooling discharges direct from chemical works. Other sources are the textile industry which use insecticides to 'moth proof' fibres and fabrics. Insecticides may contain several heavy metals in various quantities. Mothproofers are used by industry in the catchment of Esholt sewage treatment works. The residues are discharged to sewers and traces pass through treatment to rivers. A small source of mothproofer occurs in a direct discharge in Horsforth area and another from Rodley sewage treatment works. The principal problem for the Aire from chemical wastes is from Esholt sewage treatment works. Significant levels of herbicide residues are discharged from the works outfall, the source of these contaminants is from tankered-in waste. Copper is a problem downstream of IMI Yorkshire Alloys Ltd and Skelton Grange Power Station, as significant quantities are discharged to Stourton Beck. Oil Mill Beck receives significant levels of industrial pollution from Leeds / Bradford airport. Some industries have consent conditions to discharge effluent directly to the river where maximum permissible levels are set. The locations of these industries are shown in figure 4.5. Industrial effluent discharged to sewerage systems forms 40 % of the total load treated. Of this: 42.8 % is from the textile industry; 30.2 % food and drinks industry; and 17.4 % chemical industry (Yorkshire Water, 1994).

4.3.2.3 Agriculture

Diffuse pollution from land runoff / pesticide spraying is highly difficult to quantify. Discharges of silage, liquor, slurry and other farm waste can cause serious pollution problems. Pollution incidents have occurred over the last few years on Gill Beck, Oil Mill Beck, Meanwood Beck and on the Aire at Newlay. Surveys by the Environment Agency on Oil Mill Beck have identified a number of sources of farm pollution. Pesticides and fertilisers contain various concentrations of all heavy metals and are known to be used regularly on land at Apperley Bridge and Kirkstall respectively.

4.3.2.4 Waste disposal

There is a large quantity of a wide range of wastes generated within the Aire catchment, due largely to the urban and industrial nature of the areas surrounding the lower Aire. Many of these wastes are disposed of in the immediate locality and have been so for many years. The disposal of household, municipal and industrial wastes can lead to pollution of soil and surface waters with heavy metals, through site contamination and in leachates. There is a large number of waste disposal sites in the area, reflecting different standards of design for containment of all waste and leachate, depending on when they became operational (figure 4.5). Calverley picnic area is a reclaimed refuse tip. Unlicensed dumping of wastes occurs all along the river and is a particular problem downstream of Knostrop sewage treatment works, where the dumping of tyres and household appliances is widespread.

4.3.2.5 Atmospheric deposition

In highly industrialised and urbanised catchments, atmospheric contributions to runoff water quality have been found to be considerable. The atmosphere is an important transport medium for metals from various sources. Metals are largely contributed by motor vehicle traffic (lead, zinc, copper and chromium). Lead in petrol is the largest single source of air pollution. Other sources of metals from atmospheric deposition are industry and fossil fuel combustion. Fossil fuel combustion results in the dispersion of a wide range of heavy metals including lead, cadmium, chromium, arsenic, zinc and copper over a very large area, although not all these elements are present in significant concentrations in all types of coal and petroleum. Small amounts of metals are deposited from the sludge incinerator at Esholt wastewater treatment plant and are soon to be at Knostrop, where an incinerator is currently being built. Incinerators reduce the quantity of solid material to be disposed of and render the residue virtually inert. Gaseous emission (mg/m^3) of heavy metals from the sewage sludge incinerator at Esholt are as follows: cadmium 0.001; mercury 0.022; other metals 0.07 (Yorkshire Water, 1994).

4.3.2.6 Urban runoff

Efforts in improving water quality have focused on point sources. In many cases, only limited improvement in water quality has been achieved and non-point sources are likely to control any further improvement. Urban runoff is a major non-point source. Some 35 % of the total annual pollutant levels discharged to receiving waters in the UK comes from CSO's which operate 2 - 3 % of the time (Pain, 1993). Urban stormwater runoff contains materials that have been deposited by wet and dry precipitation, from abrasion of roads and transportation materials, from legitimate commercial industrial and residential activities and occasionally materials that have been illegally dumped or disposed (Dempsey et al., 1993). Traffic by products, gasoline, oil drippings, tyre residuals, brakewear, vehicle exhaust and metallic corrosion are also major contributors to pollutant accumulation (Ellis, 1979). Elevated levels of copper, lead, zinc and cadmium are also due to corrosion within the urban water supply network (Förstner and Wittmann, 1981).

Novotny et al. (1993) in a study of sediment contamination sources in the Milwaukee River, Wisconsin, over a period of more than 100 years, found that urban runoff was to be the most significant source. Some 40 - 75 % of metals of the total receiving stream input budgets can be derived from highway runoff sources (Novotny et al., 1993). Urban street surfaces are identified as potentially significant contributors to water pollution both as sources of chemical pollutants and as pathways for the transport of pollutants originating from adjacent areas (Sartor and Gaboury, 1984). Shown in table 4.2 are the mg/kg concentrations of various heavy metals found in urban street dirt.

Table 4.2 - Average pollutant concentration of street dirt (mg/kg) *(after Sartor and Gaboury, 1984)*

Arsenic	Cadmium	Chromium	Copper	Lead	Mercury	Zinc
15	3	200	100	1000	0.08	300

Hence urban stormwater runoff has long been recognised as a major source of pollutants to surface waters. The removal by runoff processes is responsible for the high maximum metal concentrations which have been found in stormwater suspended sediments, cadmium 670 $\mu g/g^{-1}$, copper 1660 $\mu g/g^{-1}$, lead 8500 $\mu g/g^{-1}$, zinc 8000 $\mu g/g^{-1}$ (Hamilton et al., 1984). The chemical association of metals in the neutral highway sediments (pH 6.7) indicate that their overall availability to the soluble phase of stormwater runoff is in the order cadmium > zinc, lead > copper (Hamilton et al., 1984). The transport pathways and effects of particulate associated metals depend on the size spectrum of particles and also on the chemical speciation. Measurements on metal size distributions indicate that about 50 % by mass of cadmium, copper, lead and zinc in road sediments can be associated with particles of < 500 μm. Only particles larger than 250 μm are generally removed efficiently by conventional street cleaning procedures leaving behind the finer contaminated particulates which are more readily flushed into the stormwater system (Sartor and Gaboury, 1984).

Figure 4.5 shows the present main sources of heavy metal contaminants to the River Aire in Leeds. There are at present 190 consented traders who discharge to Esholt and 328 who discharge to Knostrop sewage treatment works. Final effluent for 1996 from both sewage treatment works is illustrated in the tables below. The majority of trade discharges to Esholt are from Bradford and Shipley and several from north west Leeds (Guiseley and Yeadon), these are not shown on the map. Out of the 328 trade discharges to Knostrop, only those that contain heavy metals in their effluent are considered, mentioned along with the nature of the industry. For confidentiality reasons the name of the business remains anonymous.

Table 4.3 - Final effluent Esholt sewage treatment works, 1996 *(data from Yorkshire Water)*

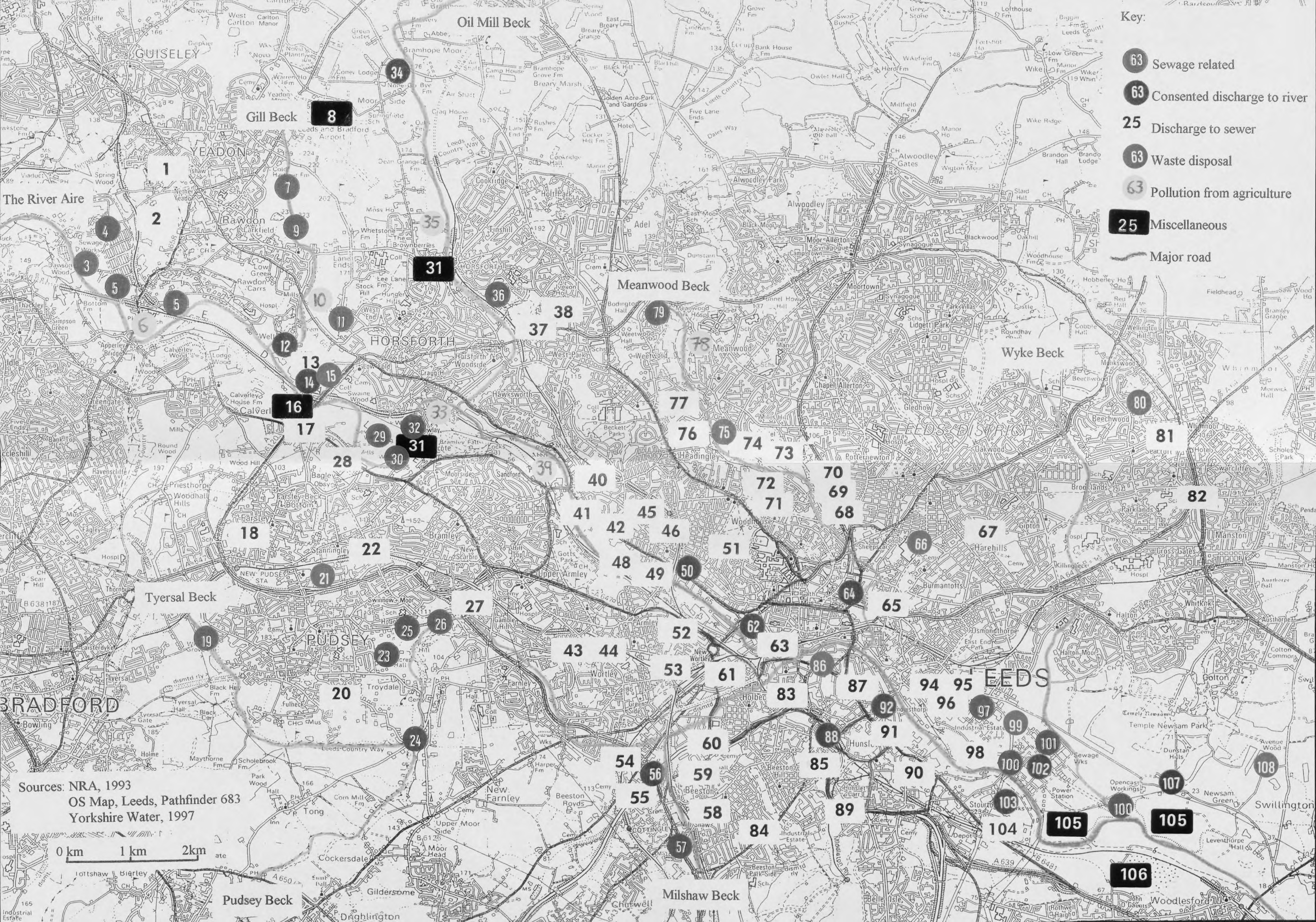
μg/l	Mean	Minimum	Maximum
Lead dissolved	1.57	1.00	2.44
Mercury filtered	0.03	0.02	0.05
Mercury total	0.05	0.02	0.10
Arsenic filtered	2.73	1.58	4.40
Arsenic total	2.84	1.93	3.91
Cadmium filtered	0.18	0.10	0.47
Cadmium total	0.30	0.10	0.65
Copper filtered	12.00	1.00	20.60
Copper total	22.40	7.56	37.00
Zinc total	49.30	32.50	60.00
Chromium filtered	7.54	4.69	8.38
Chromium total	4.52	1.00	11.60

Table 4.4 - Final effluent Knostrop sewage treatment works, 1996 *(data from Yorkshire Water)*

µg/l	Mean	Minimum	Maximum
Lead dissolved	2.12	1.00	3.67
Mercury filtered	0.02	0.02	0.02
Mercury total	0.02	0.02	0.03
Arsenic filtered	2.40	1.85	3.05
Arsenic total	2.91	2.02	6.43
Cadmium total	0.15	0.10	0.25
Copper filtered	6.23	4.73	8.93
Copper total	10.66	5.95	20.20
Zinc total	32.66	16.00	72.00
Chromium filtered	3.36	1.00	7.57
Chromium total	13.74	1.96	33.30

Figure 4.5 - List of present industries / sources

1 Metal Platers (Cu, Cr, Zn)
2 Metal Platers (Cu, Cr, Zn)
3 Esholt Sewage Sludge Incinerator (Cd, Hg)
4 Esholt Sewage Treatment Works (all)
5 Final Effluent Outlets - Esholt STW (all)
6 Pestcide Application (Cu, Pb, Zn)
7 Final Effluent, Rawdon WPC Works (all)
8 Leeds / Bradford Airport (Cu, Pb, Zn)
9 Problematic CSO's, Gill Beck (all)
10 Pollution from Agriculture, Gill Beck (Cu, Pb, Zn)
11 Stanhope Hotel Private Sewage Treatment Works
12 Colourflex (Dyers) (Cr, Cu, Zn)
13 Chemical Manufacture & Formulation (Cr)
14 Sandoz Pharmaceutical Products (Cr, Cu)
15 Waste Disposal Site (Cd, Zn)
16 Former Refuse Tip (Cd, Zn)
17 Tower Hydraulics Ltd (Engineering Works) (Pb, Zn)
18 Photographic Works (Zn)
19 Problematic CSO's, Tyersal Beck (all)
20 Printing Works (Cu)
21 Waste Disposal Site (Cd, Zn)
22 Metal Platers (Cr)
23 Smalewell Sewage Treatment Works (all)
24 Union Bridge Mill Sewage Treatment Works (all)
25 Site of Sewage Pollution, Pudsey Beck (all)
26 Problematic CSO's, Pudsey Beck (all)
27 Photographic Works (Cu, Cr, Pb, Zn)
28 Metal Processors (Cd, Cr, Cu, Zn)
29 Rodley Sewage Treatment Works (all)
30 Final Effluent Rodley WPC Works (all)
31 Moth Proofers - Direct Discharge (Cr)
32 Site of Sewage Pollution, River Aire (all)
33 Pollution from Agriculture, River Aire (Cu, Pb, Zn)
34 None-Go-Bye Farm (Cu, Pb, Zn)
35 Pollution from Agriculture, Oil Mill Beck (Cu, Pb, Zn)
36 Site of Sewage Pollution, Oil Mill Beck (all)
37 Printing Works (Cu)
38 Photographic Works (Cr)
39 Pollution from Agriculture (Cu, Pb, Zn)
40 Printing Works (Cr)
41 Photographic Works (Cr)
42 Photographic Works (Cu, Zn)
43 Metal Platers (Cr, Cu, Pb, zn)
44 Metal Platers (Cr, Cu, Zn)
45 Photographic Works (Cu)
46 Photographic Works (Cu)
47 Photographic Works (Cr)
48 Photographic Works (Cr, Cu, Pb, Zn)
49 Photographic Works (Zn)
50 Associated Dairies (Cu, Zn)
51 Photographic Works (Cr)
52 Engineering Works (Cd, Cu, Pb, Zn)
53 Printing Works (Cr)
54 Engineering Works (Cr, Cu, Zn)
55 Miscellaneous Manufacturing Works (Pb)
56 Pland Stainless Ltd (Cd, Cr, Cu, Zn)
57 Problematic CSO's, Milshaw Beck (all)
58 Engineering Works (Cr, Cu, Zn)
59 Engineering Works (Cr, Cu, Zn)
60 Engineering Works (Zn)
61 Photographic Works (Cr)
62 Doncaster - Monkbridge Iron Works (Pb, Zn)
63 Engineering Works (Cr)
64 Shell (UK) Ltd (Cu, Zn)
65 Engineering Works (Pb, Zn)
66 Waste Disposal Site (Cd, Zn)
67 Printing Works (Cr)
68 Tannery (Cr)
69 Engineering Works (Cr, Cu, Zn)
70 Photographic Works (Cu)
71 Printing Works (Cr)
72 Printing Works (Cr)
73 Engineering Works (Cr, Cu, Zn)
74 Photographic Works (Cr)
75 Waste Disposal Site (Cd, Zn)
76 Engineering Works (Cr, Cu, Zn)
77 Tannery (Cr)
78 Pollution from Agriculture Meanwood Beck (Cu, Zn)
79 Problematic CSO's, Meanwood Beck (all)
80 Waste Disposal Site (Cd, Zn)
81 Printing Works (Cr)
82 Engineering Works (Zn)
83 Metal Platers (Cd, Cr, Cu, Zn)
84 Printing Works (Cu)
85 Photographic Works (Cr)
86 Waste Disposal Site (Cd, Zn)
87 Metal Processing (Cd, Cr, Zn)
88 Brown Bros (Vehicle Wash) (Zn)
89 Photographic Works (Cr)
90 Metal Platers (Cd, Cr, Cu, Zn)
91 Chemical Manufacture & Formulation (Cu, Zn)
92 Oil Rail Terminals (Pb, Zn)
93 Metal Platers (Cd, Cr, Cu, Zn)
94 Metal Platers (Cd, Cr, Cu, Pb, Zn)
95 Miscellaneous Manufacture (Zn)
96 Fell Mongers (Cr)
97 Knostrop Sewage Sludge Incinerator (Cd, Hg)
98 Environmental Works (Zn)
99 Waste Disposal Site (Cd, Cr, Cu, Hg, Pb, Zn)
100 Final Effluent Outlets - Knostrop STW (all)
101 Knostrop Sewage Treatment Works
102 Skelton Grange Power Station (Cd, Cu, Pb, Zn)
103 IMI Yorkshire Imperial Ltd (Cu)
104 IMI Yorkshire Alloys Ltd (Cr, Cu)
105 Open Cast Mining (all)
106 Mining Spoil Heaps (all)
107 Skelton Open Cast Coal Mining (all)
108 Waste Disposal Site (Cd, Zn)



Sources: NRA, 1993
OS Map, Leeds, Pathfinder 683
Yorkshire Water, 1997

Figure 4.5 - Present sources of heavy metal pollution

CHAPTER 5

METHODOLOGY

5.1 Sampling Methodology

5.1.1 Introduction to sampling methodology

In order to establish heavy metal concentrations of soil and sediment, many analytical techniques have been used. To yield reliable and meaningful results, the sampling procedure must be conducted so that the characteristics of the sampled material coincide with those of the entire unit, for which the information is required. A representative sample must be collected for analysis which fulfills this criteria, but which is manageable for the analytical technique employed.

This study allows for the inherent lateral and vertical variability of soil materials. The extent of this variation is seldom known beforehand and hence sufficient samples must be taken to characterise variability (Grimshaw, 1989). In the soil environment, pedogenic processes may stratify soil components, especially heavy metals. 'The total mass of a trace element in a sample is small (μg/g) and is not always homogeneously distributed and in many cases can be considered as a major constituent in a very minor phase, the smaller the volume of that phase, the more difficult adequate sampling becomes' (Hamilton, 1980). Hence, the sample should be of sufficient size to allow for the heterogeneity of environmental samples and be taken from various depths in the soil profile.

On return to the laboratory, the samples were analysed and tested as soon as was possible after collection. The analytical techniques selected should be efficient and yield accurate and reproducible results. Various types of soil and sediment samples were collected, including contemporary within channel and river bed sediment, floodplain surface and subsurface soils, suspended sediments and sediment cores. Each requiring different sampling techniques. These are discussed individually in the following sections.

5.1.2 Contemporary within channel sediments and floodplain soils

Contemporary sediments, which are fine grained, within channel river alluvium, were sampled from both sides of the river at regular intervals between Apperley Bridge, upstream, to Swillington Bridge, downstream (figure 5.1). The sampling interval was generally 0.5 km, or more frequent, but in certain areas was dictated greatly by access, particularly through the city centre of Leeds. Overall, 72 contemporary within channel sediment samples were collected, using a stainless steel trowel, cleaned prior to collecting each sample to reduce contamination. Stainless steel is the most durable material for sampling devices.

Soil samples were collected across the floodplain surface and subsurface at approximately 1 km intervals, from floodplains on both sides of the river (figure 5.1). Lateral variations in the chemical composition of surface sediments act as a guide to local pollution centres. Throughout the city centre of Leeds, from between 10 - 20 km downstream of the study area, there are no floodplains and only contemporary within channel sediments were collected. Samples were taken, from the floodplain surface (0 - 20 cm) and subsurface (20 - 50 cm) along transects with increasing distance from the river, sampling overbank deposits, then at 25 m intervals to the edge of the valley side. A total of 74 surface and 64 subsurface samples were collected.

For all samples usually about 100 g of sediment was collected, where particle-size was to be analysed larger samples were taken. Samples were returned to the laboratory in polythene bags, clearly labelled, but not in contact with the soil. Contemporary within channel sediments, floodplain surface and subsurface soils were tested for pH, organic matter content, total metals (nitric-perchloric digestion) and a selection of the samples tested for particle-size analysis and sequential extraction. AAS was used to analyse the samples.

5.1.3 Contemporary river bed sediments

The dispersal of heavy metals in a river bed depend on hydrological factors such as the current velocity and turbulence, the depth and morphology of the channel and

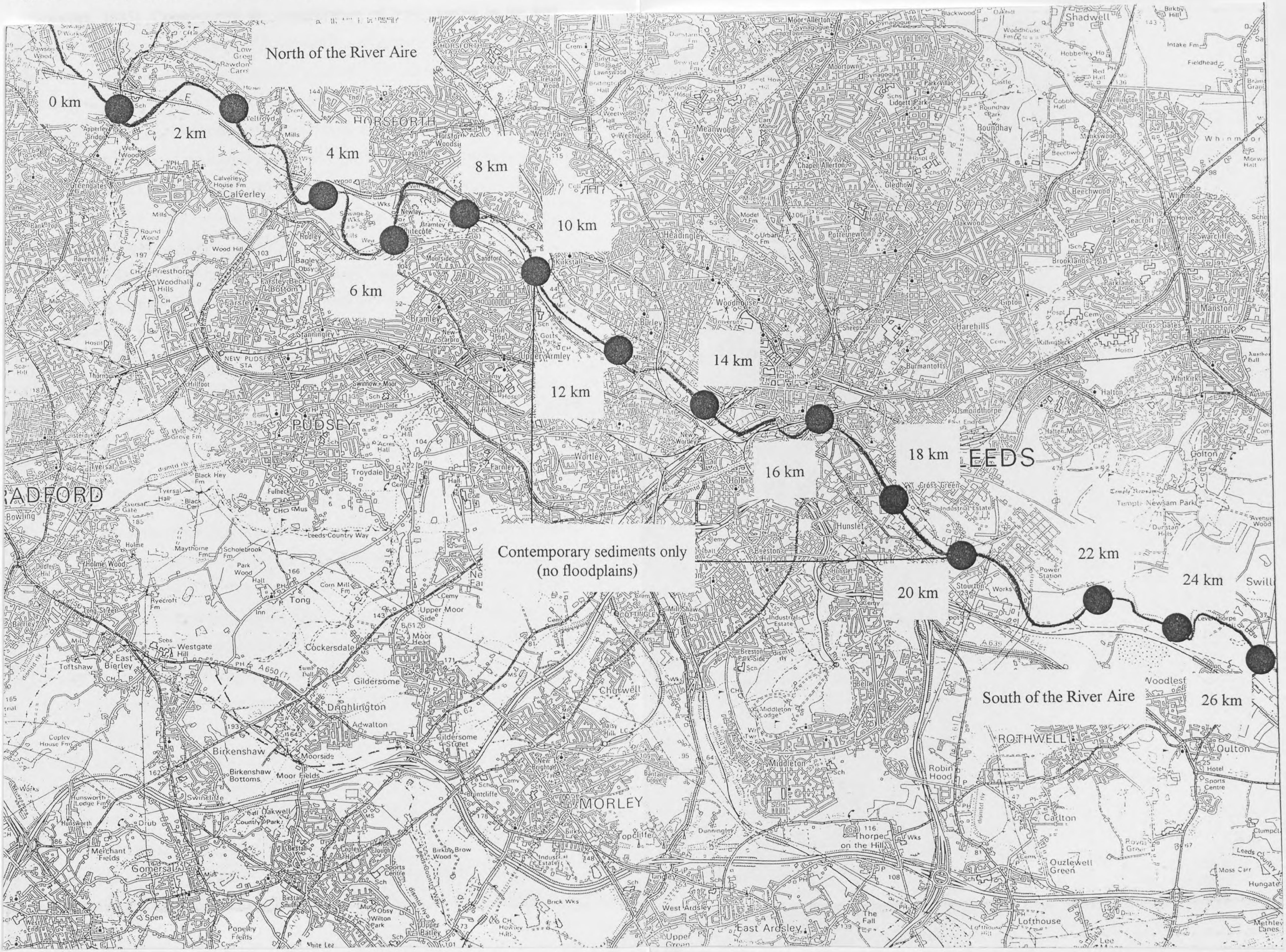


Figure 5.1 - Sampling sites for contemporary & floodplain soils

on physical parameters such as the density and size of the transported particles (Horowitz, 1985). Consequently the concentration of heavy metals in the bed sediments exhibit non-uniformity. Fine grained, contemporary river bed sediments were collected using a sediment grab technique at 1 km intervals downstream of the study area (a total of 23 samples). The sediments were taken from the centre of the channel, or as close to the centre that could be reached. Again about 100 g of sediment was collected in labelled polythene bags. These sediment samples were tested for pH and total metals (nitric-perchloric digestion), and analysed by AAS.

5.1.4 Suspended sediments

Suspended sediment plays a key role in the geochemical and biological cycling of heavy metals in aquatic systems. Many problems are associated with using this sample medium. Of particular concern, are the short and long-term spatial and temporal variations in the distribution and concentration of suspended sediment and associated heavy metals that commonly occur in fluvial systems. However, suspended sediment sampling and subsequent chemical analysis are a requisite for any type of budget or flux calculation.

Suspended sediments collected by LOIS were analysed over a flood event at Thwaite Mills on the River Aire (figure 5.2) and from various high flow events on several Ouse tributaries, including the Aire, Calder, Nidd, Swale, Ure, Wharfe and the Ouse itself (figure 5.3). The degree of variability in the concentration of particulate-associated contaminants is highly dependent on the origin of the sediment, the nature of the sediment and the processes governing the erosion and transport of the sediment (Droppo and Jaskot, 1995). The purpose of analysing suspended sediment from other Ouse tributaries was to compare heavy metal concentrations in sediment from different river catchments, such as urban and industrial and mining and rural.

The collection of representative samples is of paramount importance, as it is impossible to sample and analyse an entire water body. Unfortunately representative sampling in fluvial cross-sections to determine suspended sediment concentration and the subsequent quantification of associated metals, has long been a subject of controversy (Horowitz, 1995). Suspended sediment concentrations display marked spatial and temporal variability. In a stream cross-section, for measurement, the sampling device is required to provide a representative sample at a particular point or zone within the channel. For this, three major requirements must be fulfilled:

(1) flow velocity in the sampler intake should be the same as stream velocity;
(2) the presence of the sampler should cause a minimum disturbance to the flow at the sampling point; and
(3) the sampler intake should be orientated into the flow in both the vertical and horizontal planes (Bradley, 1984).

Thwaite Mills, River Aire, (figure 5.2) lies approximately 2 miles outside Leeds city centre (NGR SE 32700 31200) very close to Knostrop sewage treatment works. The mill, once water-powered, crushed stone to produce putty and paint in the nineteenth century. At Thwaite Mills, water samples were collected by an Epic bulk water sampler at an Environment Agency gauging station. The sampler, triggered by stage is set to extract water samples of about 500 ml at 2, 3, and then 4 hour intervals, over the flood event. The sampling period ran from 09.30 a.m. 10th February to 08.30 a.m. 13th February 1996, collecting a total of 24 samples. Approximately 450 ml of the water is filtered off for the suspended sediment which is dried on pre-weighed filter paper in an oven at 80°C and the dry weight of the sediment recorded. The suspended sediment and filter paper then went forward for sequential extraction and subsequent AAS analysis. Because the samples are collected for the analysis of the water, they do not yield a sufficient mass of solid material for the analysis of any techniques other than sequential extraction.

For the Ouse tributaries a total of 25 samples (5 from the Aire, 2 Calder, 1 Nidd, 8 Ouse, 5 Swale, 2 Ure and 2 Wharfe) were collected by hand. This involved dropping a 1 l plastic bottle into the middle of the river during events. The samples

Figure 5.2 - Thwaite Mills, River Aire

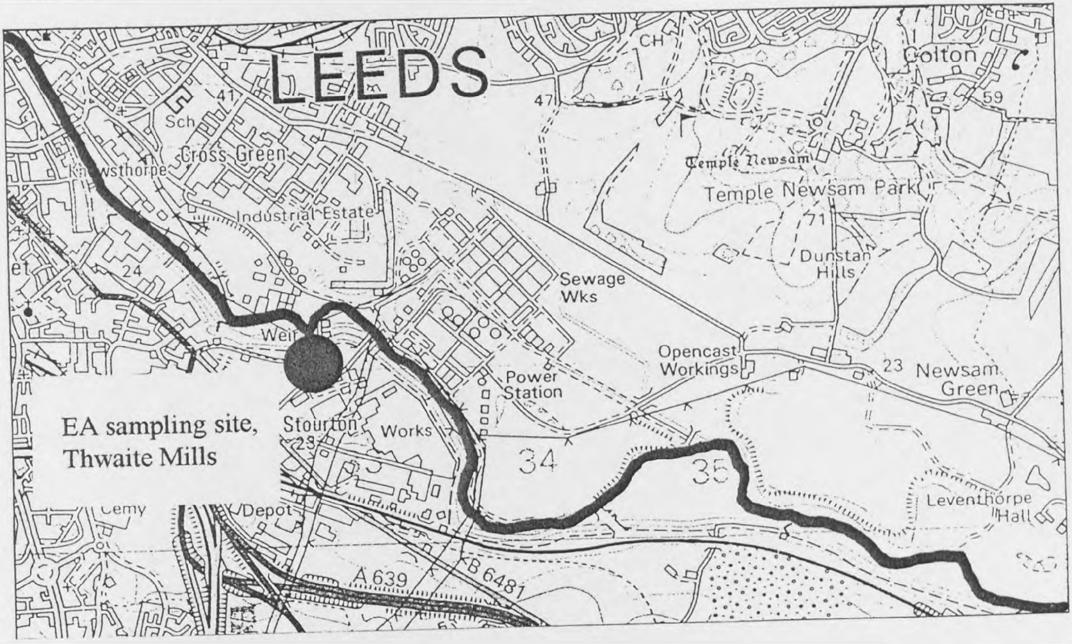
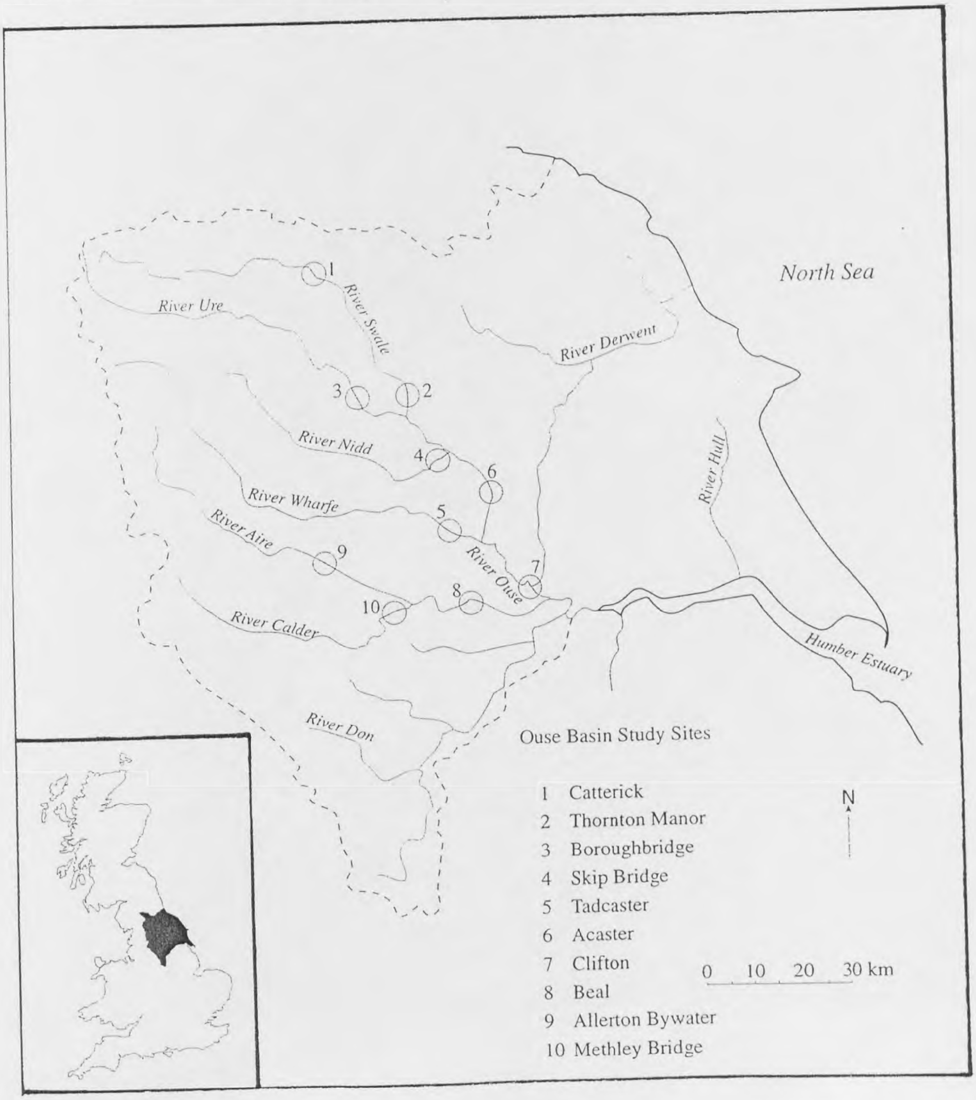


Figure 5.3 - Sampling locations on the Yorkshire Ouse tributaries



were treated and analysed in exactly the same way as those from Thwaite Mills. The sample locations can be seen in figure 5.3.

Triggering methods and sampling frequency are important technical problems because automatic samplers are triggered by changes in stage. However, temporal variations in suspended sediment and associated heavy metal concentrations can occur with and without detectable changes in discharge. Furthermore, many fluvial systems display hysteresis loops with regard to discharge and suspended sediment; that is, the suspended sediment peak may precede, or lag behind, the discharge peak. Thus stage may not be the most appropriate method to trigger automatic samplers to obtain adequate coverage of temporal changes. Manually sampling suspended sediment is likely to produce the least precise estimates of the annual flux of suspended sediment and associated heavy metals. However, when resources are limited and temporal variations are not important to the end use of the chemical analyses, this type of technique is acceptable.

5.1.5 Sediment cores

Sediment cores provide a historical record of events occurring in a watershed and enable a reasonable estimate of the background level and changes in input to a river system over an extended period of time (Förstner and Wittmann, 1981). Sediment cores have been used to evaluate heavy metal accumulations because:

(1) they are relatively independent of weathering;
(2) sedimentary deposits, in general, increase at a fairly constant rate per year;
(3) sedimentary material serves as scavengers for trace metals; and
(4) they are usually found outside the sphere of human modification, but frequently contain an anthropogenic anomaly that can be specifically dated (Wolfenden, 1977).

Location of the cores was determined by an initial survey of the study area to find the most favourable and accessible sampling sites. The sites had to fulfil the following conditions:

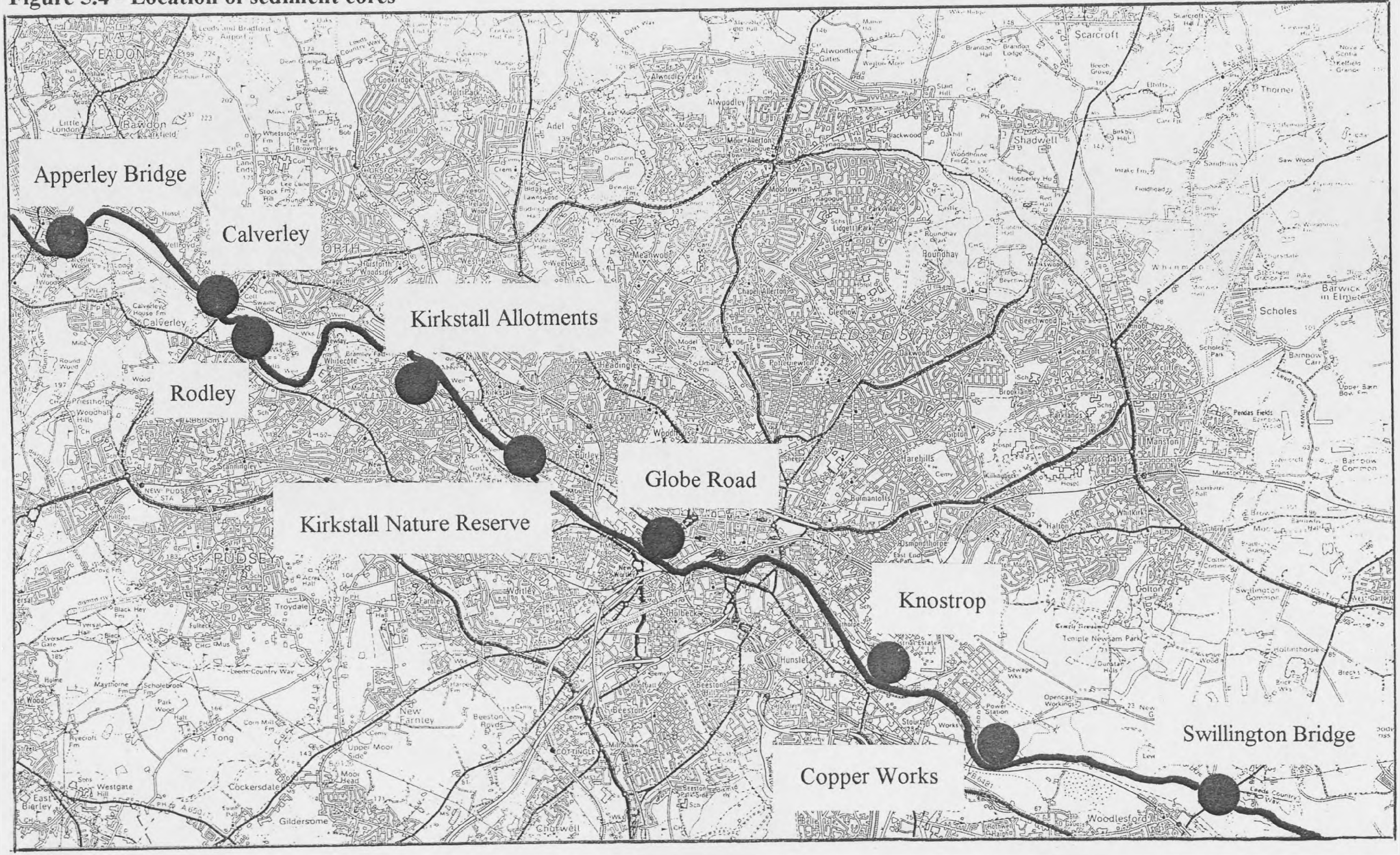
- the site had to be free of underground cables of electric, gas, water and telephone origin;
- vehicle access was available within practical carrying distance of extremely heavy equipment to the site;
- the floodplain was extensive enough to be in accordance with Environment Agency regulations, to prevent river bank instability, no ground drilling is permitted within 8 m of the bank; and
- permission was obtained from the landowner, private or public.

As a result of the highly developed Aire catchment in Leeds, site location was restricted. Sixteen cores were sampled at nine locations (figure 5.4), however, only one core at each location is considered in the present study. The length of the sediment cores varied between 2.9 and 5.6 m, regulated by the depth to the underlying bedrock, where coring ceased. From the cores used a total of 201 individual samples were collected.

Sediment cores with a diameter of 8 cm were sampled using a petrol driven Van Walt corer. The meter long steel corer was driven into the ground using a vibrating engine. The corer containing the sediment was then carefully extracted to avoid loss of sample using a manual jack. Individual samples were taken at regular intervals along the length of the sediment section and stored in separate polythene bags. Additional meter long extension poles were fitted to the corer allowing sampling at depths of up to 8 m.

All samples were tested for pH, organic matter content, total metals (nitric acid digestion) and sequential extraction (approximately one sample from each metre section of the core). The solutions analysed by ICP-AES. An additional method was carried out on a limited number of samples to help date the sediments (radiocarbon dating techniques) and to quantify heavy metal inputs over time, the method for which is outlined below.

Figure 5.4 - Location of sediment cores



5.1.5.1 Radiocarbon dating

Pieces of wood were found in two separate cores, one at Kirkstall Nature Reserve at a depth of 465 cm and the other at Stourton, near a copper works, at a depth between 480 - 500 cm. These samples were sent to Beta Analytic Radiocarbon Dating Laboratory in the USA. The materials were measured by the radiometric technique, analysed by synthesising the sample carbon to benzene (92 % C), measuring for C^{14} content in a scintillation spectrometer and then calculated for radiocarbon age. The 'conventional C^{14} age' is then calibrated into calendar years. Radiocarbon dating can be used to interpret the pollution history in the core.

5.2 Laboratory Analysis

5.2.1 Introduction to Laboratory Analyses

To determine the chemical and physical properties of the soil and sediment collected, pH measurements, organic matter content, particle-size distribution, total metal content and the selective sequential extraction of metals into specific chemical fractions have been undertaken. For suspended sediment, which was not collected in sufficient quantity, only sequential extraction has been carried out. These procedures are outlined in this section.

On return to the laboratory samples were air dried, lightly ground using a pestle and mortar, to pass a < 2 mm aperture plastic sieve. This fraction was retained and used for each analysis unless otherwise indicated. For some experiments oven dry sediment was required and where stated the sample was dried in an oven at 105°C for at least 12 hours.

Serious losses of heavy metals may occur by sorption on the materials to which the samples are exposed during storage and measurement, invalidating the final results. Likewise, several heavy metals are incorporated in plastics during their manufacture and are often present in a leachable form (Scott and Ure, 1972). Zinc is especially troublesome. To prevent losses of metals, or contamination of samples through past uses of equipment, or metals leached from plastic, prior to use all containers, glassware, etc. were soaked in 15 % nitric acid for 48 hours to remove metals from inner surfaces (Massee and Maessen, 1981). After soaking in acid, the equipment is rinsed well in distilled water and oven dried.

The concentration of heavy metals in total metal and sequential extractions were determined using a Pye Unicam atomic absorption spectrophotometer with SP9 computer and a Maxim System ICP-AES (section 5.2.8). All metal concentrations were the mean of three assays. Metals that were determined by AAS include cadmium, copper, lead and zinc. ICP-AES which is more sensitive and able to detect metals at much lower concentrations than AAS, also determined arsenic, chromium and mercury.

All reagents used in the analysis were AnalaR grade or better. Analytical precision and accuracy was determined by blank duplicates, replicate samples and standard reference material (section 5.2.9).

5.2.2 pH

The pH of soil and sediment can give valuable information regarding associated soil properties and the likely mobility and bioavailability of several heavy metals (Hesse, 1971). In general, the capacity of soil for most heavy metals is increased with increasing pH, with the maximum under neutral and slightly alkaline conditions (Adriano, 1986). The relative mobility of some metals in soils is influenced greatly by pH. In acidic soils (pH 4.2 - 6.6) cadmium, mercury and zinc are relatively mobile, arsenic and chromium are moderately mobile and copper and lead are slowly mobile. In neutral to alkaline soils (pH 6.7 - 7.8) arsenic and chromium are relatively mobile, cadmium, mercury and zinc are moderately mobile and copper and lead remain slowly mobile (Adriano, 1986). The adsorption of metals increases from near nil to near 100 % as pH increases through a critical range 1 - 2 units wide (Benjamin and Leckie, 1981). This means that a small shift in pH may cause a sharp increase or decrease in adsorbed metal levels. The onset of adsorption is characteristic for each metal.

Procedure

50 ml of distilled water is added to 20 g of air-dried soil (ratio 1:2.5). The mixture is stirred occasionally and soaked for 20 minutes to allow structural aggregates to breakdown and the soil particles to reach chemical equilibrium with the solution. Each sample is then filtered and tested using a Jenway Microprocessor pH meter, calibrated to pH 4 and 7.

5.2.3 Organic matter content by loss on ignition

All soils contain organic matter, usually in greatest amounts in the surface horizon although the proportion varies considerably from one place to another. Some heavy metals exhibit rather high affinities for soil organic matter and knowledge of its percentage content can help explain the distribution of metals within the soil profile. Usually the amount of organic material in a soil or sediment is found by the loss in weight of the sample as the organics are burnt off (Bradley, 1984). However, this is not a true measure of organic matter as other losses may occur. For example, loss of water due to dehydration of silicates or organic colloids (Davies and Lewin, 1974); oxidation of reduced compounds (Bradley, 1984). This error is relatively more serious for soils low in organic content, but is considered to be a good approximation in all other soils (Grimshaw, 1989). Some controversy exists over the exact temperature for ignition purposes at which optimal results can be obtained. At lower temperatures of 375°C variations due to water losses are prevented, whilst complete combustion is not assured. At higher temperatures above 500°C where complete combustion is guaranteed, losses of volatile minerals have been reported (Grimshaw, 1989). For a wide range of soils 550°C has been found to give satisfactory results and was used in the method described below.

Procedure

A known quantity of oven dry soil / sediment was weighed into a crucible and heated in a Carbolite muffle furnace at 550°C for 6 hours, cooled and reweighed. The percentage of organic matter was calculated using the equation below:

$$\text{Loss on ignition} = \frac{\text{weight loss (g)}}{\text{oven dry weight (g)}} \times 100$$

5.2.4 Grain-size effects

One of the most significant factors controlling sediment capacity for retaining heavy metals is grain-size (Horowitz, 1985). In general, metals are not homogeneously distributed over the various grain-size fractions and large differences in total metal concentrations are observed in sediment samples from a single locality (Leenaers, 1989). Within the grain-size spectrum the fine grained fraction, consisting mainly of clay minerals show high metal contents. In the silt and fine sand fractions, the metal concentrations generally decrease as that fraction is dominated by the quartz components with low metal contents. Therefore, the fraction < 63 µm was used in some analyses for the reasons outlined in section 2.4. Salomons and Förstner (1984) suggested that separation of grain-sizes prior to analysis, obtained better results than applying methods to correct for grain-size differences once the techniques had been carried out.

Sediment (< 63 µm) was used for total metal analysis for contemporary within channel sediment, contemporary river bed sediment and floodplain soils. With regard to the sediment cores, the fraction < 2 mm was used. The reason being that grain-size differed markedly between core sites and with depth in an individual core, where sediment usually increased in coarseness with depth. At depth in some cores it would be very difficult to get sufficient, if any, material of grain size < 63 µm. When considering the results from the sediment cores, the lack of correction for grain size will have to be taken into account.

With regard to sediments being analysed by sequential extraction, sediments < 2 mm were used, as it was found in a preliminary study, regardless of the fraction used from a sample, the chemical speciation pattern was essentially the same. The results of this study are included in Appendix I. Leenaers (1989), in sediments from the River Geul, also found that virtually no difference existed between the < 63 µm and the > 63 µm fractions. In terms of both the total amounts of lead, zinc and cadmium that were potentially mobile and the distribution of metals over the host fractions.

5.2.5 Background concentrations

To determine the extent of anthropogenic pollution in a fluvial system, it is of primary importance to establish the natural level of these substances. This is the 'pre-civilisational' level, which is then subtracted from existing values for metal concentration, in order to derive the total enrichment caused by anthropogenic influences. The Average Shale, Global Standard Value (Förstner and Wittmann, 1981; Salomons and Förstner, 1984) was used as it fulfils the following criteria, so as to achieve representative values for metal concentration.

A large number of sediment samples must be analysed, which correspond with recent deposits in their:

(a) grain-size distribution;
(b) material composition;
(c) conditions of origin; and
(d) which are uncontaminated by civilisational influences.

The rock standard is a world-wide standard in general use and satisfies the basic requirement of being uncontaminated and based, for most elements, on a large number of sediment samples. Background concentrations used in the present study are shown in Appendix I.

5.2.6 Total heavy metal extraction

Analysis of the total concentration of heavy metals in soil and sediment involves acid digestion of the sample, primarily to solubilise the metal but also to oxidise any organic material in the sample, hence freeing the metal and removing probable analytical interferences. A variety of mineral acid mixtures are reported in the literature for extracting heavy metals from soils and sediments, most notably hydrofluoric (Allen et al., 1989), perchloric (Thompson, 1983), sulphuric (Maxwell, 1968), nitric (Harrison and Laxen, 1976) and hydrochloric (Sinex et al., 1980), either separately or in combination. Each extractant has its advantages and limitations. Hydrofluoric acid must be used to breakdown silicates for complete decomposition, however the procedure is time consuming and hazardous, requiring extra caution. For routine analysis a more moderate extraction is usually undertaken.

Two acid extraction systems have been used on soil and sediment. The majority of samples were digested using a (1 + 4) mixture of nitric and perchloric acids, according to the method of Thompson (1983). The sediment core samples, due to the very large number which were to be treated and analysed and time and financial constraints, were digested with nitric acid following the method outlined by Harrison and Laxen (1976). Neither extraction removes the total metal content from the sample matrix. However, such systems may closely reflect the metals available in the environment and therefore more suitable for the analysis of environmental materials than hydrofluoric extraction schemes (Förstner and Salomons, 1980). Thompson (1983) concluded that the metals cadmium, copper, lead and zinc could be determined satisfactorily after a (1 + 4) nitric and perchloric acid digestion and that concentrated nitric alone has a less vigorous effect than the mixed acid, but is an efficient method for cadmium, copper, lead, mercury and zinc. Sinex et al. (1980) in comparing several acid mixtures with respect to their heavy metal yields from test samples, found that nitric acid alone was not as efficient as the other mixtures and by refluxing with 90 HNO_3 - 10 HCl recovery was increased by 7 - 10 %. However, Clayton and Tiller (1979) stated that extracting heavy metals into solution using concentrated nitric acid is substantially faster than using hydrofluoric acid and that the methods provide a reasonable approximation to total metal concentration. Harrison and Laxen (1976) found that all the methods discussed gave a quantitative recovery of metals within the limits of experimental error.

Procedure nitric - perchloric acid extraction

The sample (1 g), oven dry, 63 μm soil / sediment was accurately weighed into a beaker and digested initially with just nitric acid (20 ml). Pre-treatment with nitric is essential in order to reduce the danger of explosion which may occur with hot perchloric acid in contact with organic matter. The beaker is covered and its contents heated to 150°C to oxidise the organic matter. Heating is continued and evaporated almost to drying. 10 ml of 1 + 4 nitric / perchloric acid mixture is added and the solution digested until dense white fumes of acid appear. After cooling, the residue is dissolved in 1M HCl and filtered (Whatman No. 1) made up to 50 ml with hydrochloric acid. Metal concentrations were then determined by AAS.

Procedure nitric acid extraction

Concentrated nitric acid (20 ml) was added to oven dry < 2 mm soil / sediment (2 g) in a covered, lipless, tall-form beaker and allowed to stand overnight. The beaker was then placed on a hot plate and the solution refluxed for 8 hours. The watch glass was then removed, the contents evaporated down to approximately 5 ml. After cooling, the solution was then filtered (double Whatman No. 1) and the filtrate made up to 50 ml with 0.5 % nitric acid. Metal concentrations were then determined by ICP-AES.

5.2.7 Sequential extraction

In assessing the environmental impact of trace metals, information on total concentration alone is not sufficient, as this implies that all forms of a given metal have an equal impact on the environment. However, certain fractions may be enriched in several elements thus their chemical forms and availability is an important consideration. The solid material can be partitioned into specific fractions which can be extracted selectively by using appropriate reagents. The use of sequential extraction although more time consuming, furnishes detailed information regarding the origin, mode of occurrence, biological and physicochemical availability, mobilisation and transport of heavy metals (Tessier et al., 1979).

Geochemical sequential extraction procedures were used to differentiate chemical forms of metals in sediments. The technique was not carried out on every sample collected, where possible representative samples were chosen. Sequential extraction was determined for representative floodplain surface and subsurface soils, contemporary within channel sediments and fresh flood sediments and for all suspended sediments. For the sediment cores, speciation was determined for one sample in each meter long sediment section, averaging between 5 - 6 samples from each sediment core. Analyses for arsenic, cadmium, chromium, copper, lead, mercury and zinc on a phase specific, operationally defined basis were carried out according to the method originally devised by Tessier et al. (1979), and adapted by Lum et al., (1982) and Bradley (1984), which partitions sediment-associated metal into five chemical fractions.

Procedure

0.5 g oven dry sediment was weighed into a 50 ml, high density, polypropylene centrifuge tube. For suspended sediments, the filter paper containing a known weight of sediment was placed in the centrifuge tube and extracted in exactly the same way. The extractions were:

(A) Exchangeable metal ions

The samples were extracted for 10 minutes with 8 ml of 1 M magnesium chloride at pH 7 (adjusted with ammonium acetate solution), with continuous agitation.

(B) Surface oxide and carbonate bound metal ions

The residue from (A) was extracted for 5 hours with 8 ml of 1M sodium acetate adjusted to pH 5 with acetic acid. Continuous agitation was maintained through the extraction

(C) Metals bound to Fe and Mn oxides

The residue from (B) was extracted for 6 hours at 90°C (+/- 5°C) with 20 ml of 0.04 M hydroxylamine hydrochloride in 25 % (v/v) acetic acid, with occasional agitation.

(D) Organically bound metal ions

The residue from (C) was extracted with 3 ml of 0.02 M nitric acid and 5 ml of 30 % hydrogen peroxide, adjusted to pH 2 with nitric acid (Tessier et al., 1979) by slowly heating the mixture in a water bath to 90°C (+/- 5°C). The samples were periodically agitated and after two hours a second 3 ml aliquot of 30 % hydrogen peroxide was added and the mixture heated to 90°C as before. After 3 hours, 5 ml of 1.2 M ammonium acetate in 10 % (v/v) nitric acid was added and the samples were diluted to about 15 ml and agitated for 30 minutes. The addition of ammonium acetate is to prevent adsorption of extracted metals onto the oxidised sediment.

(E) Residual metal ions

The residue from (D) was extracted with 10 ml of aqua regia (90 HNO_3 : 10 HCl), for 3 hours at 90°C (Sinex et al., 1980), then extracted for a further 3 hours with a second aliquot of 10 ml of aqua regia.

Separation of sediment from the extracting solution was effected by centrifugation (3000 r.p.m.) for 30 minutes and by filtration. The concentration of heavy metals in the extracts was determined by AAS (cadmium, copper, lead and zinc) or ICP-AES (arsenic, cadmium, chromium, copper, mercury, lead and zinc) depending on the type of sediment extracted. The analysis of sediment core samples were completed on ICP-AES largely due to the vast number of samples, in which all the metals of interest could be analysed simultaneously.

5.2.8 Criticisms of sequential extraction techniques

The use of selective chemical extraction schemes is not without criticism and a number of workers have cast doubt on the validity of the final results (Guy et al., 1975; 1978; Rendell et al., 1980). The doubts arise for two reasons:

(1) the chemical extractant may attack phases other than those intended; and

(2) once metals are liberated from one phase they may become associated with another sediment phase rather than staying in solution.

This may lead to serious misinterpretation of extraction data because the metal concentrations determined in the extract do not represent metal levels in the sediment fraction supposedly attacked (Rendell et al., 1980). Consequently the chemical fractions reported may not provide such clear-cut distinctions in reality. However, the method of Tessier et al. (1979) has been widely applied for the sequential extraction of sediments and soils and with the exception of the final extraction phase, the extractants employed were the same as those used in the present study. The method appears to have been well tried and tested and such schemes at present may give the best approximation to metals in a system where conditions are rapidly changing.

Magnesium chloride was selected as the initial reagent in the sequential extraction procedure, as sodium acetate, most extensively used in soil and sediment analysis, is thought to also possibly attack carbonates (Tessier et al., 1979).

Reagents recommended for dissolving selectively the carbonate fraction in sediment generally make use of sodium acetate (NaOAc) and / or acetic acid (HOAc) at acid pH values (Chester and Hughes, 1967). The procedure selected used 1 M NaOAc, adjusted to pH 5 with HOAc. Gupta and Chen (1975) and McLaren and Crawford (1973) have demonstrated that lower pH values lead to a partial attack of Fe and Mn oxides.

The most successful methods for leaching Fe and Mn oxides have to combine reagents to reduce these metals to their ferrous and manganous forms respectively and reagents capable of keeping in solution the relatively large amounts of metals liberated (Tessier et al., 1979). Gupta and Chen (1975) found that heavy metal concentrations were consistently higher in the leachates obtained with hydroxylamine hydrochloride and acetic acid. Tessier et al. (1979) found that the extraction of reducible iron to be essentially complete after 6 hours, any longer time would have increased the possibility of attacking fractions D and E.

Hydrogen peroxide is often used to oxidise organic matter in soil and sediment analysis even though oxidation of all forms of organic matter may not be complete. More efficient methods for destroying organic matter could be used but these may also effect a partial attack on silicate lattices. Hence a treatment with hydrogen peroxide in a nitric acid medium was adopted, representing a compromise between complete oxidation and alteration of silicate material.

Bradley (1984) found that the aqua regia extraction for the residue did not extract all of the metals present; metals from the silicate matrix were not removed. Förstner and Salomons (1980) suggest 'that for this type of study it is not necessary to obtain full digestion of all sediment components including metals bound into the internal structure of silicates and other detrital minerals, since the pollution effects usually are associated with the surface of the sediment particles with which the autochthonous precipitates'.

Selectivity of the extraction reagents toward specific geochemical phases is an important performance criterion for a sequential extraction procedure designed to determine the speciation of heavy metals. The accuracy of determining metal concentrations in each of the fractions is difficult to calculate since it must include an assessment of the instrumental detection limit, the analytical precision and the accuracy of the extraction method. The latter factor is the most difficult to determine since there are no certified reference materials (CRM's) available for sequential extraction and unless a standardised extraction procedure is developed, there is not likely to be one in the future. For this reason very few investigations have considered the accumulative errors and how precisely the final results may compare with the actual concentration in each phase. A study by Li et al. (1995) concentrated almost exclusively on the accuracy on the sequential extraction method based on Tessier et al. (1979). Precision was estimated to be about 5 % for each extraction step and the overall recovery of a total metal reference material for 15 elements averaged 92 %. Using a very similar procedure of sequential extraction for metals in urban particulate matter, Lum et al., (1982) found that for each extractant, precision was ‘generally better than 10 % provided that the concentration was ten times greater than the limit of detection’.

Despite these criticisms the sequential extraction technique does simulate to a reasonable degree the various environmental conditions to which the sediment may be subjected to; deductions can then be made about the trace metal levels likely to be observed under these conditions in the environment (Tessier et al., 1979).

5.2.9 Methods of analysis

5.2.9.1 AAS

At present, Atomic Absorption Spectrophotometry is the most widely and intensively used analytical method in environmental geochemistry. Since it’s development, by Walsh (1955), there have been many advances in AAS techniques. More recent developments of nonflame atomisers, like the graphite furnace have increased sensitivity by several orders of magnitude. Along with these advances, a growing literature on the problems and interferences has also risen.

The technique utilises the absorption of excited atoms of an element, from a light source, by the population of atoms in the ground state present in the volatilised sample. To produce atoms in the excited state for elements of interest, a specific hollow cathode lamp is used, multiple lamps are also available. The lamp has a cathode manufactured from a pure sample of the element to be studied. Radiation of a characteristic wavelength is discharged from the lamp and is passed through the flame. The volatilised sample is produced by aspirating the liquid sample into a long narrow flame, produced by a variety of gas mixtures and serving to decompose the sample to produce atoms which are distributed along a long absorption path (Parkinson and Rowland, 1989). Ideally the flame temperature should decompose the sample into atomic form with the minimum of excitation of ground state atoms. Each of the elements present in an atomic vapour phase will absorb radiation at a limited number of wavelengths over an exceedingly narrow spectral region (c. 0.01 Å). The wavelength bands which each element can absorb are different for each element. The amount of energy absorbed by the atoms is measureable and is proportional to the concentration of absorbing atoms (Fletcher, 1981).

A variety of gas mixtures have been used, but the air / acetylene flame has the most general application and was used in the present study. Its temperature (~2200°C) is sufficiently high to ensure breakdown of most compounds but is not so high as to cause significant ionisation for elements other than the alkalies (Fletcher, 1981). For optimum sensitivity the burner height and fuel to oxidant ratios and pressures should be determined separately for each element. Hollow cathode lamps must be run at their specified lamp currents. Too low a current may give insufficient sensitivity but too high a current will shorten the life of the lamp. As a general rule, best sensitivity is obtained between 50 - 70 % of the maximum current and best precision between 75 - 90 % (Parkinson and Rowland, 1989).

Freedom from interferences is often cited as one of the principal advantages of AAS. However, interferences do exist, especially in the use of AAS for routine analysis. If samples and standard solutions differ in bulk composition, a variety of interferences can cause enhancement or depression of the analyte signal. Matrix interferences can change the analytical result, possibly caused by the viscosity or nature of the sample solution, for example, as the solution becomes more concentrated, it flows more slowly through the burner and absorption is therefore decreased (Kahn, 1968). Accuracy is limited mainly by interference effects produced when trace elements are determined in solutions containing major sample constituents (sodium, potassium, calcium, magnesium, iron, aluminium) not present in the calibration (Thompson, 1983). As the concentration of the major constituents are variable no allowance can be made during calibration. Chemical interferences are usually the result of incomplete dissociation of the compounds of the element being determined. Ionisation interference takes place when a substantial proportion of the atoms in the sample become ionised, causing them to absorb at a different radiation line. Since the different line may be outside the passband of the detector, such atoms are in practice lost to the determination

(Kahn, 1968). Background absorption can give large errors when low concentrations of an element are to be measured in a sample, especially in the ultraviolet part of the spectrum, i.e. below 300 nm.

It is realised that no single analytical technique can be used for all analyses. Some of the requirements for an analytic method to be acceptable are:

(1) sensitivity, specificity and accuracy;
(2) rapidity of analysis and ease of operation;
(3) low cost of equipment; and
(4) reliability of results and reducing interference effects (Förstner and Wittmann, 1981).

Although AAS is a precise technique and is easy to operate, this does not imply a guarantee for the validity of the data obtained. AAS measurements do not provide low enough detection limits or the necessary sensitivity for many samples which can be adequately analysed by ICP-AES.

5.2.9.2 ICP-AES

The use of Inductively Coupled Plasma Atomic Emission Spectrometry in geochemical studies is now rapidly spreading. The ICP is an optically thin emission source formed by coupling radio frequency power into a stream of argon gas. The argon is constrained into three concentric streams in a plasma torch fabricated from fused silica. Plasma is a conducting gaseous mixture containing a large concentration of cations and electrons. Once argon ions have been formed in the plasma, they are capable of absorbing sufficient power from an external power source to maintain the temperature at a level at which further ionisation will sustain the plasma indefinitely (Skoog and Leary, 1992). The sample is injected either as an aerosol or as a thermally generated vapour and is carried into hot plasma through the central tube in a third stream of argon and heated to a high temperature (c. 8000 K, Skoog and Leary, 1992) and thereby atomised to a large extent. The emission spectrum is recorded using high resolution optical instruments combined with a computer. A wide range of elements can be identified by the characteristic wavelength of the spectral lines and their concentration determined by the line intensity (Fifield, 1995).

The ICP has analytical characteristics that make it a uniquely powerful analytical tool. The use of ICP-AES for the analysis of soil and sediments has several advantages over atomic absorption spectrometry. These are (after Fifield, 1995):

(1) the detection limits obtainable by ICP-AES are normally lower than can be obtained by AAS;
(2) the range of linear calibration is wide, always exceeding 4 orders of magnitude above the detection limit;
(3) unlike AAS, a wide range of possible emission lines is always available allowing a convenient concentration range to be chosen;
(4) interference effects from the chemical matrix of the analyte are small;
(5) emission intensities are such that short integration's (typically 5 seconds) can be used after signal stabilisation (typically 20 seconds) so that relatively small volumes of sample solution are required for the analysis; and
(6) many elements can be determined simultaneously.

Despite these advantages, some limitations of ICP-AES use still occur. The most serious limitation stems from the fact that the sensitivity depends critically on the injector gas flow rate. If this parameter can be kept stable then sensitivities and backgrounds are stable for many hours, so that no recalibration is required (Thompson, 1983). Another limitation stems from the change in background emission caused by the major constituents of a complex mixture (Fifield, 1995). If low levels of metals are to be measured a correction has to be applied for the background shift. Although this undoubtedly improves the accuracy of the determination, the error in correction is often substantial when compared with the detection limit and it also increases the time of analysis.

5.2.10 Quality control

For trace metal analysis in particular, sample contamination can be important but difficult to detect. Hamilton (1976) noted that at least 20 % of a laboratory workload should be devoted to laboratory care, standardisation and development of methods acceptable for a wide range of elements in many different matrices. The lower limits at which concentration of metals can be measured in a sample are ultimately determined by the precision in establishing the value of the analyte metal in the 'blank'. The reliability of analytical results depends greatly upon minimising the level and the variability of the blank. When contamination is measureable by the analytical method it becomes significant.

All reagents and equipment used may contaminate the sample to some degree. Practical limits of detection in the analyses of real life samples are also established by the level and variability of contaminants. Hamilton (1980) commented that 'some of the commonly used laboratory paper tissues, selected because they are free from loose fibres, contain significant levels of leachable zinc; the tips of disposable pipettes often contain zinc, cadmium and copper; markings on glassware can contain a variety of elements such as barium and lead, while virtually all types of filter paper contain a host of elements'.

Of the data generated for this study, the majority is used to show relative changes in metal concentration through time and space, but also generally to compare absolute concentrations of metals with other studies and to assess the toxic effects of these metals. Hence quality control is highly important. An attempt has been made throughout to produce the best quality of data compatible with instrumental and other resources, using identified methods and techniques of analysis. In addition, to avoid contamination during and to check the quality of the analysis, certain procedures were carried out and these are outlined below.

Grinding the bulk sample until the metals are evenly distributed throughout the sample can introduce errors. There is no problem in physically grinding the sample but quite severe problems can exist in carrying out this operation without the introduction of contaminants or selective loss of part of the sample as finely divided dust (Davies, 1980). To limit this the samples were air-dried in a clean, dust-free laboratory and stored in sealed, clean polythene bags. Grinding equipment was cleaned between each sample to reduce the possibility of cross contamination and lids were used when sieving to prevent the loss of very fine particles.

All equipment was acid washed, prior to use (section 5.2.1). Replicate samples were used to detect and distinguish systematic and random errors and the accuracy of the extraction technique. The use of high quality reagents is desirable in most methods and are essential for preparing standard calibration solutions since contamination may be introduced through the use of inferior grade reagents. AnalaR grade reagents, used in this study is acceptable (Allen et al., 1989). Quality control during analysis was checked by periodic calibrations of standard solutions when using either the AAS or ICP-AES (every 4th and 6th sample respectively).

Each type of analysis involves some form of sample preparation, also an estimation of the contribution of an element added to the sample as a contaminant, conventionally estimated in so-called ‘blanks’ (Davies 1980). In most determinations a correction must be made for the background concentration or ‘blank’ value. A treatment blank which is introduced during the preparation stage, will distinguish contamination introduced particularly by digestion acids and filter papers. This blank should be run in the same way as the samples and in the calculation the value is subtracted from the sample readings (Allen et al., 1989).

Accuracy and precision for total metal analysis can be controlled by the use of reference materials inserted into every batch of samples. The samples are ‘certified’, that is, the concentration of certain elements in the sample is accurately known after many analyses have been performed by many laboratories, usually by several different analytical methods. Theoretically, if the analytical result agrees with the certified value, then the accuracy of the method under test may be considered to lie within the specified limits. Stream sediment and soil reference materials from Canada were used. The samples were prepared, blended and bottled at CANMET (Canada Centre for Mineral and Energy Technology). For the stream sediment, thirty five laboratories provided analytical data and provisionally recommended values for 65 elements. Also from CANMET, CCRMP (Canadian Certified Reference Materials Project) soil samples were used. Mean values for 70 - 230 accepted analytical results from 10 - 30 laboratories for the various constituents contributed to the recommended values set.

CHAPTER 6

HEAVY METAL LEVELS IN CONTEMPORARY RIVER SEDIMENT OF THE AIRE CORRIDOR

6.1 Introduction

River sediment and associated heavy metals are stored in a variety of depositional environments, either temporarily within the channel or spread across floodplains during floods. Contemporary fine-grained sediment accumulates within the channel, laid close to river banks and gets flushed downstream by larger than normal flows. Contemporary sediment has been shown to represent the current quality of the river system (Salomons and Förstner, 1984). The sampling and analysis of contemporary river bed and suspended sediments (see Chapter 7) are particularly important, because heavy metal concentrations associated with them are orders of magnitude higher than in the dissolved phase in the water column and also because riverine transport of heavy metals is dominated by sediment. River bed sediments function as the main storage for most pollutants in fluvial systems (Renwick and Ashley, 1984) and should be regarded as a major, if not the major source of suspended sediment (Horowitz, 1985). The dispersal of heavy metals in a river bed depend on hydrological factors such as the current velocity and turbulence, the depth and morphology of the channel and on physical parameters such as the density and size of the transported particles (Horowitz, 1985). Chemical (e.g. pH, redox potential) and biological (e.g. bioavailability) factors are also important. For the geochemical cycling of metals in the hydrosphere, bed-load remains stationary for much of the time and metals are only slowly leached or abraded from the surfaces (Bradley, 1987). Fine-grained contemporary within channel and river bed sediments were collected at regular intervals throughout the Aire catchment in Leeds and analysed for total metal concentration by AAS.

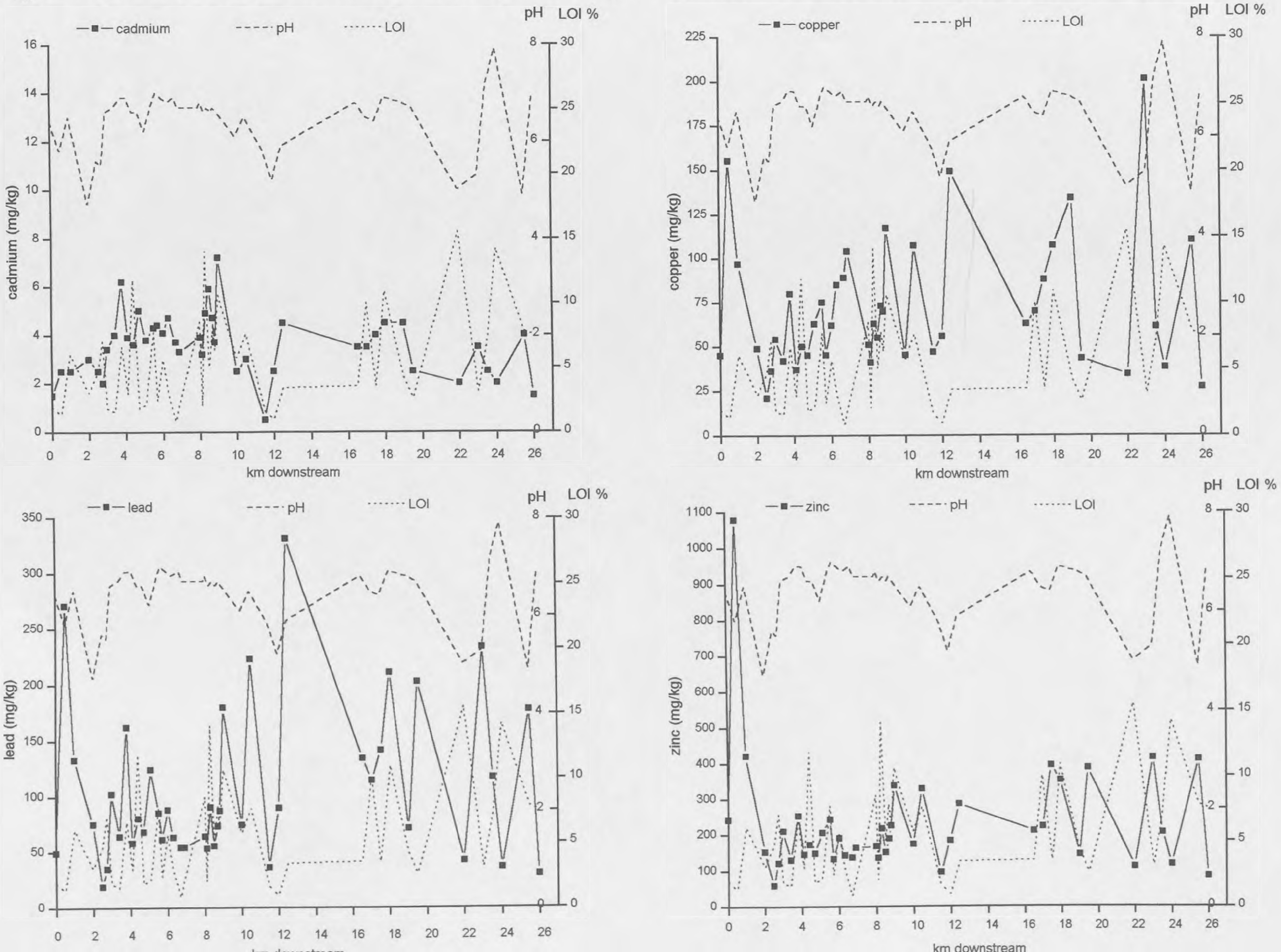
Between January and the end of February 1995, Northern England experienced heavy rainfall causing widespread flooding. One result of this was the deposition of fine-grained sediments within the channel and across floodplains in the region. This provided an opportunity to investigate the chemical speciation of sediment-borne metals that could be related to a single flood and to compare to the chemical partitioning of heavy metals in fine-grained within channel sediment, deposited before this event. Sequential extraction procedures give an insight into the chemical associations of heavy metals with specific sedimentary phases and provide the key to understanding and predicting metal transport and environmental availability, as well as identifying sources and sinks for aquatic metal constituents. This enables inferences to be made of their likely effect on the environment at present and when chemical conditions change. The heavy metal concentration of fine-grained contemporary within channel sediment from Apperley Bridge was determined using sequential extraction by AAS.

6.2 Heavy Metal Concentrations in Contemporary Within Channel Sediment

Fine-grained contemporary within channel sediments were sampled at 72 sites, from both sides of the river and analysed for total heavy metal concentrations, pH and loss on ignition. The results are presented in figures 6.1 and 6.2. The north side of the river had significantly more samples taken, because of access and availability of suitable sites. The results show very large variations in metal concentration between the north and south side of the river and with distance downstream.

The spatial pattern of concentration is relatively similar for each of the metals studied on the north side of the river (figure 6.1). A sharp rise in total metal concentration occurs from the onset of the study reach for all the metals, except cadmium, where only a small increase is observed. Metal levels peak in concentration at 0.5 km downstream, where the highest concentration of zinc (1079 mg/kg) in contemporary within channel sediment is observed. A sharp decline in metal concentration occurs from 0.5 - 2.5 km downstream, where the lowest determined levels of copper (21 mg/kg), lead (19 mg/kg) and zinc (58 mg/kg) are found. Cadmium concentrations generally increase gradually from the start of the study reach, to peak in concentration (6.2 mg/kg) at 3.8 km downstream. Metal levels fluctuate greatly between 3.8 - 8.0 km downstream. Other major peaks in cadmium concentration occur at sites 8.5 km (5.9 mg/kg) and

Figure 6.1 - Total metal concentration, contemporary within channel sediment, north of the river

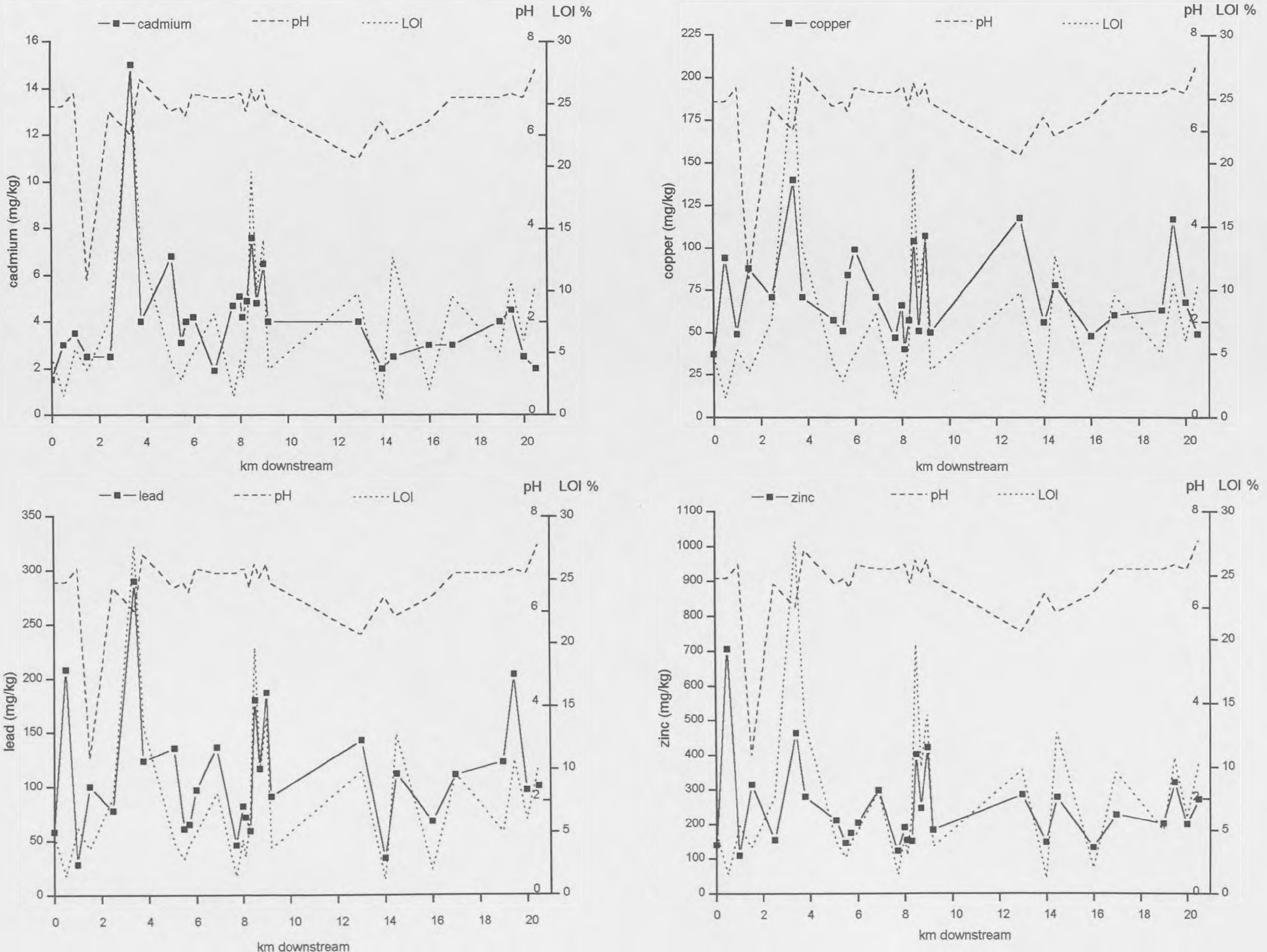


9.0 km downstream (7.2 mg/kg). Copper, lead and zinc also peak in concentration at 9.0 km downstream and again at 10.5 km, but decline steeply at 11.5 km downstream, where low levels of metals are observed, particularly for cadmium (0.5 mg/kg). Total metal concentrations increase sharply at 12.5 km downstream, forming major peaks in concentration for cadmium and copper, but particularly lead, where the highest level (331 mg/kg) is found in contemporary within channel sediment on this side of the river. Concentrations decrease once more up to 16.5 km downstream. Metal levels fluctuate greatly through to the end of the study reach, peaks generally occurring at sites 18.0 km, 19.5 km, 23.0 km (particularly for copper where the highest recorded concentration of 201 mg/kg is observed at this site) and 25.5 km downstream.

Sediment pH appears to follow metal concentration closely. Generally as pH increases metal concentration increases and vice versa. However, the relationship reverses between 12.5 - 17.5 km and 23.0 - 26.0 km downstream for cadmium and copper and 12.5 - 16.5 km and 23.0 - 26.0 km downstream for lead and zinc. The resulting correlation coefficients for these distances downstream (table 4, Appendix II) show a strong negative relationship between metal concentration and pH, for example, copper = -0.783, zinc = -0.837. The relationship between loss on ignition and total metal concentration is complex and shows no clear pattern. It does, however, follow the pH trend in places, particularly through the centre of the study region between 9.0 - 19.5 km downstream, where a correlation coefficient of 0.554 was determined (table 4, Appendix II).

In contemporary within channel sediments taken from the south side of the river (figure 6.2) the metals again show very similar patterns of concentration. A major peak occurs in total metal concentration at 0.5 km downstream for copper, lead and particularly zinc (where the highest concentration is recorded at this site, 705 mg/kg). Metal concentrations decline sharply from this site to increase equally sharply at 3.4 km downstream, where high concentrations of cadmium (15 mg/kg), copper (140 mg/kg), lead (290 mg/kg) and zinc (463 mg/kg) are observed. Total metal concentrations similar to the north side of the river, fluctuate greatly between

Figure 6.2 - Total metal concentration, contemporary within channel sediment, south of the river



3.8 - 8.3 km downstream. Two peaks in concentration are observed at 8.5 km and 9.0 km for all the metals. From this site cadmium concentrations remain at a relatively consistent level, with a small peak at 19.5 km downstream, through to the end of the catchment study. Copper, lead and zinc all peak in concentration at 13.0 km downstream, decrease at 14.0 km and then increase up until 16.0 km, where concentration steadily increases up to 19.5 km downstream. Concentration from this site decreases for cadmium and copper through to the end of the study, whereas lead and zinc both show a slight increase in concentration in the last sample taken.

Sediment pH shows a positive relationship with total metal concentration between 5.7 - 9.2 km downstream (correlation coefficients for lead = 0.586, zinc = 0.555), but generally exhibits a negative relationship - as pH increases total metal concentration decreases, for example, copper has a correlation coefficient of -0.329 (table 4, Appendix II). Loss on ignition appears to show a much closer relationship with total metal concentration on the south side of the river, than the north side and shows the same trends.

There is considerable geographic variation in the concentration of contaminants in contemporary within channel sediment, as a result of dispersal mechanisms from a range of diffuse sources, where a number of physical (e.g. grain size, river discharge) and chemical (e.g. pH, organic matter content) processes are interacting. Taking both the north and south sides of the river together, peaks in metal concentration occur at approximately the same distances downstream. However, there is no overall relation between heavy metal concentration in contemporary sediment and distance downstream.

At 0.5 km downstream from the start of the study reach, large peaks in metal concentration occur for copper, lead and particularly zinc. This site lies immediately downstream from Esholt sewage treatment works (Chapter 4, figure 4.5), where large quantities of heavy metals are discharged in final effluent (table 4.3). Major peaks in metal concentration occur at 3.4 km downstream on the south side of the river and 3.8 km on the north side. These samples were taken downstream of a waste disposal site, a former refuse tip, a private sewage treatment works and consented discharges from Sandoz Pharmaceutical works and Colourflex (dyers, which discharges quantities of zinc, chromium and copper). These are all situated on the north side of the river, but contemporary sediments from the south side contain much higher levels of heavy metals, particularly cadmium.

Smaller peaks in metal concentration occur between 5.0 - 7.0 km downstream, reflecting sewage and waste water pollution from Rodley sewage treatment works and from Oil Mill Beck, a highly industrial, sewage and agriculturally polluted tributary of the River Aire, from agricultural pollution on the Aire at Newlay and also direct sources from Rodley and the Horsforth area of ‘mothproofers’, an insecticide likely to contain quantities of heavy metals. Two peaks in concentration occur very close together at 8.5 km and 9.0 km downstream, particularly for cadmium, lead and zinc. Sources here include agricultural pollution from fertiliser applications at Kirkstall and atmospheric deposition and road runoff of metals from motor vehicle traffic.

At Armley, metal concentration in contemporary within channel sediment increases, at 12.5 km (north side) and 13.0 km (south side) downstream, particularly for lead and copper. A likely source includes vehicle exhaust, where a very busy road passes over the river. On the south side of the river at 14.5 km downstream (no samples were collected on the north side), copper, lead and zinc levels increase, possibly due to consented discharges and atmospheric deposition of metals from nearby engineering and iron works and vehicle exhausts, as traffic density increases with increasing distance towards the city centre. Metal concentration generally increases between 17.0 - 19.0 km downstream on both sides of the river, reflecting metal inputs from atmospheric deposition from vehicle exhausts, metal plating and processing works (figure 4.5, numbers 87, 93, 94, 96), consented discharges from Shell (UK) Ltd., Oil Rail Terminals Ltd. and Brown Bros. vehicle wash (potential source of zinc). Meanwood Beck also joins the River

Aire in this vicinity and is significantly polluted by sewage and agricultural activities.

The influence of Knostrop sewage treatment works is evident on the north side of the river at 23.0 km downstream. The sewage works discharges significant quantities of metals in its final effluent (table 4.4). Skelton open cast coal mine and spoil heaps, Skelton Grange Power Station and IMI Yorkshire Imperial Ltd. and IMI Yorkshire Alloys Ltd. all contribute to the elevated metal concentrations that are observed at the site of 25.5 km downstream, particularly for copper which is high in effluents from the IMI works.

Heavy metals are derived from a variety of sources in this fluvial system. The sources differ in size and in the quantity and quality of their output, producing the observed spatial distribution of heavy metals in contemporary within channel sediment. Metal concentrations in contemporary within channel sediments are generally lower than those of contemporary river bed sediments. The level of heavy metal pollution is assessed using UK and Dutch policy on contamination (section 3.5). UK policy, as outlined by ICRCL (1983, 1987 and 1990), sets 'trigger concentrations', defined as those values below which a site could be regarded as uncontaminated. In contemporary within channel sediments (table 5, Appendix II), 70 % of the samples exceed the trigger concentration of 3 mg/kg cadmium, set for domestic gardens and allotments. 3 % of the samples also exceed the trigger concentration of 15 mg/kg for parks, playing fields and open spaces. Only 9 % (north side) and 3 % (south side) of the copper in contemporary sediment samples exceed 130 mg/kg, set for any uses where plants are to be grown. 21 % of the samples have zinc concentrations exceeding the trigger concentration of 300 mg/kg for any use where plants are to grown.

According to Dutch policy A-values and C-values are proposed. Concentrations not exceeding the A-value are considered clean. If C-values are exceeded, clean-up is considered necessary, the urgency of which is determined by human exposure, metal mobility and ecological factors. Over 90 % of contemporary within channel sediment samples contain more than 0.8 mg/kg cadmium and 36 mg/kg copper, the A-values set for these metals (table 5, Appendix II). In 55 % of the samples, lead exceeds the A-value of 85 mg/kg and 82 % of the zinc with an A-value of 140 mg/kg. In contemporary within channel sediment samples, 3 % of the cadmium and 2 % of the copper and zinc also exceed the C-values of 12 mg/kg, 190 mg/kg and 720 mg/kg respectively. In these sediments, according to both UK and Dutch guidelines, cadmium exceeds concentrations set to the greatest extent and lead exceeds the limits the least.

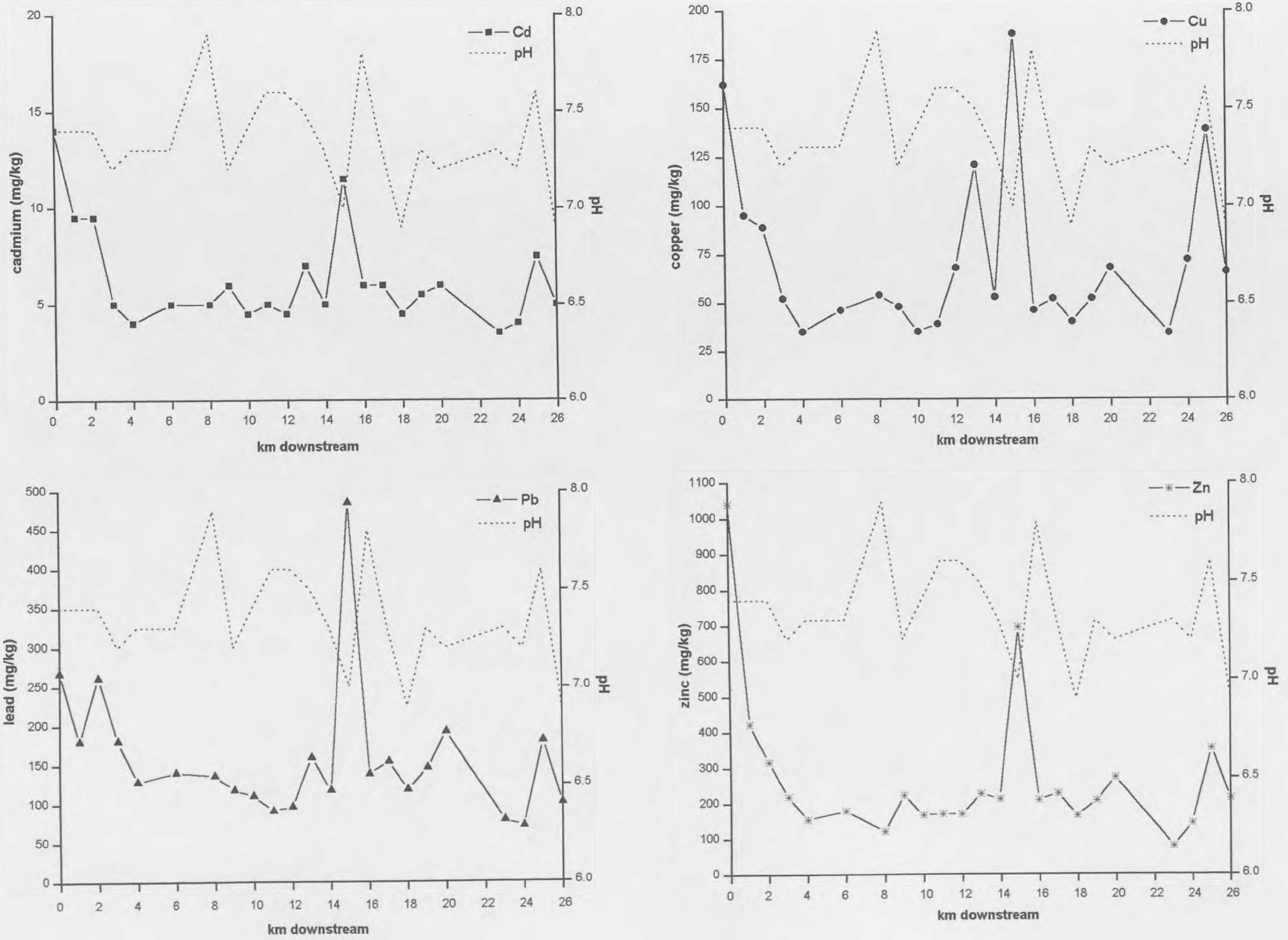
Metal concentrations in contemporary within channel sediment show wide variations with distance downstream. Concentrations are highest at sites 0.5 km and 23.0 km, immediately downstream of effluents discharged from Esholt and Knostrop sewage treatment works respectively and between 3.0 - 4.0 km, 10.5 - 13.0 km and 17.0 - 19.0 km downstream, reflecting a range of metal sources including agriculture, industry and vehicle exhausts.

6.3 Heavy Metal Concentrations in Contemporary River Bed Sediment

Twenty three fine-grained contemporary river bed sediment samples were taken from the River Aire and analysed for total heavy metal concentrations and pH. The results are shown in figure 6.3 and also table 3 in Appendix II. These results show a wide spatial variation in the distribution of heavy metals in contemporary river bed sediments. All the metals analysed show a very similar pattern of total metal concentration with distance downstream.

Total concentrations of heavy metals at the start of the study reach (0 km) are high, particularly for cadmium (14.9 mg/kg) and zinc (1038 mg/kg), the highest concentrations in contemporary river bed sediment of any of the sites. Metal levels decrease downstream up to 4 km, where concentrations steadily begin to rise, peaking in concentration between 8 and 9 km. From 12 km downstream heavy metal concentrations begin to increase again, reaching a peak at 13 km, a significant peak for copper, decreasing in concentration at 14 km, but all rise to a major peak at 15 km. Copper and lead in particular, where the highest metal

Figure 6.3 - Total metal concentration, contemporary river bed sediment



concentrations are detected at this site (188 and 485 mg/kg respectively), but also cadmium and zinc (11.5 and 695 mg/kg respectively). Heavy metal concentration decreases sharply from this site, however, a significant peak occurs for all the metals at 20 km downstream. The lowest levels detected throughout the catchment are recorded at 23 km for cadmium (3.5 mg/kg), copper (34 mg/kg) and zinc (79 mg/kg) and for lead at 24 km downstream (71 mg/kg). From here concentrations rise sharply again at 25 km, particularly for copper and decrease for the last site sampled at 26 km downstream.

The pH of samples appears to follow the total metal concentration quite closely, producing positive correlations (table 4, Appendix II). If pH decreases, there is a corresponding decrease in total metal concentration. This occurs between 2 - 3 km, 17 - 18 km and 25 - 26 km downstream for all metals and between 8 - 9 km for copper and lead. When pH increases a rise in total metal level occurs and does so between 4 - 8 km, 18 - 19 km and 24 - 25 km downstream. However, throughout the middle of the catchment, this relationship reverses, i.e. as pH decreases, metal concentration increases or vice versa. This trend is observed between 8 and 16 km downstream, producing correlation coefficients of -0.603 for cadmium and -0.707 for zinc (table 4, Appendix II), for example.

The heavy metals are derived from a variety of sources in this fluvial system that differ in the quantity and quality of their output. The diffuse sources of the metals contribute to the somewhat random spatial pattern of distribution. The variation in the concentration of contaminants in contemporary river bed sediments is also a result of geographically and / or temporarily discontinuous sedimentation and variable transport rates (Graf, 1994). No relation occurs between heavy metal concentration in contemporary river bed sediments and distance downstream, as a result of no single point source of these metals. The metal pollution of sediments is mainly produced by industrial and urban waste disposal which is not restricted to one locality (section 4.3.2, figure 4.5).

At the start of the study catchment, immediately downstream from Esholt sewage treatment works, total metal concentrations in contemporary river bed sediments are high, especially zinc and cadmium. Significant quantities of metals are released from the sewage works (table 4.3), which treats both domestic and industrial waste from 190 consented traders. Total lead peaks in concentration at 2 km downstream, possibly the result of high levels of lead in Gill Beck which joins the River Aire at this site. All the metals slightly increase in concentration from 4 km downstream. Potential sources include a discharge consent from Sandoz Pharmaceutical works and Colourflex (high in zinc, chromium and copper), a waste disposal site, a former refuse tip at Calverley Bridge, which may be leaching heavy metals, and atmospheric deposition from vehicle exhausts and a metal processing works.

The peak in total metal concentration of copper and lead at 8 km and cadmium and zinc at 9 km downstream may be the result of metal pollutants in effluent from Rodley sewage treatment works, agricultural pollution of the Aire at Newlay and Kirkstall, and inputs from the tributary Oil Mill Beck, which receives significant quantities of metals from industry and sewage from Leeds / Bradford airport and is also a site affected by pollution from agriculture.

The next major peak in metal concentration occurs at 13 km in samples collected at Armley. The most likely sources of metal contaminants here are atmospheric deposition from vehicle exhausts, since a very busy road passes over the river and there is also an engineering works nearby. An extremely large peak in concentration occurs at 15 km downstream, particularly for lead, but also for copper. Sources of metals include atmospheric deposition of metals from iron and engineering works and as this site was located in the city centre of Leeds, where traffic and road density are at their greatest, deposition of lead from vehicle exhausts. Milshaw Beck also joins the River Aire here and is likely to contribute to total metal levels, including a consented discharge from Pland Stainless Ltd. (stainless steel products) and sewage inputs from unsatisfactory CSO's on the beck.

Consented discharges from Brown Bros. vehicle wash (potential source of zinc) and Oil Rail Terminals Ltd., along with vehicle emissions and atmospheric contributions from metal processing and chemical manufacture plants, probably give rise to the small increase in metal concentration at 17 km downstream. Total metal concentrations peak again at 20 km downstream. The sources include an effluent outlet from Knostrop sewage treatment works and consented discharges to the river from IMI Yorkshire Imperial Ltd. (high in copper, chromium and tin) and Skelton Grange Power Station which is coal fired. Both are also likely to contribute to atmospheric sources of heavy metals.

Heavy metal concentrations peak again at 25 km, downstream from Wyke Beck where the majority of effluent from Knostrop sewage treatment works is discharged. Knostrop treats domestic sewage and industrial waste from 328 traders. Significant quantities of metals are released in effluent from the sewage treatment works (table 4.4). Nearby open cast coal mines at Skelton and spoil heaps are also likely to contribute significant amounts of metals to the river.

For current sediments in the Aire valley, contemporary river bed sediments exhibit higher total metal concentrations than contemporary within channel sediments, illustrating their importance as a store and potential source of heavy metals. The levels of metals found in contemporary river bed sediments have been applied to guidelines of contamination (section 3.5) according to the UK system and the Dutch system (table 5, Appendix II). 100 % of the cadmium in contemporary river bed sediment samples was above the ICRCL trigger concentration of 3 mg/kg for domestic gardens and allotments. 13 % of the copper and 22 % of the zinc was above the concentration of 130 and 300 mg/kg respectively, set by ICRCL, for any use where plants are to be grown. In respect to Dutch policy, a considerably more stringent system in sediment samples, 100 % of the cadmium, 87 % of the copper and 91 % of the lead and zinc exceed the A-values. If concentrations do not exceed the A-value, the site is considered clean. 4 % of the cadmium and zinc also exceed the C-value, where clean-up of the site is considered necessary by the Dutch system.

According to both systems, cadmium is the metal which exceeds guidelines to the greatest extent. Throughout the entire reach studied total metal concentrations are highest at the start of the study area and at 15 km and 25 km downstream. Peaks in metal concentration reflect various input sources and variable transport and sedimentation rates providing a spatial distribution, on which sewage treatment works appear to have the greatest influence on metal concentration.

6.4 The Chemical Speciation of Contemporary Within Channel Sediment

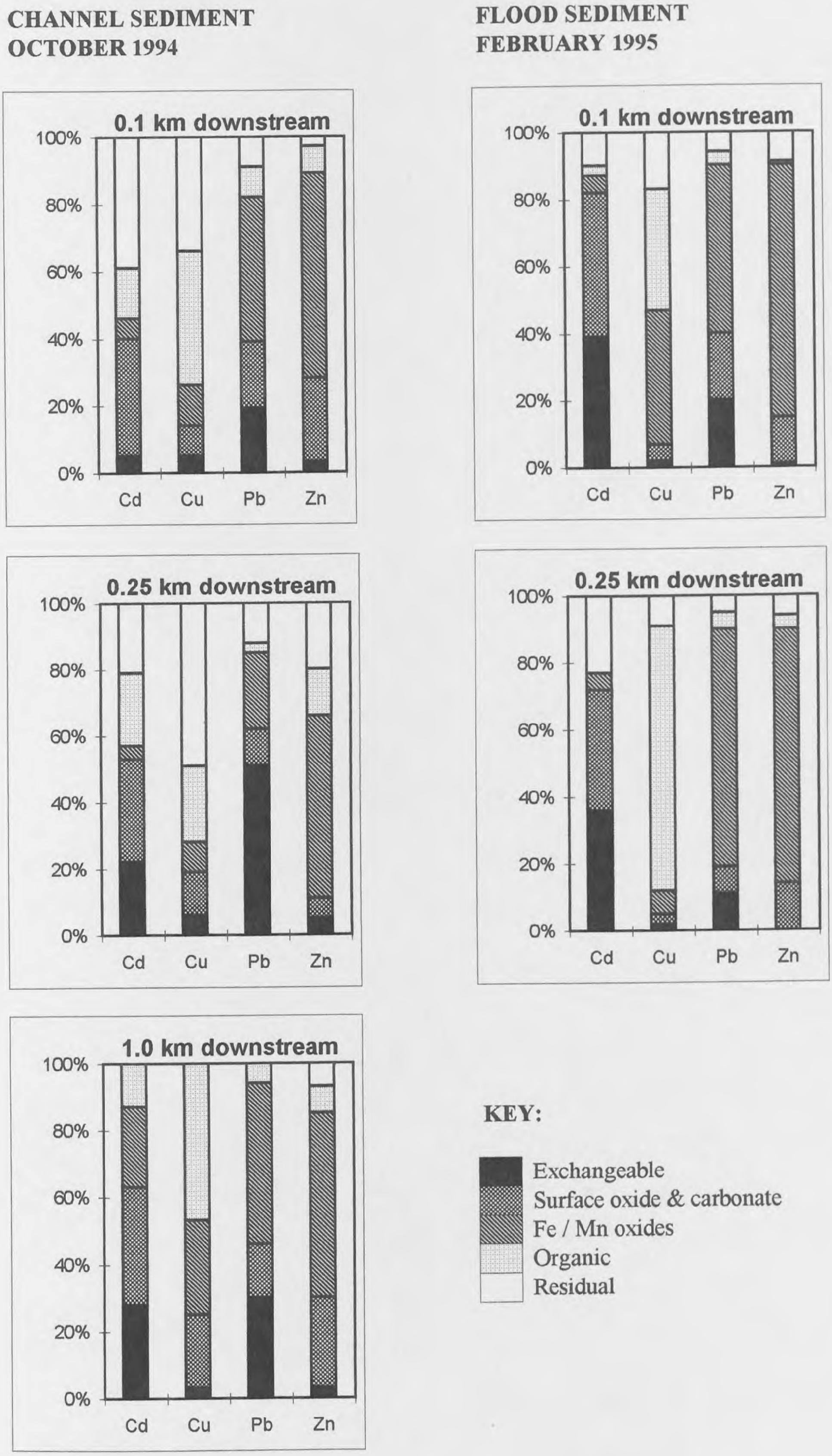
6.4.1 General patterns

Five fine-grained contemporary within channel sediment samples were selected for sequential extraction from Apperley Bridge. The speciation patterns observed are taken to represent contemporary within channel sediment throughout the River Aire, in Leeds, as it was not possible to analyse all sediments using this technique and the results found are consistent with those presented in other studies. Apperley Bridge regularly floods, providing an opportunity to investigate flood effects on the chemical speciation of heavy metals in contemporary within channel sediment. Fine-grained contemporary within channel sediments were sampled at three sites along the River Aire at Apperley Bridge in October 1994. Two of these sites were resampled immediately after floods in February 1995, once river level had fallen.

Figure 6.4 shows the chemical speciation of contemporary within channel sediment and table 6 in Appendix II shows all the results including pH and loss on ignition data. These results show that metals are partitioned between a variety of operationally- or chemically-defined fractions. In all samples, with the exception of copper (dominated by the organic fraction), metals are primarily associated with Fe and Mn oxides (lead and zinc), with the surface oxide and carbonate fraction (cadmium and zinc) and an operationally defined exchangeable component (cadmium and lead).

Cadmium was the only one of the metals analysed in contemporary sediments for which a large percentage (40 - 82 %) of the total metal was consistently associated

Figure 6.4 - Chemical speciation, contemporary within channel sediment (% in each fraction)



with the exchangeable or surface oxide and carbonate fractions. The organic fraction predominated over all other forms of sediment-associated copper (45 % of total copper present on average). The residual component also accounted for a significant proportion of total sediment copper. Almost all particulate lead (43 - 71 %) was associated with Fe and Mn oxides, with the exception of sediment collected in October 1994 at a distance of 0.25 km downstream, where the majority of sediment lead (51 %) was accounted for by the exchangeable fraction. Lead is consistently found within the first three sequential extraction fractions. The organic and residual components together only accounting for a maximum of 18 % of total sediment lead. Zinc was found to be predominantly in the Fe and Mn oxide fraction, which accounted for 55 - 76 % of total zinc present. The surface oxide and carbonate fraction was also associated with a significant proportion of total sediment zinc, on average 17 %.

These results are similar to those reported in other studies. Macklin and Dowsett (1989) in a study of contaminated river sediment in the Tyne Basin, England, found a significant proportion (50 - 80 %) of cadmium in fine sediments to be in exchangeable or surface oxide and carbonate bound forms. Other researchers (Bradley and Cox, 1990; Salomons and Förstner, 1980) have also found a strong affinity between the organic fraction and copper. Copper more than any other metal shows a tendency to prefer the organic fraction (Förstner and Wittmann, 1981). This can be partly explained by the high stability constants exhibited by complexes involving copper and organic matter (Smith and Martell, 1976; Stumm and Morgan, 1970). A high percentage of total lead and zinc in the Fe and Mn oxide fraction has also been reported by Hudson-Edwards et al. (1996) and Macklin and Dowsett (1989). These results are consistent with the known ability of the Fe and Mn oxide coatings to scavenge heavy metals in fresh water sediments (Jenne, 1968; Whitney, 1975).

6.4.2 Flood effects

The major difference between contemporary within channel sediments deposited before October 1994 and during the February 1995 flood is the greater percentage of total cadmium that is held in the exchangeable or surface oxide and carbonate fractions in the more recent material. 18% of cadmium was bound to the exchangeable component in sediment collected in October, compared to 38% in contemporary within channel sediment sampled after the flood. For copper, a greater proportion is associated with the Fe and Mn oxide fraction in flood sediment from 0.1 km and the organic fraction in flood sediment sampled from 0.25 km downstream. At both sites significantly less copper is found within all fractions, in particular the residual component. The percentage of lead within each fraction is very consistent between contemporary within channel sediment sampled before and after the flood at 0.1 km downstream. However, at 0.25 km downstream the majority of lead (71 %) is associated with the Fe and Mn oxides in flood sediment, compared to 51 % being bound to the exchangeable fraction in contemporary within channel sediment deposited before October 1994. Zinc also shows a significant increase in the Fe and Mn oxide fraction at both sites in the flood sediment, with reductions occurring in most other chemical fractions. Copper, lead and zinc at 0.25 km downstream decreased in the residual fraction as the total metal concentration increased.

The nature and extent to which any metal is present within the solid phase will depend upon the chemistry of the metal itself, the type of source area and the range of physical, chemical and biological actions and interactions prevailing in the fluvial system. Metals will migrate differentially according to the pH, redox potential and the presence of organic matter in the environment. The flood sediments have a higher pH than those deposited before October 1994, but also have a lower loss on ignition. The breakdown of organic matter possibly producing the lower pH levels recorded in the earlier sediment. The higher pHs in flood sediment may prevent the leaching and solubilising of sediment cadmium, accounting for its greater percentage associated with the exchangeable and surface oxide and carbonate fractions. Other chemical factors such as the scavenging effects of Fe and Mn oxides are known for concentrating metals from solution and appear to be very important in flood sediments for copper, lead and zinc. Salomons and Förstner (1980) suggested from a study of sediment samples taken from the River Rhine and Ems Estuary, that a significant decrease of residual associations for copper, lead and zinc occurred as the total metal concentration increased due to anthropogenic pollution. This study showed that the surplus metal contaminants introduced by human activity into the aquatic system usually exist in relatively unstable chemical associations and are therefore predominantly available for biological uptake. Metal values may also be modified by input sources to the channel, variable both in terms of its metal concentration and in the rate and timing of input. These and other physical factors, including varying rates of metal transport and deposition result in wide variations in chemical speciation at a point.

The accuracy of sequential extraction techniques is much more difficult to assess than for total metal determinations, due to the many extraction steps involved (Li et al., 1995). In addition there are no standard reference materials available for sequential extraction, as there is no agreement on standard methods of extraction. In order to estimate the accuracy of the sequential extraction scheme employed, the sum of the concentration from the five steps were compared with values obtained for total metal concentration. The recovery rates for the samples for the five steps were 68 - 84 % of the total concentration for all metals determined, with an average of 74 %, with the exception of cadmium, where much higher levels of cadmium were recorded in the sequentially extracted samples. The high recovery rates for most metals indicate that metal determinations from the sequential extraction for sediment samples can be achieved with acceptable accuracy.

The chemical associations of cadmium, copper, lead and zinc in contemporary within channel sediments were analysed using sequential extraction techniques. Cadmium is primarily associated with the exchangeable and surface oxide and carbonate metal ions, copper with the organic fraction and lead and zinc with the Fe / Mn oxides. During the flood a greater percentage of total cadmium in contemporary within channel sediments is held in the exchangeable or surface oxide and carbonate bound fractions, whereas the Fe and Mn oxides increase in importance for sediment-associated copper, lead and zinc.

6.5 Conclusions

The dispersal of metals downstream in contemporary within channel and river bed sediments is a highly variable and complicated phenomenon. This arises from many factors, the most important of which include the proximity of a stream reach to a metal source, initial metal concentration at source and the range and extent of physical, chemical and biological factors operative on metal species. These illustrate the complexities caused by such factors as tributary streams and multiple or variable metal sources. Large sewage treatment works at Esholt and Knostrop appear to have the greatest effect on concentration of sediment-associated metals. Heavy metal concentrations in contemporary river sediments are highest overall between 0 - 1 km, 12 - 15 km and at 25 km downstream. These levels are influenced by Esholt sewage treatment works at the start and Knostrop sewage treatment works towards the end of the study reach. The high concentrations observed between 12 - 15 km occur through the city centre of Leeds, where traffic and industrial density is the greatest.

Contemporary river bed sediments show higher concentrations of heavy metal pollutants than contemporary within channel sediments and are the main store and sink for metals in the Aire channel. Cadmium appears to be the most problematic of the metals, as it exceeds guidelines in UK and Dutch policy to the greatest extent and because the majority of the metal is associated with the exchangeable and surface oxide and carbonate fractions. Both of these chemical associations are easily remobilised and available for biological uptake.

CHAPTER 7

HEAVY METAL CONCENTRATIONS ON SUSPENDED SEDIMENT

7.1 Introduction

The importance of suspended sediment in the transport and biogeochemical cycling of contaminants in the aquatic system is now well recognised (Förstner and Wittmann, 1981; Hart, 1982; Ongley, 1982). Many authors (Bradley and Lewin, 1982; Gibbs, 1973, 1977; Salomons and Förstner, 1984) have found that heavy metal discharges contributed by suspended sediment constitute a large percentage (c. 90 %) of the total metal flux. The relationship between sediment concentration and metal concentration is important in this context as it may reflect the change in total surface covering by the metals and thus the total mass of metal transported at a given discharge (Leenaers, 1989). A river with increasing discharge has a greater capacity to transport sediment in suspension. Suspended sediment may be supplied from within-channel sources (e.g. channel bank and bed) or from valley sides during storms. Furthermore, a constant supply of sediment is not maintained during a flood as source areas become exhausted. The relative concentration of elements in the solid or aqueous phase and the proportion between each chemical fraction is determined by the concentration of the metal and of competing metals, the concentration of other ions capable of forming inorganic complexes, organic chelates and by a number of chemical (e.g. pH, redox potential) and physical (e.g. grain size) properties of the sediment (Förstner, 1993). Sequential extraction techniques can be used to determine these chemical associations of heavy metals with operationally-defined fractions, whereby the 'bioavailability' and environmental mobility of metals may be estimated.

There is an increasing need to understand more fully the sources of pollutants and the processes and mechanisms of their movement from land to sea (Neal et al., 1997). This includes infrequent, high magnitude flood events, when the vast majority of sediment-associated contaminant transport takes place (Horowitz, 1995). To evaluate the relationships between river discharge, suspended sediment and associated metal levels in chemical fractions under various stages of flood, a high flow event at Thwaite Mills, River Aire, which occurred in February 1996 is considered. The Rivers Aire, Calder, Nidd, Swale and Wharfe all join the River Ouse and pass through to the Humber Estuary and out into the North Sea. Variations in water and sediment quality for these rivers relate to regional differences in geology, climate, landuse and population distribution. The Humber rivers provide the major urban and industrial pollution sources to the North Sea and also to the UK coastal area (Neal et al., 1997) and are therefore the subject of much concern and study. To compare heavy metal levels on suspended sediment between different catchments and to assess their chemical speciation, samples were collected and analysed from several Ouse tributaries. The heavy metal concentration of suspended sediment from the River Aire and Ouse tributaries has been determined using sequential extraction by AAS and ICP-AES respectively.

7.2 Flood Effects on Sediment-Associated & Dissolved Metal Concentrations at Thwaite Mills, River Aire

In February 1996 a flood event with a discharge peak of 72 m^3/s occurred in the catchment of the River Aire. This was recorded at Thwaite Mills. Figure 7.1 shows the flood hydrograph, the suspended sediment concentrations and total metal levels and figure 7.2 dissolved metal concentrations and pH. Tables of the data are included in Appendix III.

Suspended sediment levels closely follow river discharge during the flood event (figure 7.1). The peak of sediment concentration arrives just before the first discharge peak, as the river system is ‘flushed’ of fine material, its source being exhausted before maximum discharge. The second discharge peak coincides with the peak of suspended sediment concentration. However, the maximum concentration of suspended sediments in the second peak (304 mg/l) is much lower than that of the first peak (484 mg/l).

Similarly, particulate bound metal concentrations show a strong dependence on river discharge and suspended sediment concentrations. Metal levels decline during

Figure 7.1- Discharge, sediment & total metal concentration, Thwaite Mills

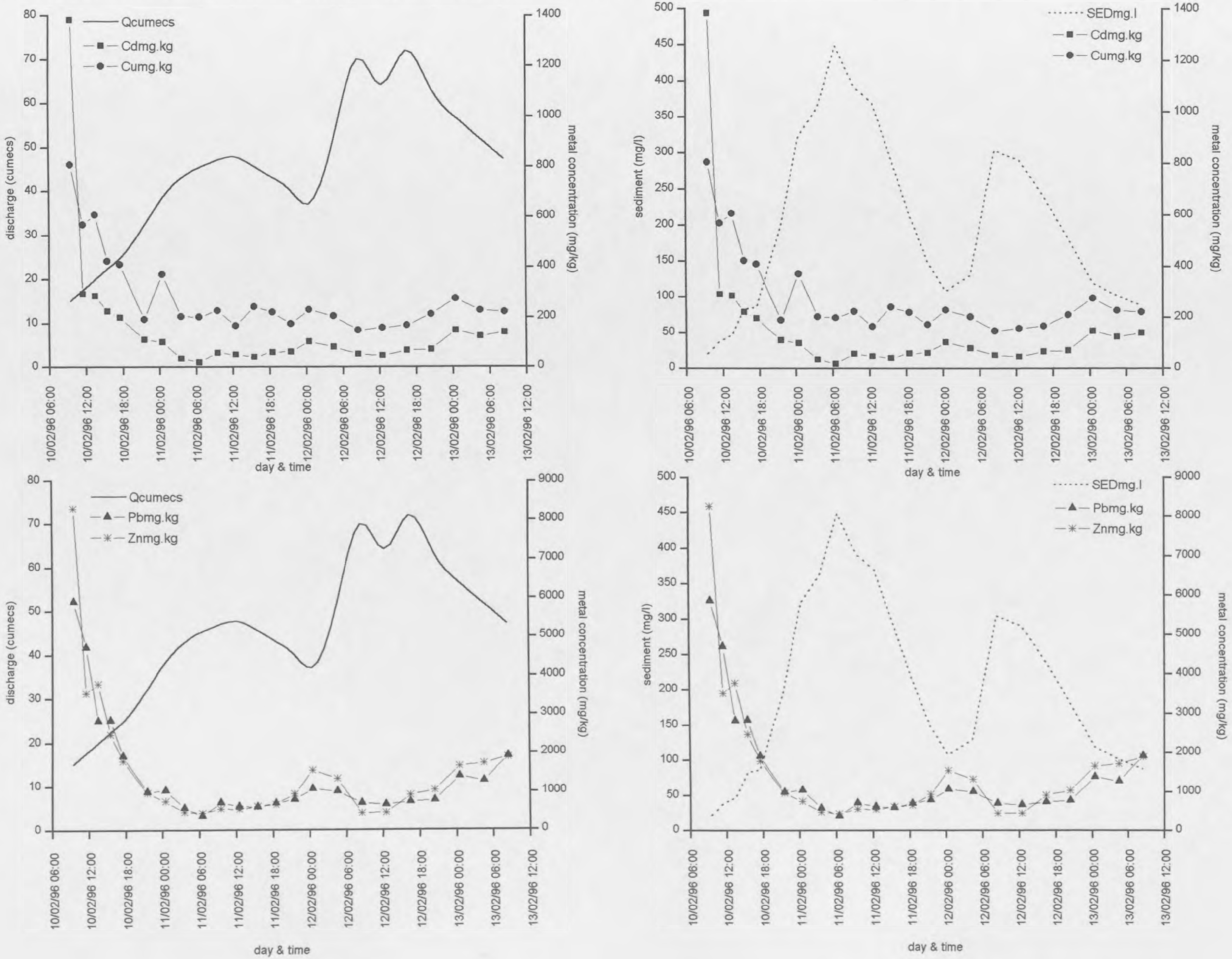
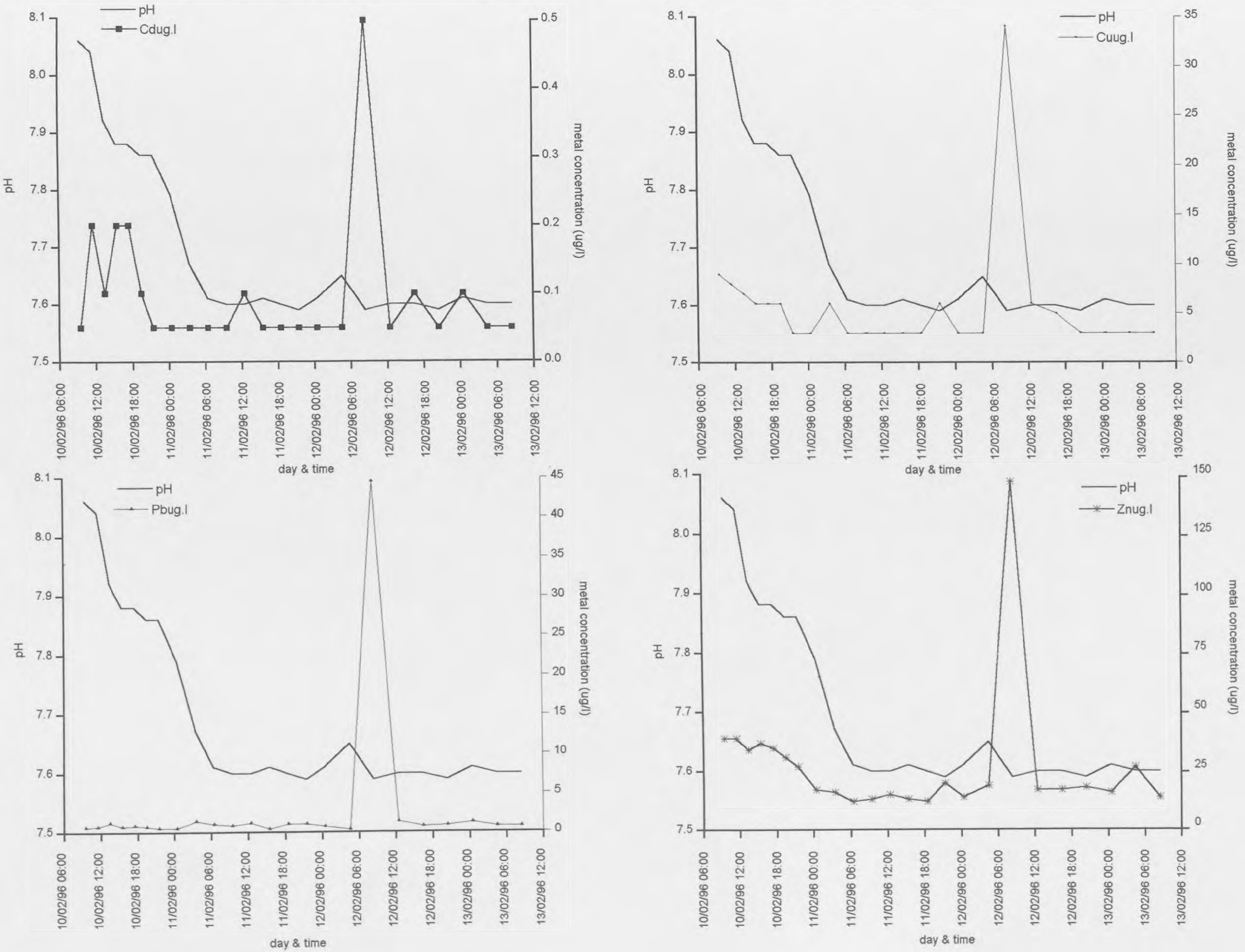


Figure 7.2 - Dissolved metal concentrations (ug/l) & pH, Thwaite Mills



the flood event, particularly in the first 6 - 12 hours and rise very slightly at the end of the event. Sediment associated metal concentrations are lowest just before the first flood peak, at the peak of sediment concentration. They rise on the falling limb of the hydrograph as sediment concentrations decline. This 'dilution' effect has been clearly demonstrated by many authors (e.g. Bradley and Lewin, 1982; Grimshaw et al., 1976), who observed that at times of flood, the concentration of heavy metals carried in solution and bound to suspended particles decreased as a result of mixing with relatively clean water and sediment. The lower concentrations of metals during the sediment peak may also be due to new sediment source areas and to a higher percentage of relatively coarse material which is transported at higher discharges. This coarser material exhibits a lower exchange capacity for heavy metals and particle size has been noted to influence the partitioning and transport of metals (Hart, 1982; Lum et al., 1982). A lower concentration in suspended sediment occurs at the second flood peak as the finest sediments in the river bed may be suspended at relatively low shear stresses. Therefore, fine-textured bottom sediments will be carried away at the beginning of the flood, whilst towards the end of the event sediments are coming from more distant sources with a more limited supply.

The gradual decline in total metal levels (copper, lead and zinc) from the start of the event illustrates the dilution effect. Cadmium, however, does not show this to the same degree, a large drop in concentration occurs between the first two samples. The reason for this could be due to other processes: (1) analytical problems arising from very low cadmium concentrations; and (2) changes in pH and in the oxidation-reduction potential (Eh). At the onset of flooding, metals may be 'desorbed' or dissolved from their hosts (e.g. Fe / Mn oxides, organic matter) in response to pH and Eh changes and taken into solution. The adsorption / desorption behaviour of metal ions at the solid / water interface is strongly pH dependent (Leckie and James, 1974). The data shows that a significant decrease in pH occurs at the onset of the event and is accompanied by an initial rise in dissolved cadmium species in particular, but also a slight increase in dissolved lead. Tessier et al. (1980) also found that cadmium was readily desorbed from solid phases. Hydrous oxides, clay minerals and organic matter generally exhibit strong cation exchange properties in alkaline solution, strongly binding many metals to their surfaces. However, as pH decreases, the surface charges and attractive forces become diminished and the concentration of dissolved metal ions increases (Williams et al., 1974).

Towards the end of the flood event slight increases in total metal concentrations occur. This may reflect metals being reabsorbed or coprecipitated by the sediment, driven by the small increase in pH that occurs at approximately 00:00 hours, 13/2/96, and the resulting decreases in the concentration of dissolved metal levels. At the discharge and suspended sediment concentration peaks, especially during the second flood peak, where sediment metal concentrations are the lowest, dissolved concentrations of metals are the highest, the result of a sharp decrease in pH. Particulate-bound metal levels closely mirror changes in pH.

To establish changes in heavy metal concentration during the flood and the relationship with discharge and suspended sediment concentrations, Pearson coefficients of correlation were determined from the raw data, for two phases of the sediment peak. That is, the rising and the falling sediment limbs (table 7.1 a). The Pearson method of correlation was chosen, despite the small number of samples, to compare the results directly with those found in other studies. The amount of suspended sediment is positively correlated with the river discharge (= 0.711) on the rising limb of the flood. However, a poor correlation between discharge and suspended sediment concentration was found (= 0.118) on the falling limb. Considering metal concentration with discharge on the rising limb, a strong negative correlation was found (Cd = -0.561, Cu = -0.825, Pb = -0.767, Zn = -0.695), but such values were not reported for the falling limb. The relationship between sediment concentration and metal concentration was also considered. On the rising limb of the flood, copper, lead and zinc showed strong negative correlations to the amount of sediment present (Cu = -0.739, Pb = -0.789, Zn = -0.724) and cadmium gave -0.560. However, strong negative correlations were also found for cadmium, lead and zinc on the falling limb (Cd = -0.788, Pb = -0.740, Zn = -0.883). Similar correlations between metal concentration and

Table 7.1 - Correlation coefficients between discharge, suspended sediment concentration & sediment-associated metals, Thwaite Mills

(a) Discharge with suspended sediment & total metal concentrations

	flood data (n = 23)	rising limb (n = 11)	falling limb (n = 12)
SS	**0.4916**	**0.7107**	0.1182
Cd	**-0.4693**	-0.5607	-0.0390
Cu	**-0.7847**	**-0.8245**	-0.2949
Pb	**-0.7127**	**-0.7670**	-0.1049
Zn	**-0.6417**	**-0.6951**	-0.1043

Suspended sediment with discharge & total metal concentrations

	flood data (n = 23)	rising limb (n = 11)	falling limb (n = 12)
Q	**0.4916**	**0.7107**	0.1182
Cd	**-0.4420**	-0.5598	**-0.7884**
Cu	**-0.5940**	**-0.7391**	-0.3945
Pb	**-0.6944**	**-0.7893**	**-0.7402**
Zn	**-0.6794**	**-0.7239**	**-0.8831**

(b) Total metal concentrations with chemical speciation

Flood event (n = 23)

	A	B	C	D	E
Cd	**0.7971**	**0.6462**	**0.9866**	**0.8958**	**0.7783**
Cu	**0.7493**	**0.9701**	**0.9020**	**0.7601**	**0.7895**
Pb	**0.9703**	**0.9417**	**0.9684**	**0.9236**	**0.9809**
Zn	**0.9872**	**0.9594**	**0.9971**	**0.9697**	**0.9803**

Rising limb (n = 11)

	A	B	C	D	E
Cd	**0.8765**	**0.7386**	**0.9853**	**0.9004**	**0.8897**
Cu	**0.8403**	**0.9701**	**0.8807**	**0.8041**	**0.7180**
Pb	**0.9689**	**0.9376**	**0.9703**	**0.9156**	**0.9846**
Zn	**0.9918**	**0.9638**	**0.9984**	**0.9661**	**0.9778**

Falling limb (n = 12)

	A	B	C	D	E
Cd	**0.9595**	**0.9831**	**0.7718**	0.4173	0.4892
Cu	0.4996	**0.6021**	0.5397	0.3952	**0.7591**
Pb	**0.9005**	**0.7518**	**0.8043**	**0.9322**	**0.9471**
Zn	**0.8758**	**0.8308**	**0.9654**	**0.9918**	**0.9811**

SS = suspended sediment concentration
Q = discharge
n = number of samples
A = exchangeable metal ions
B = surface oxide & carbonate metal ions
C = metal ions bound to Fe & Mn oxides
D = organically bound metal ions
E = residual metal ions

figures in bold are significant at the 95 % confidence level discharge have been found by Bradley and Lewin (1982; cadmium = -0.96, lead = -0.62). The metals also showed strong negative correlations to the amount of sediment present (e.g. lead = -0.694, zinc = -0.679).

In view of these observations it is clear that a dilution effect occurs during the flood with a negative relationship between metal levels and river discharge. In addition, sediment-associated metal concentrations exhibit a strong tendency to decrease with increasing sediment concentration and appear to be largely controlled by pH.

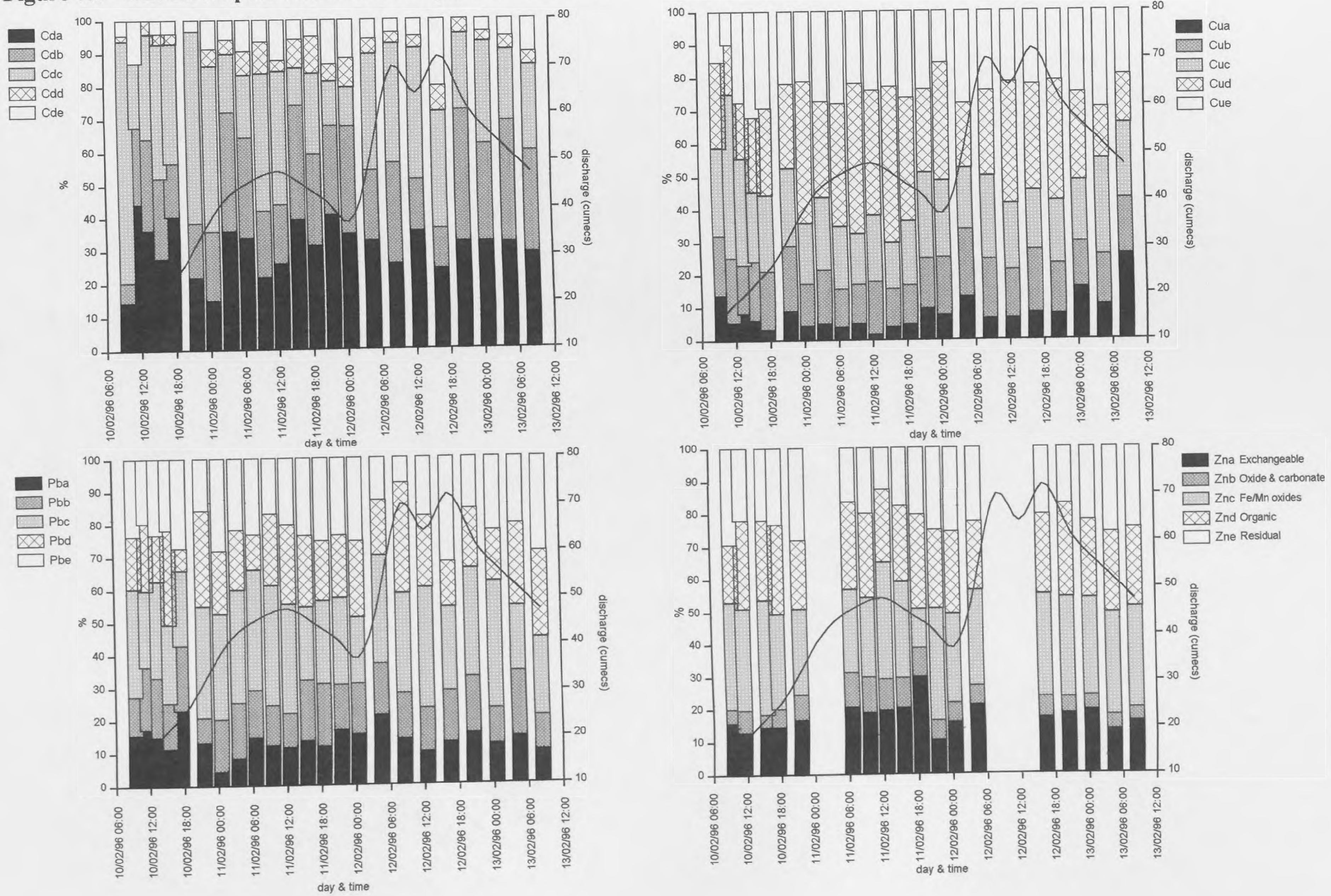
7.3 Chemical Partitioning of Heavy Metals on Suspended Sediment through a flood event at Thwaite Mills, River Aire

The chemical fractions which the metals were found on the sediment also varied during the event (figure 7.3), with a tendency for certain metals to be concentrated in specific fractions. In particular, the organic fraction accounted for, on average, 30 % of the copper, while significant amounts of both lead and zinc were contained in the Fe and Mn oxide fraction. The majority of cadmium (> 85 %) was transported within the first three sequential extraction components.

At the first flood peak, 41 % of the cadmium, 34 % of the lead and 36 % of the zinc were present in the Fe and Mn oxide fraction. Through the falling hydrograph, however, up to 41 % of the cadmium was present in the exchangeable fraction, whilst for lead and zinc both the exchangeable and residual components became more important.

At the second flood peak, 36 % of the cadmium was present in the Fe and Mn oxide fraction. This fraction was most important on the rising limb, while the exchangeable and surface oxide and carbonate fractions became important as flood discharges began to decline, accounting for between 60 - 75 % of total sediment cadmium. Throughout the flood, the organic fraction contained the majority of the copper, however, as the discharge subsided the exchangeable and Fe and Mn oxide fractions became more important. Prior to the peak flow, the majority of lead was

Figure 7.3 - Chemical speciation & discharge, Thwaite Mills



present in the Fe and Mn oxide fraction. At the flood peak, the residual fraction accounted for 32 % of the lead. The Fe and Mn oxide fraction accounts for 31 % of zinc at the second flood peak. This amount remains constant as the discharge subsides, with the residual fraction increasing its percentage of total sediment zinc.

The Pearson coefficients of correlation were calculated between the chemical fractions and the total concentration of each element studied, for the whole food event and for both the rising and falling flood limbs (table 7.1 b). The data shows that the Fe and Mn oxide fractions of cadmium and zinc were strongly correlated with the total cadmium (= 0.987) and total zinc (=0.997) concentration. For copper, the surface oxide and carbonate fraction was the most important (= 0.970). The residual and exchangeable fractions of lead were most strongly correlated with total lead concentration. For the chemical fractions studied, the Fe and Mn oxide fraction was very strongly correlated with total cadmium & zinc concentrations on the rising limb of the flood (Cd = 0.985, Zn = 0.998). For copper, the surface oxide and carbonate fraction was most strongly correlated to total copper concentration on the flood rising limb (= 0.970). The Fe and Mn oxide and residual fractions, on the rising limb, were both strongly correlated with total lead concentration. On the falling limb of the hydrograph, the concentration of cadmium in the exchangeable and surface oxide and carbonate fractions was very strongly correlated with the total amount of cadmium present. These fractions were found to occupy a greater percentage of total cadmium as the flood discharge declined. For copper, only the surface oxide and carbonate and the residual fractions were significantly positively related to the total copper concentration on the flood falling limb. Total lead and zinc concentrations were most strongly correlated with the residual (Pb = 0.947, Zn = 0.981) and the organic (Pb = 0.932, Zn = 0.992) fractions on the falling limb of the flood. The residual fraction was found to increase its percentage of bound zinc on the falling limb of the flood.

From the flood event, it is demonstrated that sediment-associated concentrations of cadmium, copper, lead and zinc vary with discharge as does the form in which they are bound to the sediment. Tessier et al. (1980) in a study of water and suspended sediment on a river in south-eastern Quebec found that 26 % of cadmium was in the exchangeable fraction compared to 12 % in the residual phase. In both the Mersey and Humber Rivers the dominant phases for cadmium were the exchangeable, carbonate and Fe and Mn oxides (Gunn et al., 1992). These studies suggest that following an increase in salinity and / or a slight lowering of pH an appreciable percentage of the cadmium would be solubilised. The speciation of particulate copper contrasted with cadmium, with a high percentage bound to the organic fraction in samples taken from the Humber and Mersey river systems (Gunn et al., 1992). The distribution of particulate lead and zinc was characterised by the importance of the Fe and Mn oxide fraction. These results are in agreement with the known ability of Fe and Mn oxide coatings to scavenge trace metals from solution (Jenne, 1968; Whitney, 1975) and are consistent with results found by Tessier et al. (1982) where 14 % of total copper, 40 % lead and 24 % zinc were found in this fraction.

The pattern which has emerged from this study is that cadmium is transported mainly within the first three sequential extraction fractions, particularly the Fe and Mn oxide component at the peak of flow. During the falling hydrograph much of the soluble cadmium is scavenged by the exchangeable fraction of the sediments. Copper is transported largely in the organic and residual components of the sediments. Lead is transported mainly in the Fe and Mn oxide fraction and as discharge falls much of the soluble lead is scavenged by the exchangeable and surface oxide and carbonate components of the sediment. For Zinc, large concentrations are transported within the Fe and Mn oxide and organic fractions.

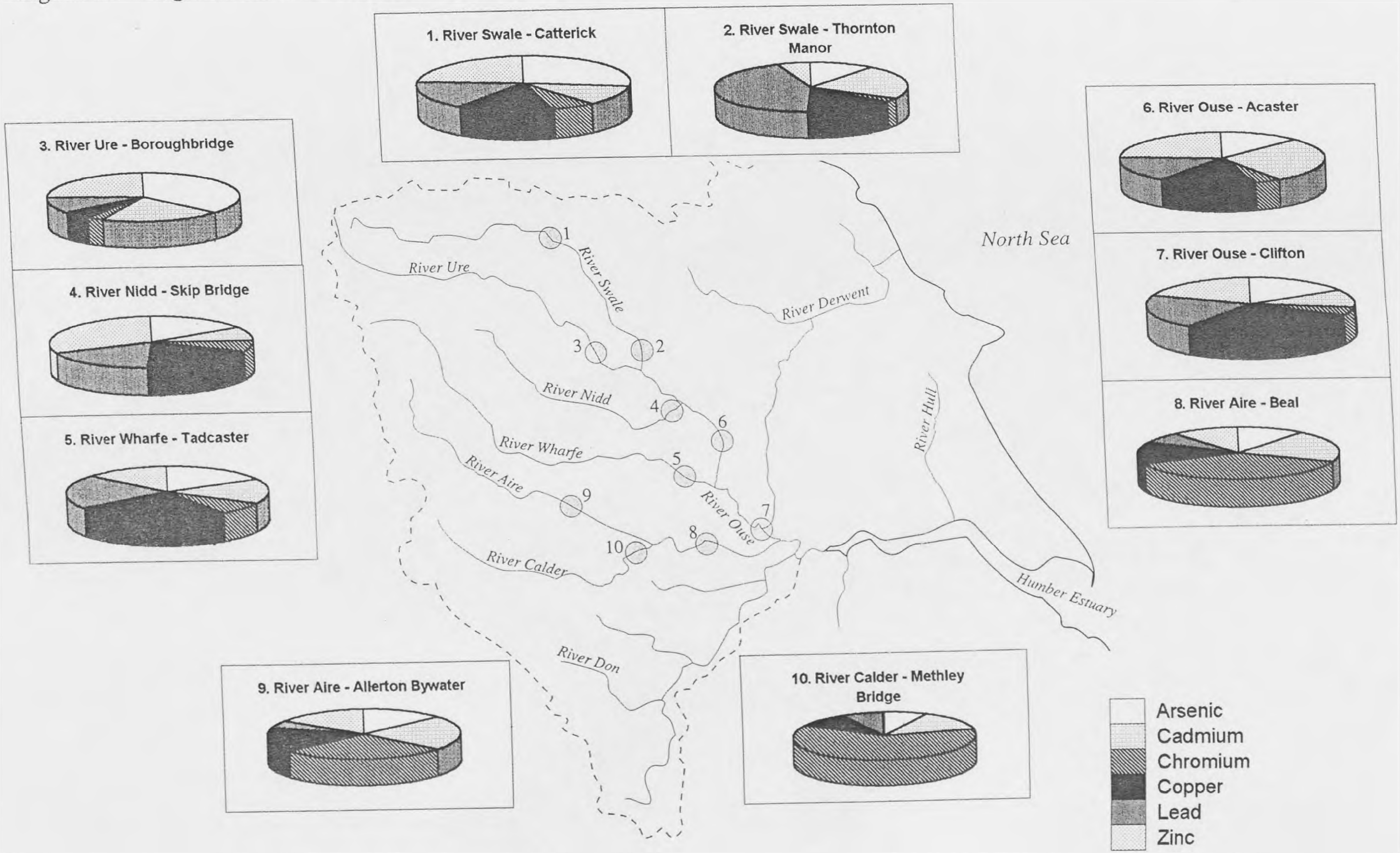
7.4 Spatial Variation in Heavy Metal Concentrations on Suspended Sediment from the Major Ouse Tributaries

The Ouse tributaries sampled exhibit a wide range of landuse types, with large areas of urbanised and industrialised regions in West Yorkshire and open moorland of the Pennines. River water is of variable quality, receiving effluent from mines, industry and urban conurbations and diffuse inputs from agricultural land (Robson and Neal, 1997). Ten different river sites (figure 5.3) have been sampled during high flow events, however, the exact discharge conditions are not known. These include the major rivers draining to the Humber Estuary (Aire and Ouse) together with selected major tributaries to those rivers (Calder, Nidd, Swale, Ure and Wharfe). Regional variations in total heavy metal concentrations (i.e. the sum of each sequential extraction fraction, figure 7.4 and table 6, Appendix III) are interpreted in relation to catchment geography (landuse, industry, etc.) and the chemical partitioning of heavy metals on suspended sediment are investigated (figure 7.5 and table 7, Appendix III).

Figure 7.4 shows metal concentrations at each site as a percentage of the regional total. Arsenic shows highly variable concentrations across the Humber catchment area, showing no consistent trends. Cadmium occurs in elevated concentrations mainly in Rivers Aire, Calder, Ouse (at Acaster) and Swale (at Thornton Manor). Chromium shows a very clear pattern of concentration and occurs in high levels in both the Aire and Calder. Copper shows a more variable pattern in the Ouse tributaries and is consistently higher at sites on the Aire, Ouse, Nidd and Swale. Lead is similar to chromium in that concentrations are highest at few locations, in particular the Swale and Wharfe. Zinc is highly variable throughout the catchment and occurs in high concentrations at all rivers, particularly the Ouse, with the exception of the River Calder.

Heavy metal concentrations therefore show significant variation across the Humber catchment area. The main features relate to: lead-zinc mineralisation in the northern catchments (Nidd, Ouse and Swale) and industrial and domestic effluents from the southern catchments (Aire and Calder). Higher concentrations in the north are related to heavy metal inputs from the base metal rich regions of the Pennines, for example, those drained by the Nidd, Ouse and Swale. There is extensive vein mineralisation in these areas which have been widely mined in the past (Gill, 1987; Macklin, 1992) and historical lead-zinc mining activity has led to contamination of stream and floodplain sediments with mining spoil. As a result these rivers are important sources of lead and zinc, and also copper and cadmium. In the southern catchments, large pollutant discharges from industry and sewage

Figure 7.4 - Regional variations in total metal concentrations



works are made to the Rivers Aire and Calder and result in much higher concentrations of cadmium, chromium and copper. High concentrations of chromium were found only on the Aire and Calder which is common from textile industry in this region. For some determinands the resultant regional distribution derives from a mixture of the above factors; in the case of zinc and copper, for example, there are both industrial and mineralogical sources.

Other studies have observed similar trends (Macklin et al., 1997; Neal et al., 1997; Robson and Neal, 1997). The dominant pattern for most of the heavy metals is one of lowest concentrations in the cleaner northern rivers and highest in the more industrial / urban rivers (cadmium, chromium) clearly reflecting the contribution of pollutant sources (Neal et al., 1997). A reverse pattern is observed for lead with the higher concentrations occurring in the northern rivers, particularly the Swale. The differences reflect the presence of lead-zinc mineralisation in the bedrock of the northern area where mine waste, derived from old spoil heaps and floodplains contaminated by mining, presently constitutes the primary source of contaminant heavy metals (Macklin et al., 1997). For other components there is no discernible pattern between the rivers to the north and south of the area. In the case of zinc there are lithogeneous sources to the north and industrial sources to the south which may mask any distinct regional trends. For most of the metals northern concentrations were found to be roughly comparable with concentrations deriving from the industrial catchments further south (Robson and Neal, 1997). In the southern rivers relative concentrations were highest for chromium (Neal et al., 1997).

7.5 Chemical Speciation of Heavy Metals on Suspended Sediment from the Major Ouse Tributaries

The form of a metal is known to be the main influence on its fate, behaviour and effect on aquatic life, hence chemical speciation was studied on suspended sediment from the Ouse rivers (figure 7.5 and table 7, Appendix III). The results are as follows:

River Aire:

For both sites on the River Aire, arsenic shows wide variations in chemical speciation and there is no single dominant host fraction. Cadmium is found consistently within the first three sequential extraction fractions, the surface oxide and carbonate fraction generally accounting for more than 50 % of total sediment cadmium. The majority of chromium occurs in the Fe and Mn oxide fraction (40 - 62 %), with significant amounts also in the organic and residual components. The residual and organic fractions are also important for copper, the former fraction being more significant than the latter, generally accounting for more than 75 % of total sediment copper. Lead is found predominantly within the Fe and Mn oxide fraction, which generally accounts for more than 70 % of total sediment lead. The surface oxide and carbonate and organic fractions also account for significant amounts of lead. The residual fraction contains the majority of zinc, accounting for up to 98 % of the total amount present.

River Calder:

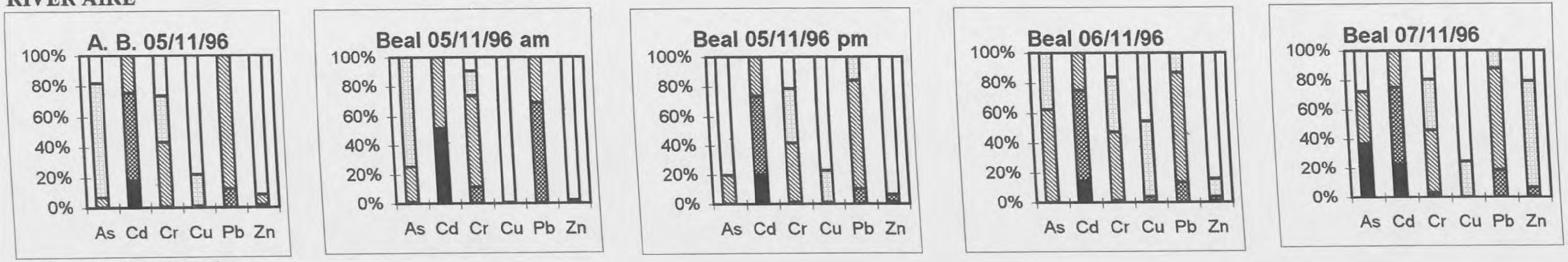
The chemical speciation of the two samples taken from the River Calder show great consistency with each other. A significant proportion of total sediment arsenic is found within the residual component for both samples. Cadmium is dominated by the surface oxide and carbonate fraction and the Fe and Mn oxides, which account for between (50 - 62 %) and (36 - 42 %) of total sediment cadmium respectively. Chromium occurs almost entirely within the last three sequential extraction fractions. The Fe and Mn oxide component contained the majority of the lead. In the River Calder, the surface oxide and carbonate fraction contained almost all the zinc, the remainder being found within the residual fraction.

River Nidd:

The single sample taken from the River Nidd shows that arsenic is mainly associated with the organic fraction (84 %). The exchangeable fraction contained the majority of the cadmium (60 %), the remainder was associated with the Fe and Mn oxides (40 %). The Fe and Mn oxide and residual components predominate for chromium, together accounting for nearly all sediment chromium present. The last

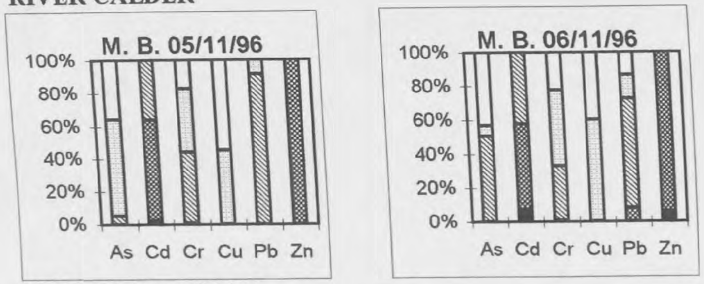
Figure 7.5 - Chemical speciation, Ouse tributaries

RIVER AIRE



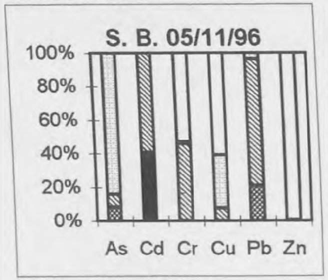
A.B. - Allerton Bywater

RIVER CALDER



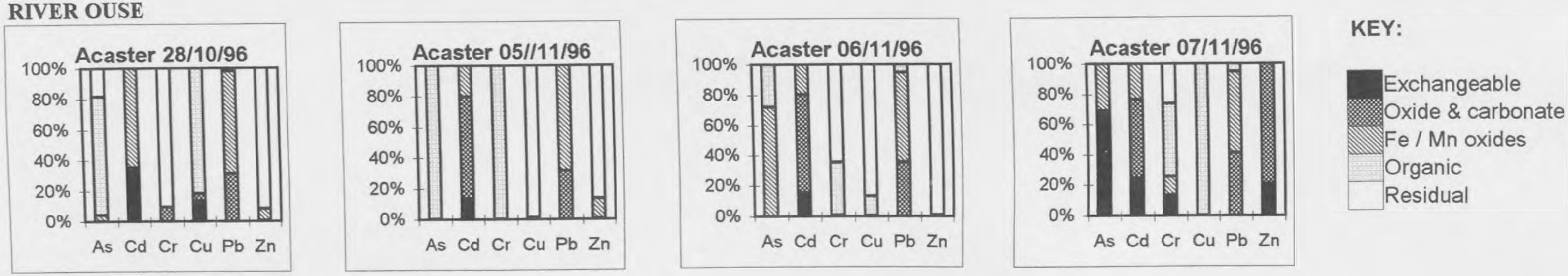
M.B. - Methley Bridge

RIVER NIDD



S.B. - Skip Bridge

RIVER OUSE



three sequential extraction fractions contain all the copper, the residual fraction accounting for the majority (61 %) of total sediment copper present. For lead, the surface oxide and carbonate fraction and Fe and Mn oxides account for a very high percentage of total sediment lead, 21 % and 75 % respectively. Almost all sediment zinc is found within the residual component.

River Ouse, Acaster:

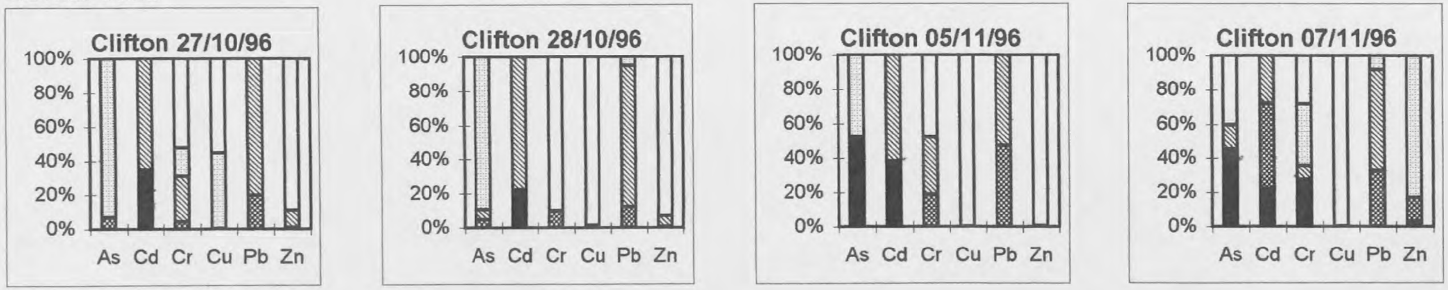
Arsenic occurs in various concentrations in the fractions of each sample taken on the Ouse at Acaster. Cadmium is only found within the first three sequential extraction fractions, the surface oxide and carbonate fraction predominates, accounting for 65 % of total sediment cadmium. Chromium and copper both occur mainly within the organic and residual components. The surface oxide and carbonate and the Fe and Mn oxide fractions are consistently important for lead, together accounting for more than 94 % of total sediment lead. In the first three samples from the Ouse at Acaster, zinc occurs mainly within the residual fraction (up to 92 %), with small amounts also bound to the Fe and Mn oxides. The final sample collected however, has the majority of sediment zinc associated with the first two sequential extraction components.

River Ouse, Clifton:

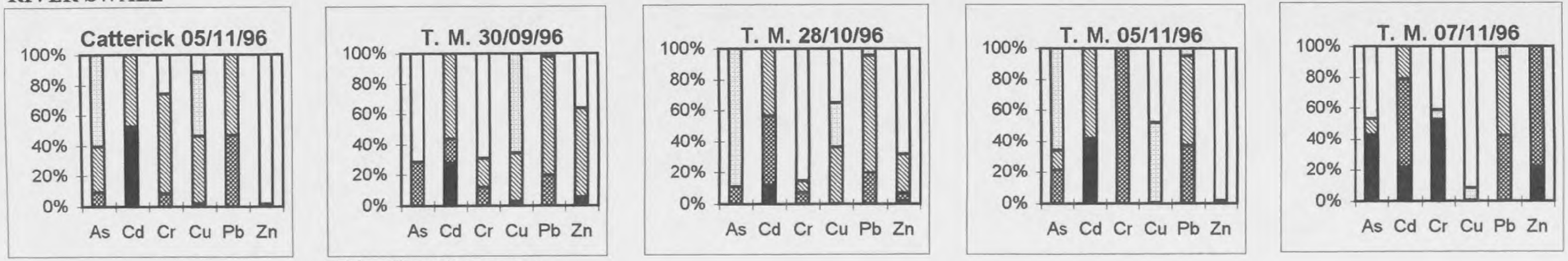
The results for the Ouse at Clifton are very similar to those at Acaster. Arsenic concentrations vary widely and show no consistent trends. Cadmium is found mainly within the first three sequential extraction fractions, the Fe and Mn oxides accounting for the largest percentage of total sediment cadmium (28 - 78 %). Chromium and copper occur mainly within the residual fraction, with smaller amounts of chromium arising in all other components. The surface oxide and carbonate fraction and Fe and Mn oxides are most important for lead, together accounting for > 92 % of total sediment lead. The residual fraction contains the majority of zinc (> 89 %), except for the last sample where the organic fraction predominates, accounting for 83 % of total sediment zinc.

Figure 7.5 - Chemical Speciation, Ouse Tributaries

RIVER OUSE

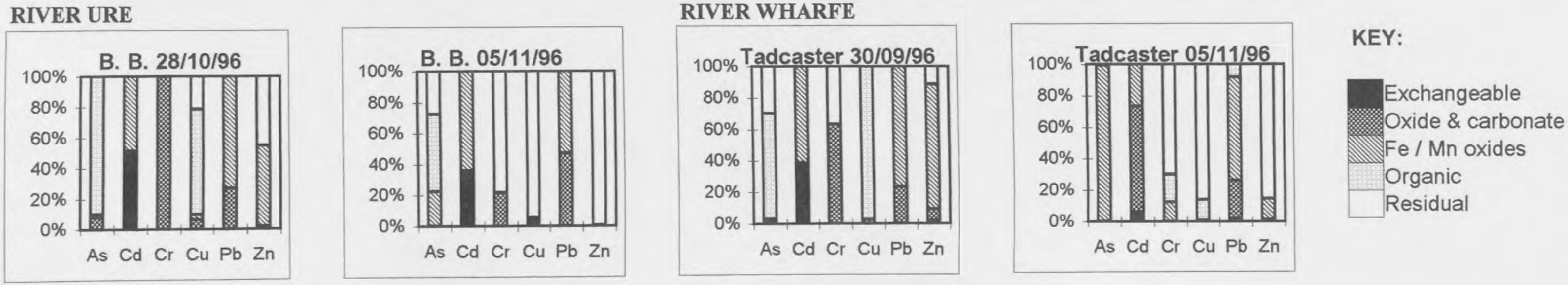


RIVER SWALE



T.M. - Thornton manor

RIVER URE



B.B. - Boroughbridge

River Swale:
Considering all samples from both sites on the Swale, similar to the results found at other sites, arsenic shows considerable variability. Cadmium only occurs at detectable levels within the first three sequential extraction fractions. The Fe and Mn oxides predominate, generally accounting for more than 60 % of total sediment cadmium. The majority of chromium occurs in the residual fraction, although significant amounts also occur in the Fe and Mn oxide and surface oxide and carbonate fractions in some samples. Lead consistently occurs at high concentrations in both the Fe and Mn oxide and surface oxide and carbonate fractions, together accounting for > 93 % of total sediment lead. The residual and Fe and Mn oxides contain the majority of zinc, with the exception of the last sample where the surface oxide and carbonate fraction accounted for 78 % of total sediment zinc.

River Ure:
The majority of arsenic in samples from the River Ure is contained within the organic fraction. Cadmium is found only within the exchangeable and Fe and Mn oxide fractions. The surface oxide and carbonate and residual fractions are important for chromium, accounting for all the sediment chromium present. The organic and residual components contained the majority of the copper (> 90 %). The surface oxide and carbonate and Fe and Mn oxide fractions consistently account for the majority of total sediment lead. The residual and Fe and Mn oxide fractions contain the most zinc.

River Wharfe:
Heavy metal concentrations between the two samples taken from the Wharfe show great variation, especially for arsenic. Cadmium is only found at detectable levels within the first three sequential extractions, the exchangeable and Fe / Mn oxides dominate in the first sample, the surface oxide and carbonate fraction in the second. Chromium in the first sample occurs in highest concentrations within the surface oxide and carbonate fraction and in the second sample in the residual component. Copper is found in the organic and residual fractions in the first and

second samples respectively. Lead is the only metal which shows consistency between the two samples taken, the majority occurring within the Fe and Mn oxides (> 65 %). Zinc occurs in high concentrations in the Fe and Mn oxide fraction in the first sample and the residual component in the second.

To summarise the above results, taking into account data from all sites, arsenic varies widely, showing no consistent trends. At all sites cadmium is found only in detectable levels in the first three sequential extraction fractions, higher levels generally occurring within the surface oxide and carbonate and Fe and Mn oxide components. Chromium occurs mainly within the last three sequential extraction components, the residual fraction in particular. Copper is associated largely with the residual and organic fractions. Lead is the most consistent metal throughout and is found within the Fe and Mn oxide and surface oxide and carbonate fractions. Zinc concentrations vary between sites and between samples collected at each site, but generally occurs in highest concentrations in the residual fraction.

Samples collected in the Rivers Aire, Ouse and Swale on 07/11/96, generally show a greater percentage of metals in the first four sequential extraction fractions and less in the residual component, as compared to samples collected before this date. This applies to metals arsenic, cadmium, chromium and most noticeably, zinc. For example, arsenic and chromium concentrations increase in the exchangeable fraction, cadmium in the exchangeable and surface oxide and carbonate components. Previous samples at these river sites, revealed zinc to be predominantly in the residual fraction. Samples collected on the 07/11/96 show zinc concentrations mainly in the organic fraction (Aire and Ouse at Clifton) and the surface oxide and carbonate and exchangeable components (Ouse at Acaster and Swale). These results may reflect a sudden change in the physical properties of the river water, such as a lower flow. These samples were collected towards the end of the event, where much of the soluble metals may become reabsorbed or coprecipitated by the sediment.

Arsenic concentrations are highly variable throughout, hence no trends have been identified. It is very likely that analytical errors played a large part in these results and concentrations of arsenic are at or around the detection limit of 0.05 ppm. However, Robson and Neal (1997) reported that determinands with specific industrial sources show the greatest variation. Cadmium occurs in elevated concentrations in the exchangeable and surface oxide and carbonate fractions at all sites, particularly on the Aire and Ouse (at Acaster), reflecting both natural and industrial sources. Chromium generally occurs in lowest percentages in the residual fraction in the Rivers Aire and Calder and is contained mainly in the Fe and Mn oxide component. These two rivers contain much higher total concentrations of chromium than any other Ouse tributary and it was expected that these rivers would have the highest concentrations of available chromium as their main source is from industry. However, large proportions of chromium are found in the surface oxide and carbonate fraction in samples from the River Swale at Thornton Manor (05/11/96) and River Ure (28/10/96). Both are rural catchments, with no obvious source of chromium and the results may be due to experimental error. Cross contamination of samples may have occurred by the transfer of airborne contaminants when samples are air dried in the laboratory or during transport, when the filter papers containing the suspended sediment are packed together to be posted. Copper occurs in fractions other than the organic and residual mainly in samples from the Swale, its main source from past metal mining activities. Lead shows great consistency throughout all the rivers, being associated with the Fe and Mn oxides in particular and surface oxide and carbonate fractions to a lesser extent. This indicates the relative importance of these fractions for transporting lead from both natural and industrial sources. The River Calder is the only site where zinc is found consistently within fractions other than the residual, the majority of zinc being associated with the surface oxide and carbonate component. Metals held within this fraction are relatively available in the Calder compared to other rivers, possibly indicating that the major source is from industry.

The results obtained for chemical speciation show a relatively high degree of consistency between the Ouse tributaries and also with data from the Humber system taken from Gunn et al. (1992) where the dominant fractions were identified as: the exchangeable, surface oxide and carbonate for cadmium; reducible (i.e. that associated with the Fe and Mn oxides), organic and residual for chromium; organic and residual for copper; and reducible for zinc. The result for zinc is the only one in disagreement with the present study, where most sediment zinc is associated with the residual fraction.

In evaluating the acid available particulate phase in sediments from the Ouse tributaries, Neal et al. (1997), found that for chromium and copper the highest acid available particulate concentrations occur on the southern rivers (Aire and Calder), indicating that the major particulate source is from industry. For copper it was found that only the acid available particulate component is elevated in the industrial rivers. In contrast, arsenic, lead and zinc had significant natural and industrial sources and showed significant acid available particulate concentrations across all rivers.

Despite large differences in total metal concentrations in the Ouse tributaries, the speciation patterns are relatively consistent with each other and with other studies. Arsenic concentrations show large variations throughout the Ouse basin with no single dominant host fraction. For the other metals, where there is significant industrial or mining input, concentrations associated with the first three sequential extraction fractions tend to be higher than in rivers without such influences.

7.6 Conclusions

The load of flood-transported metals in the River Aire is largely by river discharge and suspended sediment concentrations. At peak discharge, sediment levels increase and the concentration of solid-bound metals decrease as a result of dilution. However, although metal concentrations are lower at the peak of the flood, the mass flow of sediment-associated metals is highest. It is clear that the transport of heavy metals during flood events is substantial. The distribution of metals between solid-bound and dissolved phases is controlled to a large degree by changes in pH.

The form in which metals are bound to the sediment varies throughout the event and is specific to each metal, but appears to be influenced by adsorption and coprecipitation processes. The pattern which has emerged from this study is that significant amounts of cadmium, lead and zinc are transported in weakly-bound fractions. This suggests that sudden changes in the physical or chemical properties (e.g. discharge, pH, Eh) of the river water is accompanied by a release or sorption of the metal from sediments. Of all the metal fractions the residual may be considered as of no immediate environmental concern as ready release from this fraction is unlikely. On the rising limb of the flood, relatively large concentrations of cadmium, lead and zinc are transported in the Fe and Mn oxide fraction, and it appears to be the most important component for transporting heavy metals. This study shows the importance of various chemical fractions for the transport and cycling of metals and changes related to flood conditions. Knowledge of the partitioning of metals on the sediment is of critical importance in assessing or understanding their environmental behaviour, transport fate, bioavailability and toxicity.

Total heavy metal concentrations show significant variation in the Ouse tributaries. Lead, zinc, copper and cadmium are primarily associated with mineralisation and are highest in the northern catchments of the Nidd, Ouse and Swale. Cadmium, chromium, copper and zinc are metals associated with industrial discharges and are higher in the urban and industrial catchments of the Aire and Calder. For these rivers, although the results indicated important differences in total particulate metal concentrations, there was a high degree of consistency in speciation trends between the Ouse tributaries. Chemical controls clearly play a role in chemical speciation of suspended sediment, but the role of hydrological processes is uncertain in these samples and is likely to be very significant. Several analytical problems occur when using suspended sediment samples for chemical speciation. The chemical fractions identified are only operationally defined and can, to some extent, overlap (section 5.2.7). The quantity of sediment used in the analysis is often very small and digested using strong acids which must be strongly diluted before analysis, resulting in metal concentrations often being close to detection limits. This suggests that great caution should be taken when using these results to establish regional variations in chemical speciation. Further work needs to be carried out to support the present results, taking into consideration discharge conditions, using more samples from each site and where possible, using larger amounts of suspended sediment.

CHAPTER 8

HISTORICAL HEAVY METAL CONTAMINATION IN THE RIVER AIRE

8.1 Introduction

Once released into the river environment, heavy metals can be absorbed onto suspended matter (Zwolsman et al., 1993), transported and subsequently deposited across floodplains by sedimentation during overbank floods. Of the sites of deposition, floodplains are the most important in the river environment. Fluctuating inputs of heavy metals to river systems together with changes in inundation frequency and deposition rate are commonly reflected in floodplain sequences by varying amounts of metals in vertical sediment profiles (Macklin et al., 1992; Rang and Schouten, 1989). By acting as a focus for deposition, particulate-bound metals can remain stored in these alluvial environments for decades or even centuries (Macklin, 1996). However, once a metal has become incorporated within floodplain soils it has not entered a static environment and sediment-associated metals can be remobilised if contaminated soil or sediment is disturbed, or if environmental conditions change. This implies that pollution of the fluvial system may continue even after the original polluting source is extinguished (Macklin, 1996). In floodplain soils it is not the total amount of a heavy metal, but how it is actually stored that is important in assessing the environmental impact (Leenaers, 1989). A metal may be considered to be potentially mobile if it is stored in the non-residual fraction of a sediment. Sequential extraction techniques appear to mimic a general environmental mobility sequence of sediment-bound metals and give a reasonable indication of how they might behave should chemical conditions change. Floodplain surface and subsurface soils were collected at regular intervals across the floodplain and downstream and analysed for total metal concentration and chemical speciation by AAS.

Sediment cores provide a historical record of events occurring in the watershed of a river and enable a reasonable estimate of the background level and changes in input of a metal over an extended period of time (Förstner and Wittmann, 1981;

Salomons and Förstner, 1984; Spliethoff and Hemond, 1996). Because of their large adsorption capabilities, fine-grained sediments represent a major repository for contaminants and a record of the influence of human activity (Macklin et al., 1994; Ridgway et al., 1995). Thus they can be used for historical reconstructions (Valette-Silver, 1993). Almost without exception the studies published (Owens and Cornwell, 1995; Valette-Silver, 1993; Zwolsman et al., 1993) have shown that sediment contamination increased in the late 1800s, accelerated in the 1940s and reached a maximum in the late 1960 -70s. For some pollutants, such as lead, a decrease in concentration occurred in the 1980s following the implementation of new discharge and emission regulations. The objectives of this work were to examine changes in the concentration, forms and sources of heavy metals and to link these to anthropogenic factors. Sediment cores were taken at various locations throughout the Aire Valley (figure 5.4) and analysed for total metal concentration and chemical speciation by ICP-AES.

8.2 Heavy Metal Concentrations in Floodplain Soils

The River Aire channel is stable, indicated by a study of historical maps and the dominant process of floodplain formation is the sedimentation of fines by overbank floods (Lewin et al., 1983). The study of the floodplain sediment system assumes some considerable importance not only for quantifying fluxes and storage of sediment-associated metals, but additionally for safeguarding surface and groundwater quality and for protecting plant, animal and human health.

Floodplain surface (0 - 20 cm) and subsurface (20 - 50 cm) soil was sampled, where possible, from both sides of the river along transects with increasing distance from the channel. Sediments were sampled at 2 m from the river, then samples were taken at 25 m intervals across the floodplain to the edge of the valley side. Throughout the city centre and city outskirts, i.e. between 10 - 20 km downstream, the river banks are heavily built-up and no floodplains occur. Sampling of the floodplains was greatly determined by access, particularly on the south side of the river downstream of the city centre, often hindered by the closeness of the Aire and Calder Navigation.

Figures 8.1 - 8.4 show the total concentration of each metal in floodplain surface and subsurface soil at various sites downstream with increasing distance from the river. Metal concentrations in contemporary within channel sediment are also included in the figures for comparison purposes and are represented in the figure by a dark grey bar in between 5 m south and 5 m north of the river. Tables 1 and 2 in Appendix IV show all the results along with pH and loss on ignition data. It was not always possible at each site to get a subsurface sample, where this is the case, an 'X' is marked on the tables.

The results show that heavy metal concentrations vary greatly between each metal, both downstream and laterally across the floodplain. For cadmium, total metal levels tend to be higher in floodplain soil than in contemporary within channel sediment throughout the catchment, with exceptions at sites at 3.8, 5.1, 7.7, 8.5 and 23.0 km downstream. In overbank deposits (2 m from the river), cadmium concentrations at the start of the study are relatively low (between 2.0 - 3.0 mg/kg). From 3.0 km downstream levels increase and maintain a higher level of contamination (between 3.7 - 6.7 mg/kg), until 21.0 km downstream where concentrations decrease and are similar to those at the start of the study. Cadmium concentrations overall are highest between 4.4 and 6.0 km downstream. Laterally across the floodplain the pattern of cadmium concentration is complex. Where there is extensive floodplain development, sites showing a general decrease in concentration with distance from the river include 1.0, 4.4, 5.1, 5.5, 7.7, 8.1, 8.5, 23.0 and 26.0 km downstream. Several sites show an increase in concentration laterally across the floodplain; 0.0, 0.5, 6.0, 6.7, 8.8, 9.2, 21.0, 22.0 and 24.0 km downstream. No clear pattern can be established between cadmium concentration in floodplain surface and subsurface soils.

As with cadmium, copper concentrations tend to be higher in floodplain soils than in contemporary within channel sediment, particularly after 4.0 km downstream. Sites at 0.5, 1.0 (north of the river) and 3.8 km downstream, show generally higher concentrations in contemporary within channel sediment. Copper concentration in overbank sediment varies greatly with distance downstream. Very high

Figure 8.1 - Cadmium concentrations in floodplain soils

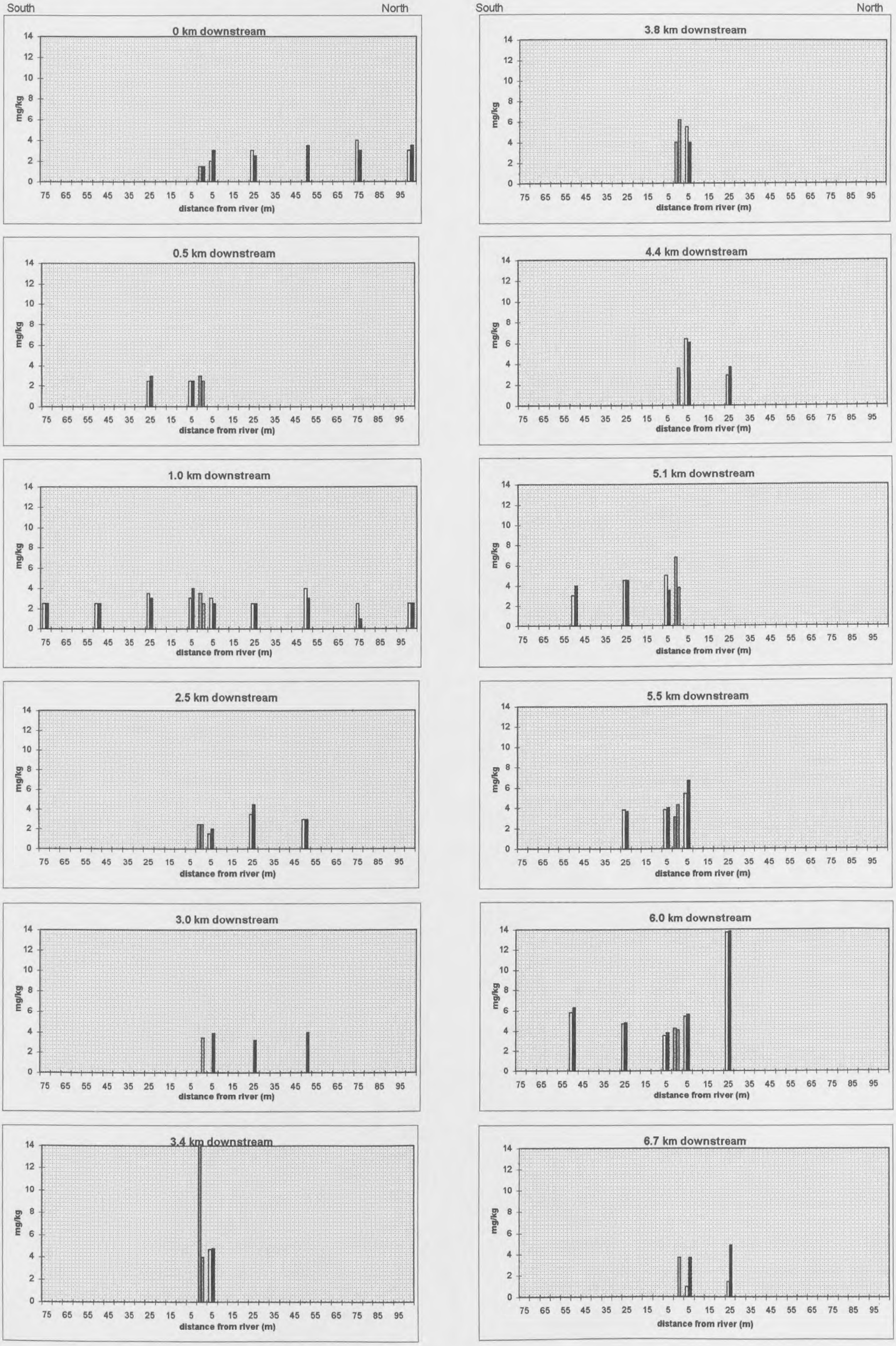
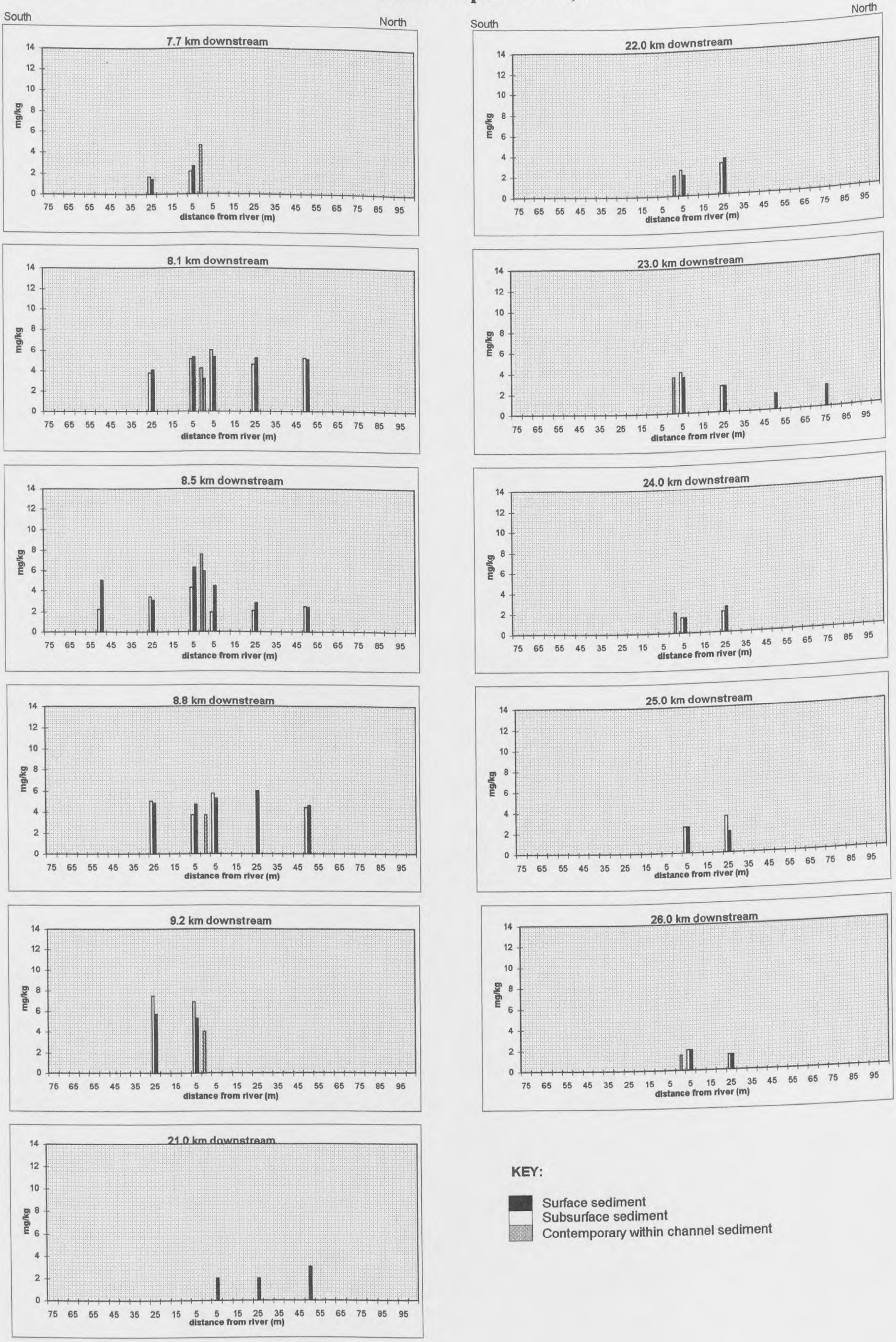


Figure 8.1 - Cadmium concentrations in floodplain soils, cont...



7.7 km downstream

8.1 km downstream

8.5 km downstream

8.8 km downstream

9.2 km downstream

21.0 km downstream

22.0 km downstream

23.0 km downstream

24.0 km downstream

25.0 km downstream

26.0 km downstream

Figure 8.2 - Copper concentrations in floodplain soils

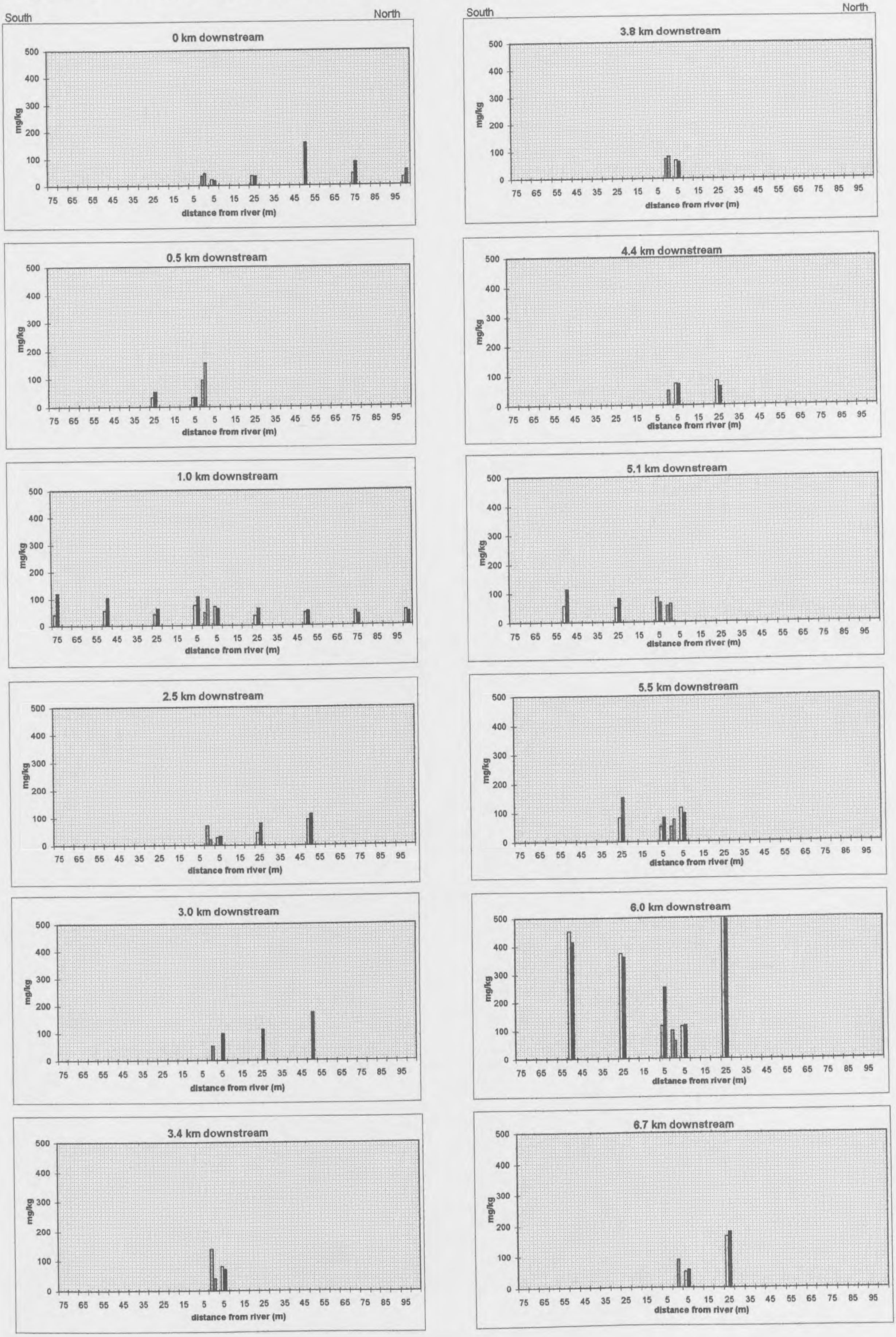
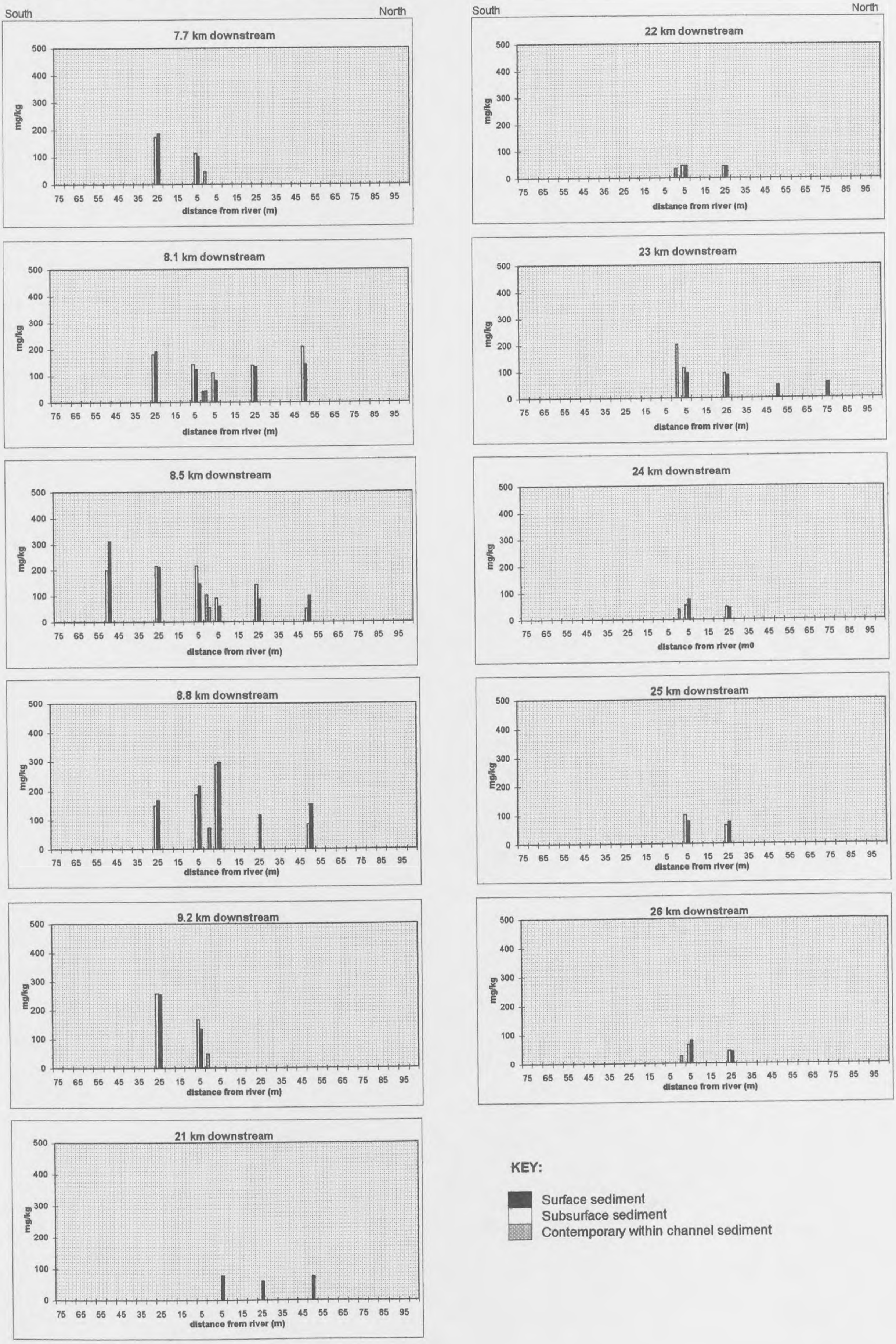


Figure 8.2 - Copper concentrations in floodplain soils, cont...



concentrations occur at 8.8 km and there's also high levels between 6.0 - 9.2 km downstream, especially on the south side of the river. Lowest concentrations are observed at the start of the study. Total copper concentrations increase laterally across the floodplain at the majority of sites, including 2.5, 3.0, 4.4, 5.1, 5.5, 6.0, 6.7, 7.7, 8.1, 8.5 and 9.2 km downstream. Sites from 21.0 km tend to show an increase in copper between contemporary and overbank sediment, levels then decreasing at 25 m across the flooplain. Again there is no relationship between copper concentrations and floodplain surface and subsurface soils.

A very similar pattern of concentration is observed for lead. Higher concentrations of lead occur in floodplain soil than in contemporary within channel sediment, with the exception of sites at 0.5, 1.0, 3.8 and 23.0 km downstream. In overbank sediment, lead concentrations show much variation, with low levels at the start of the study catchment, increasing with distance downstream. High concentrations are observed at 3.0, 5.5, 6.0 and 8.8 km downstream on the north side of the river. Elevated lead concentrations occur on the south side of the river between 7.7 and 9.2 km downstream. The pattern of lead concentration laterally in the floodplain shows no consistent trends. Sites where concentrations increase with increasing distance from the river include 0.5, 2.5, 5.5, 6.0, 6.7, 8.8, 9.2 and 22.0 km downstream. At 4.4, 7.7, 24.0, 25.0 and 26.0 km downstream, concentrations decrease laterally across the floodplain. Floodplain concentrations are highest at 3.0, 8.1, 8.5, 8.8 and 9.2 km downstream, particularly at sites with greatest distance from the river. Unlike cadmium and copper, where no dominant relationship was established, lead concentrations are highest in floodplain surface soils than in the subsurface.

For zinc, the relationship between contemporary within channel sediment and floodplain soil appears to be much more complicated than for the other metals. At sites 0.5, 1.0, 3.8 and 21.0 - 24.0 km downstream, contemporary within channel sediments have higher concentrations of zinc than floodplain soils. At some sites, for example, 0.0, 3.0, 4.4 and 5.1 km downstream, contemporary within channel sediment zinc concentrations are lower than those determined in overbank

Figure 8.3 - Lead concentrations in floodplain soils

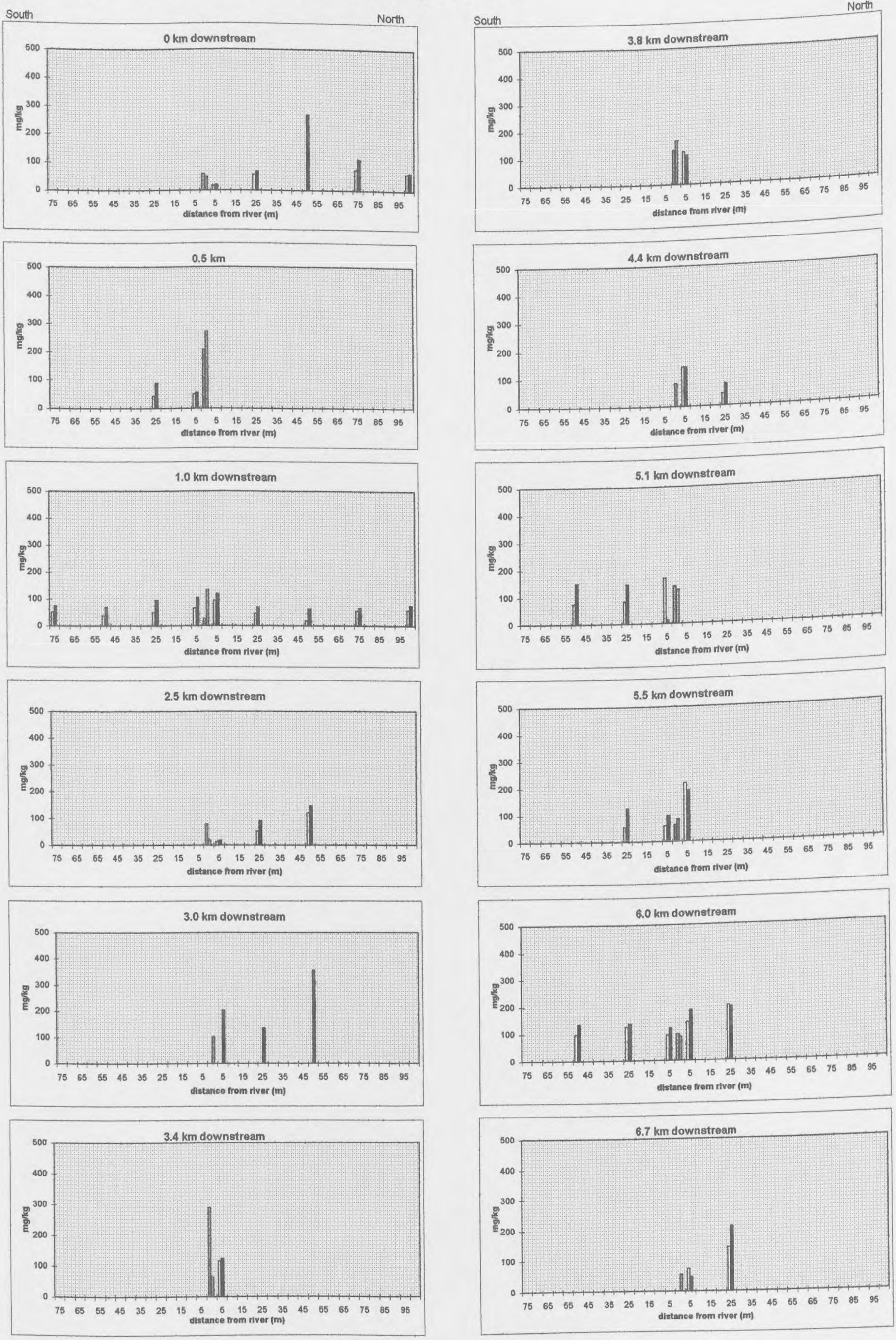


Figure 8.3 - Lead concentrations in floodplain soils, cont...

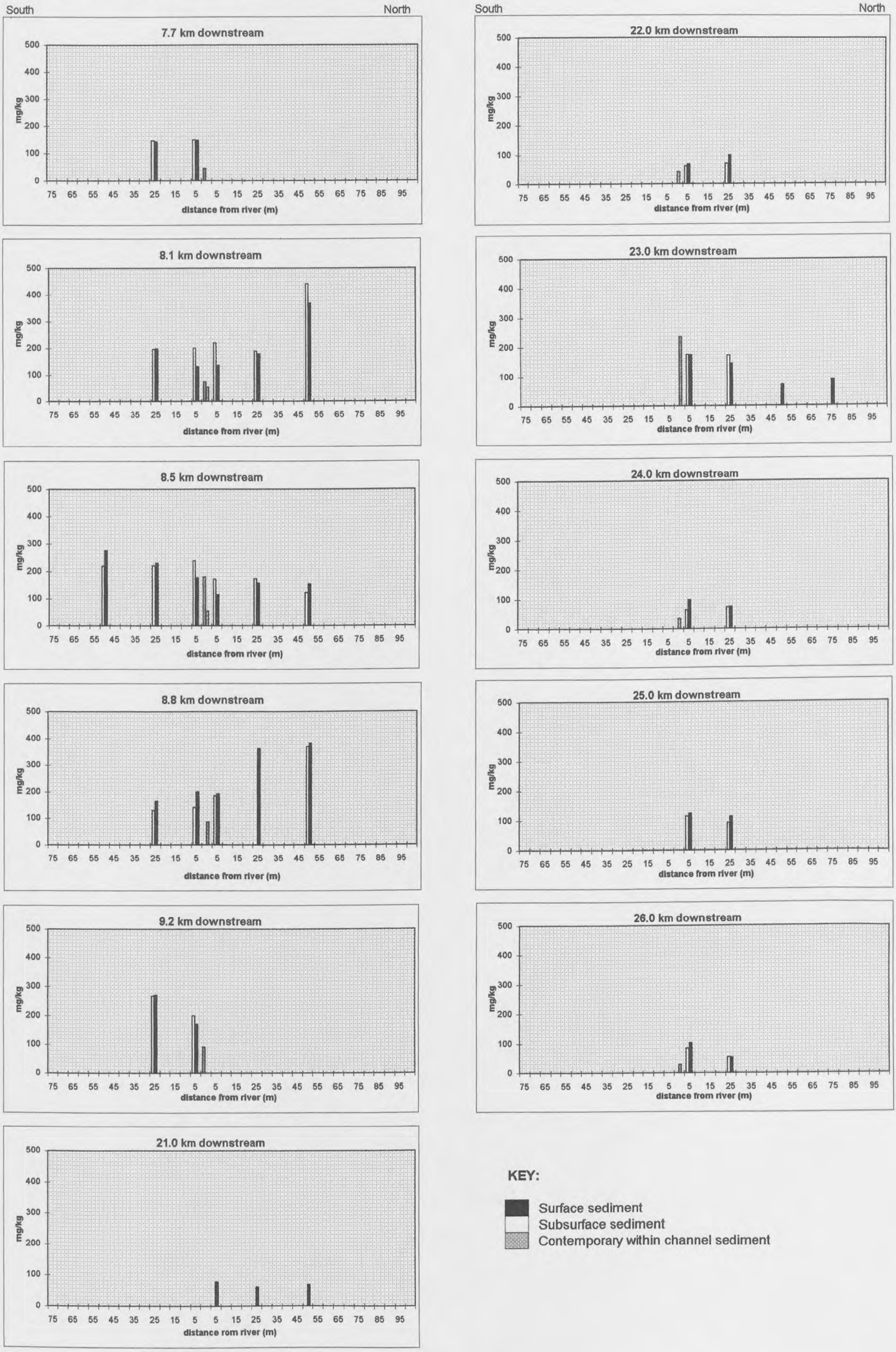


Figure 8.4 - Zinc concentrations in floodplain soils

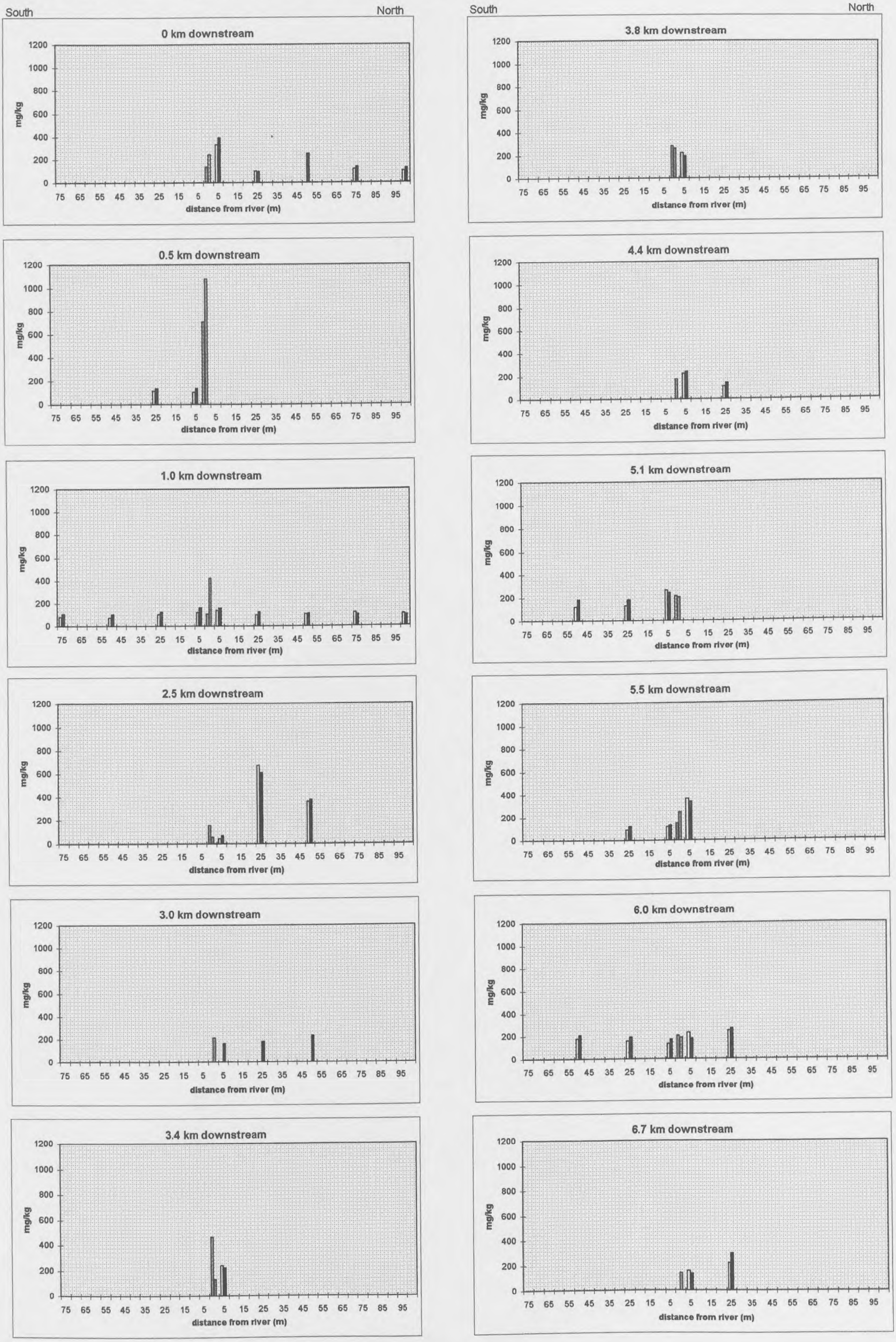
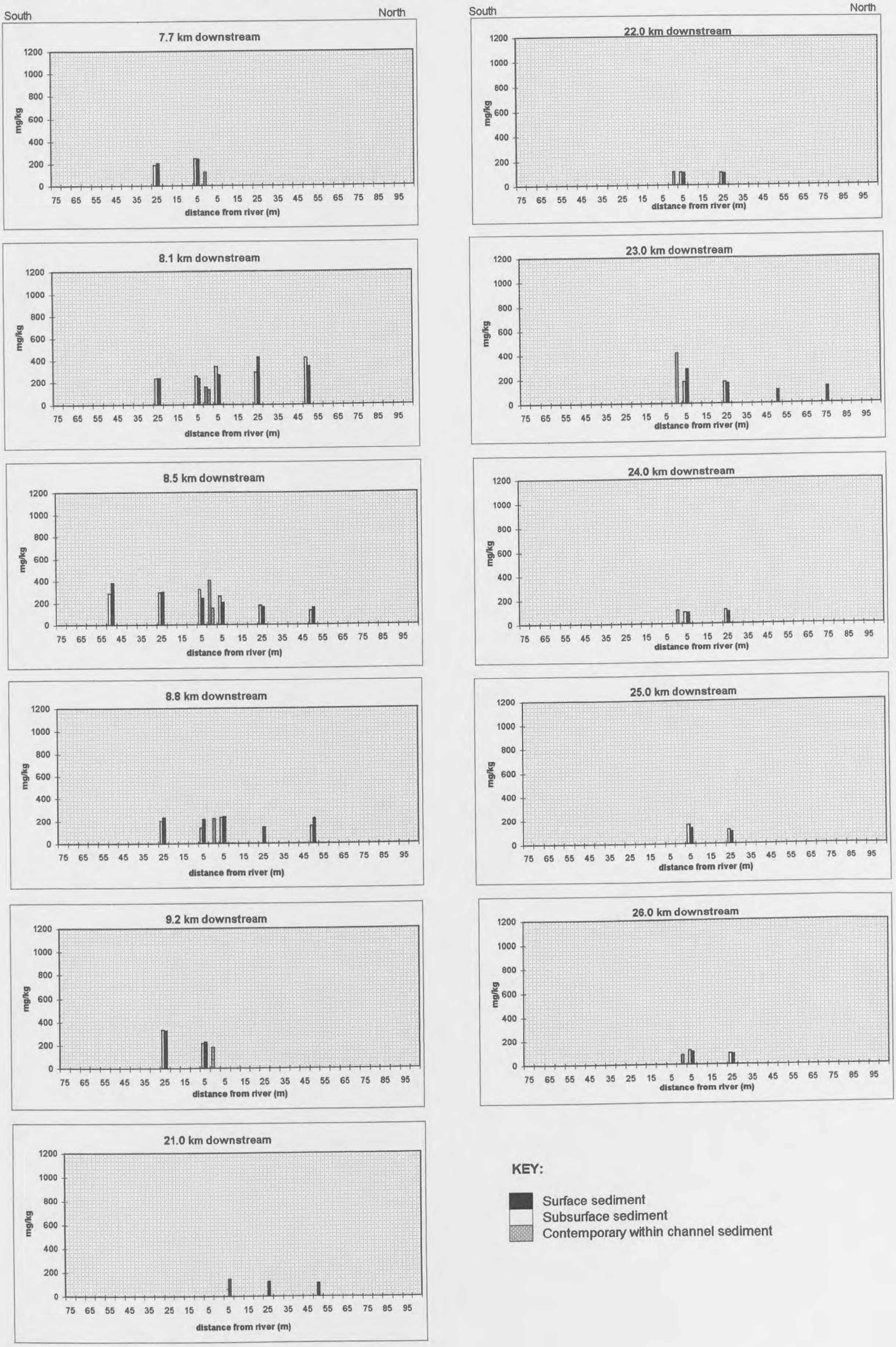


Figure 8.4 - Zinc concentrations in floodplain soils, cont...



sediments, but generally higher than levels in floodplain soils at distances greater than 2 m from the river. Zinc concentrations in overbank sediment at the start of the study catchment are high, differing from cadmium, copper and lead. Levels decline up to 2.5 km downstream and then gradually increase downstream, fluctuating greatly until 21.0 km where concentrations decline again. A peak in concentration does however, occur at 23.0 km downstream. Levels are particularly elevated at 5.5 and 8.1- 8.8 km (north side of the river) and between 7.7 - 9.2 km (south side of the river). With distance from the river, zinc concentrations generally decrease. This occurs at 0.0, 1.0, 4.4, 5.1, 5.5, 7.7, 8.5, 21.0 - 23.0 and 25.0 - 26.0 km downstream. However some sites, for example, 3.0, 6.0, 6.7, 8.1, 9.2 and 24.0 km downstream, show an increase in zinc concentrations laterally across the floodplain. Zinc concentrations between surface and subsurface soils vary greatly.

The spatial pattern of metal concentration in floodplain soils of the River Aire catchment in Leeds is considerably variable. Generally, for each metal determined concentrations are higher in floodplain soil than they are in contemporary within channel sediment, possibly indicating that contamination of the river system is now less than it was in the past. However, at selected sites, contemporary within channel sediment concentrations were higher for each of the metals than those found in the floodplain, including 0.5, 1.0, 3.8, and 23.0 km downstream. The sites at 0.5 and 1.0 and 23.0 km are likely to reflect the influence of metals in final effluent from Esholt and Knostrop sewage treatment works. Metal concentrations are elevated at 3.8 km downstream in the vicinity of consent discharges from Sandoz Pharmaceutical works, Colourflex and a private sewage treatment works (section 4.3.2). In overbank sediments, cadmium, copper, lead and zinc concentrations are highest between 6.0 - 9.2 km downstream. Potential sources of these metals include Rodley sewage treatment works, the highly polluted tributary Oil Mill Beck and agricultural pollution of the Aire at Newlay and Kirkstall (section 4.3.2).

Metal concentrations showed no clear variation in levels across the floodplain. Sites where concentrations of all metals increase laterally away from the river include 6.0, 6.7 and 9.2 km downstream. Sites where concentrations of all metals generally decrease with distance from the channel include: 4.4, 7.7, 23.0 and 25.0 - 26.0 km. Cadmium concentration shows no consistent trends. Copper and lead at the majority of sites increase in concentration with distance from the river, whereas zinc generally decreases in concentration laterally across the floodplain. Lead in particular shows elevated levels at the greatest distance from the river, including sites at 3.0, 8.1, 8.5, 8.8 and 9.2 km downstream. The likely source is atmospheric deposition of lead from vehicle exhausts from nearby roads.

The chemical analysis of floodplain soils show that they are appreciably contaminated with cadmium, copper, lead and zinc. For cadmium, 54 % of floodplain samples exceed the 3.0 mg/kg guideline set by the ICRCL for domestic gardens and allotments. 100% of floodplain sediments exceed the Dutch Policy A-value of 0.8 mg/kg (where the site is considered clean). 1.5 % of samples also exceed the C-value of 12.0 mg/kg where clean-up of the site is considered necessary. 28 % of samples exceed the ICRCL trigger concentration of 130 mg/kg of copper for any use where plants are to be grown. In floodplain soils 93 % and 14 % respectively, exceed the Dutch A-value and C-value of 36.0 and 190.0 mg/kg copper. 12 % of samples exceed the ICRCL trigger concentration of 300 mg/kg zinc for any use where plants are to be grown. 65 % and 60 % of floodplain samples for lead and zinc respectively exceed the Dutch A-values. None of the samples analysed exceed the C-values set for lead or zinc. Cadmium and copper exceeds guidelines to the greatest extent and are considered to be the most problematic in floodplain soils.

However, the levels of different heavy metals can only be mutually compared if the concentrations have been standardised. To do this, using a system devised by Rang et al. (1987), the measured concentration of the metals are combined into a 'pollution index' based on Dutch Soil Protection Policy Guidelines. The concentration of each heavy metal in one sample are converted to a dimensionless quantity by dividing by a norm concentration, enabling the concentration of different levels to be compared. The pollution index is expressed as:

$$\text{Pollution index} = \sum_{j=1}^{n} cj \,/\, (Nj * n)$$

where cj = concentration of metal j

Nj = norm value for the metal j

n = number of metals analysed

In the present research, the pollution index was calculated from the concentration of cadmium, copper, lead and zinc and the norm values of the different metals are taken from the 'test value indicating further research' (A + C / 2) as given in the Dutch Policy system (section 3.5.2). On the basis of the value calculated using the pollution index equation above, the soil samples were classified according to the degree of pollution (table 8.1 and tables 3 and 4 in Appendix IV).

Table 8.1 - Floodplain soils classified according to value of pollution index

		Number of samples (%)		
Pollution index	**Description**	**North**	**South**	**Overall**
0.0 - 0.5	Unpolluted to lightly polluted	53.4	34.0	46.4
0.5 - 1.0	Moderately polluted	39.8	50.0	43.5
1.0 - 2.0	Severely polluted	6.8	16.0	10.1
2.0 -	Very severely polluted	0.0	0.0	0.0

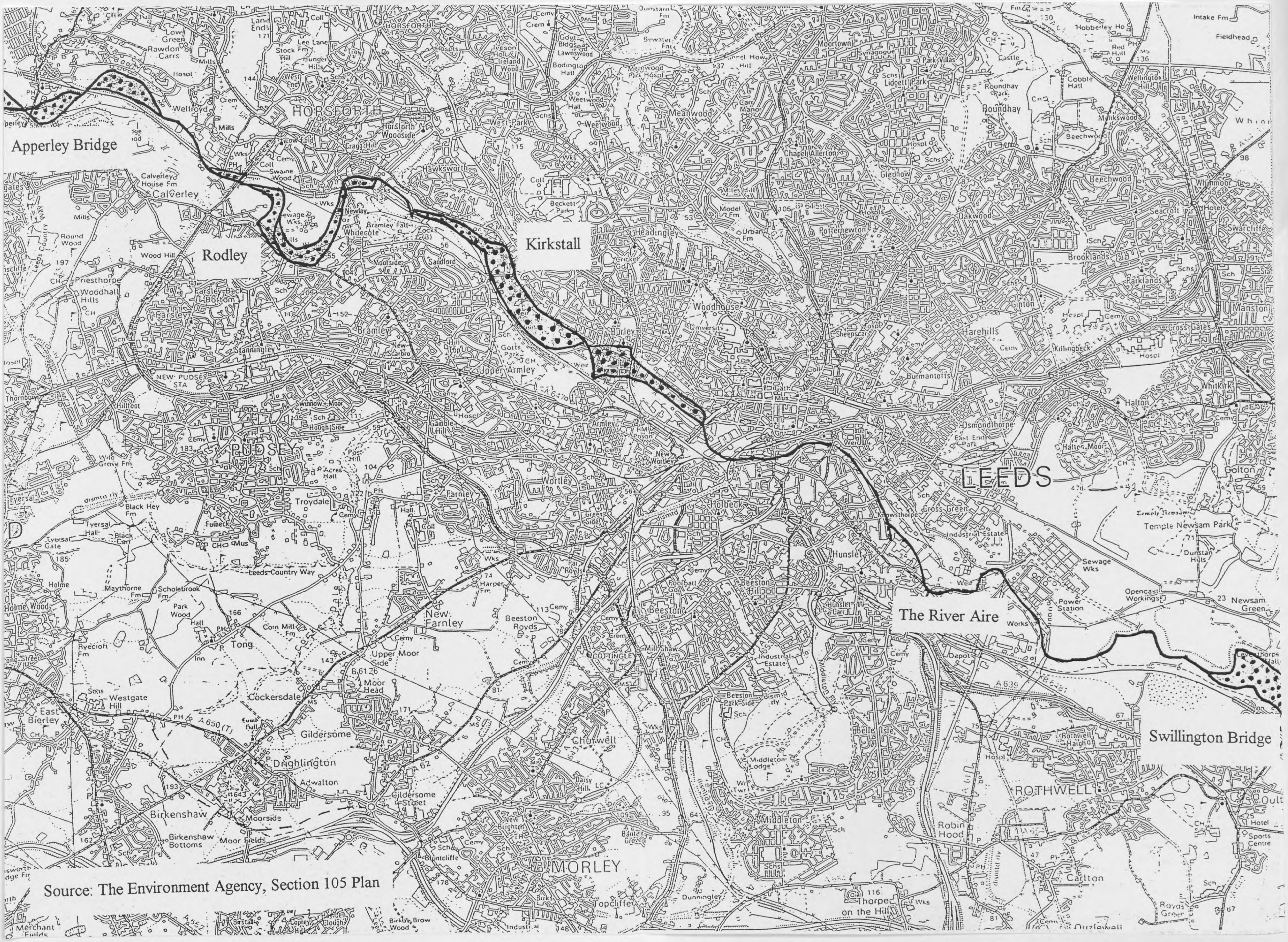
From this table, the majority of sites overall are unpolluted to lightly polluted (46.4 %) and moderately polluted (43.5 %). 10.1 % of sites are classified as being severely polluted, whereas no sites sampled fit the description of being very severely polluted. The south of the river is significantly more polluted than the north, where half the samples are moderately polluted, with 16 % also being severely polluted. Sites at the start and end of the study catchment, i.e. those between 0.0 - 1.0 km and 21.0 - 26.0 km downstream are classified as unpolluted to lightly polluted. Sites between 2.5 - 5.5 km downstream are generally moderately polluted and those between 6.0 - 9.2 km downstream are largely severely polluted.

The severely polluted sites are also those which have the highest concentration of metals in floodplain sediments and where metal concentrations generally increase laterally across the floodplain. The spatial pattern of pollution in floodplain soils appears to be also related to the frequency of flooding. Floodplains between 6.0 - 9.2 km downstream are included on the Environment Agency 'Section 105 Flood Plans', which is land liable to flood (figure 8.5). Within the River Aire in Leeds, other land also liable to flood is found at Apperley Bridge, Rodley and Swillington Bridge. However, during a flood event, the whole floodplain is not necessarily covered. Irregular bank heights downstream ensure that the bankfull discharge varies along the channel and certain parts of the floodplain receive overbank deposits more frequently than others (Bradley and Cox, 1987). Sites between 6.0 and 9.2 km downstream are frequently inundated and will consequently be burdened more by heavy metals, concentrations are higher as metal containing waste discharges into the channel upstream are numerous (section 4.3.2). These floodplains are particularly level and low lying and when inundated with floodwaters, metals are likely to be spread across the entire floodplain.

Sites where concentrations of metals generally decrease with distance from the channel include 4.4, 7.7, 23.0, 25.0 - 26.0 km downstream, which is also land liable to flood. These floodplains are higher lying and in the case of sites towards the end of the study are relatively steep. Floodwaters are therefore unlikely to inundate the whole floodplain. Overbank sediments will therefore be more frequently inundated and consequently receive more heavy metals than the higher lying soils.

To summarise, floodplain soils generally contain higher concentrations of heavy metals than contemporary within channel sediment. The lowest metal concentrations in floodplain soils occur at the start and end of the study catchment and according to the pollution index are classified as being unpolluted to lightly polluted. Floodplain samples taken between 6.0 - 9.2 km downstream contain the

Figure 8.5 - Land liable to flood



Source: The Environment Agency, Section 105 Plan highest concentrations of heavy metals and have the majority of samples within the severely polluted category. These high levels are the result of several heavy metal sources in the upstream vicinity and a relatively high frequency of floodplain inundation.

8.3 Chemical Speciation in Floodplain Soils

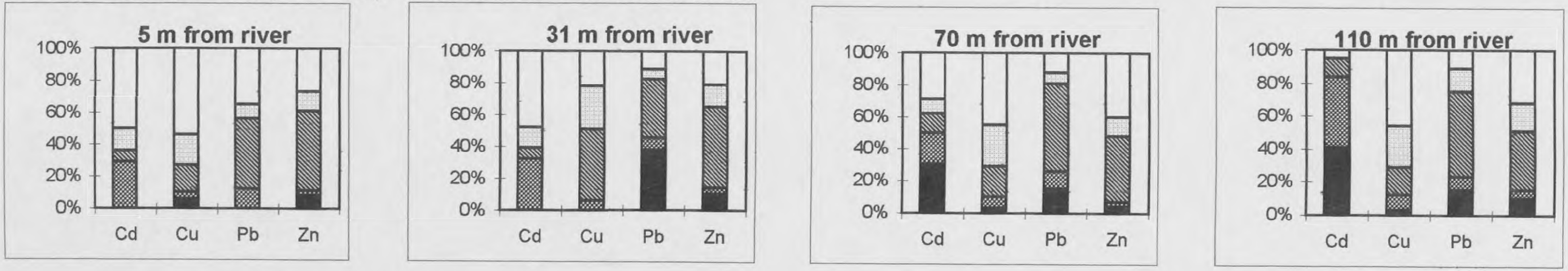
8.3.1 General patterns

Two areas were chosen for investigation to compare chemical speciation patterns and because they were two of the largest floodplain areas of the study reach. It included floodplains at Apperley Bridge and Kirkstall Abbey, from which nine samples were collected. Six floodplain surface (0 - 20 cm) samples were collected, two from kirkstall Abbey and four taken along a transect at Apperley Bridge (0.75 km downstream), as metal levels have been found to vary laterally across the floodplain with increasing distance away from the river (Bradley and Cox, 1990). Three floodplain subsurface (20 - 50 cm) samples were collected at 0.025, 0.05 and 0.40 km downstream. Because of time constraints, it was not possible to analyse all sediments for chemical speciation, and as the findings are consistent with those presented in other studies, these results are taken to represent floodplain soils throughout the Aire catchment in Leeds.

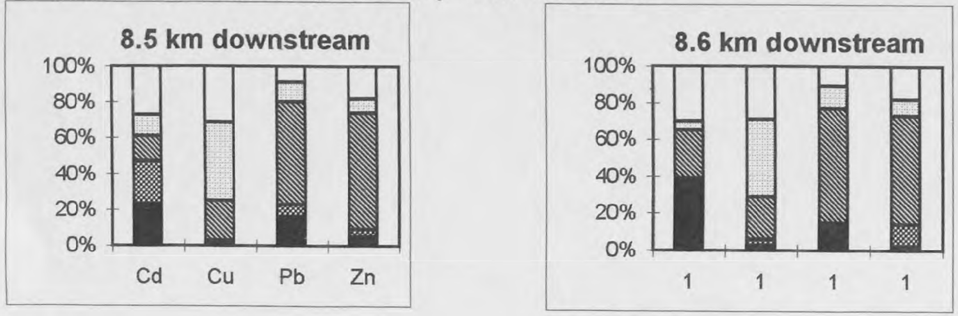
Figure 8.6 shows the chemical speciation of floodplain soils and table 5 in Appendix IV shows the complete set of results, including pH and loss on ignition data. These show that the metals are partitioned between a variety of chemically-defined phases. Cadmium is mainly associated with exchangeable and surface oxide and carbonate metal ions, copper with the organic and residual components, lead with the Fe and Mn oxides and the exchangeable fraction and zinc is associated primarily with the Fe and Mn oxides. The percentage of metal released during the first four extraction steps varies from 50 - 95 % for cadmium, 46 - 88 % for copper, 65 - 99 % and 60 - 87 % for lead and zinc respectively. These fractions, which may be considered ‘potentially mobile’ form a very large part of the total concentration.

Figure 8.6 - Chemical speciation, floodplain soils (% in each fraction)

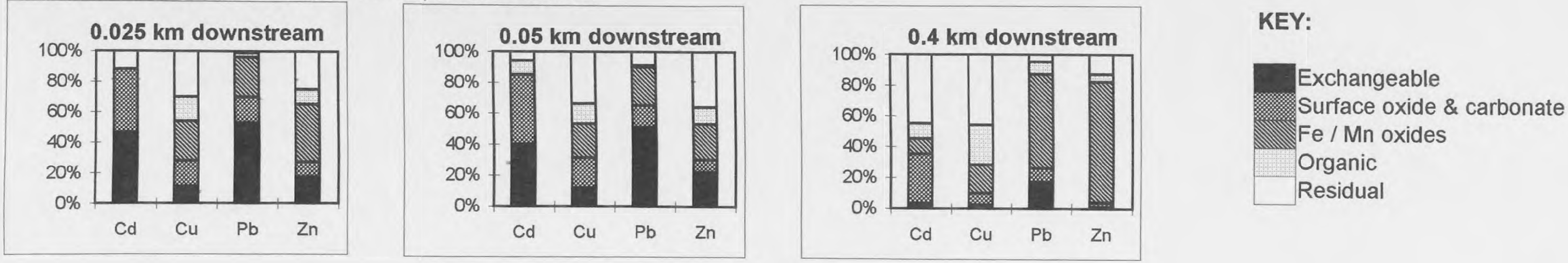
Floodplain surface soil (0 - 20 cm) - transect at 0.75 km downstream



Floodplain surface soil (0 - 20 cm) - 2 m from river



Floodplain subsurface soil (20 - 50 cm) - 2 m from river



Cadmium is mainly found in the exchangeable and surface oxide and carbonate fractions, particularly in subsurface soil. A significant proportion is also associated with the residual fraction, for example, in surface soil at 5 m and 31 m from the river. Copper is associated predominantly with the last three extraction steps, which account for between 69 - 97 % of total sediment copper. The organic and residual fractions are most important in the upper part of the profile and the Fe and Mn oxides and residual components in the lower part of the profile. Both lead and zinc are primarily found within the Fe and Mn oxides, this fraction accounting for 25 - 62 % and 23 - 78 % of the total lead and zinc present respectively. A significant proportion of lead is also associated with the exchangeable fraction, over 50 % in some floodplain subsurface soils. The exchangeable fraction contains metals which are in loosely-held surface associations and are therefore the most potentially mobile (Leenaers, 1989).

The results are consistent with those found in other studies. Bradley and Cox (1987) and Leenaers (1989) also found a significant proportion of cadmium in floodplain soils to be associated with the exchangeable fraction. McLaren and Crawford (1973) noted the importance of organic associations with copper in the soil profile. The Fe and Mn oxides have long been recognised as playing an important role in binding trace metals in soils and sediments, particularly for lead and zinc (Rao Gadde and Laitinen, 1974; Jenne and Luoma, 1977; Williams et al., 1974).

8.3.2 Lateral and vertical variations in floodplain soils

The pattern of speciation laterally across the floodplain varies for each metal (figure 8.6). Cadmium shows the most pronounced variation in speciation, with the exchangeable component significantly increasing across the floodplain away from the channel, as both the organic and residual fractions decrease. Copper shows little variation in speciation laterally across the floodplain. The only significant difference is the large proportion (45 %) of copper found in the Fe and Mn oxide fraction at 31.0 m across the floodplain, where significantly less copper is associated with the residual component at this site. The proportion of lead in the

Fe and Mn oxide fraction increases across the floodplain with distance from the river, whereas the percentage bound to the residual component decreases. For zinc the pattern reverses. There is a small reduction in the proportion of Fe and Mn oxide bound forms and a slight increase in the residual fraction away from the channel. Total metal concentrations are highest for cadmium and copper at 31 m and for lead and zinc at 110 m from the river channel.

Floodplain subsurface (20 - 50 cm) material compared to surface (0 - 20 cm) soils have a greater concentration of metals held in exchangeable, surface oxide and carbonate bound forms. In subsurface soils, a comparable decrease in the residual and the Fe and Mn oxide fraction arises for lead and particularly cadmium, with corresponding increases in the exchangeable and surface oxide and carbonate components. Less zinc is also held in the Fe and Mn oxide and more in the exchangeable fraction in floodplain subsurface soils with an exception at 0.4 km downstream. The organic component accounts for a smaller proportion of copper in subsurface samples compared with floodplain surface soils. Total metal concentrations are generally higher in surface than in subsurface soils and on floodplains at Kirkstall Abbey, at 8.5 and 8.6 km downstream.

The lower concentrations of metals associated with the exchangeable and surface oxide and carbonate fractions in floodplain surface soils corresponds to higher loss on ignition percentages in the upper part of the profile (table 5, Appendix IV). Here, the breakdown of organic matter may have produced the relatively low pHs (5.0 - 6.1) in the upper part of the profile, leading to the partial leaching of these sediment-associated metals. The exchangeable fraction contains metals which are most easily mobilised and carbonates become increasingly soluble at lower pH values (Leenaers, 1989). Less copper is bound to the organic fraction in floodplain subsurface sediments as this part of the profile was found to have generally lower loss on ignition results. These differences may also reflect fluctuations in the water table in the lower part of the profile, causing changes in the redox conditions which alter the solubility, mobility and bioavailability of sediment-associated metals. Evidence suggests that metals are redistributed in floodplain soils (Hudson-

Edwards et al., *in press*). The Fe and Mn oxides and hydroxides are particularly susceptible to alterations in redox and are soluble under reducing conditions that occur when ground water levels rise during flood events. This can release heavy metals which are then taken up by the exchangeable, surface oxide and carbonate bound fractions accounting for the greater proportion of metals observed bound to these fractions in subsurface soils. Total metal concentrations are considerably higher at 8.5 and 8.6 km downstream at Kirkstall Abbey. Peaks in concentration also occur in contemporary within channel (section 6.2) and contemporary river bed sediments (section 6.3) between 8 - 9 km downstream. Heavy metals are derived from a variety of sources in this fluvial system that differ in size and in quantity of their output. The number of waste sources discharging into the river increases with distance downstream. Sources of metals include, Rodley sewage treatment works, agricultural pollution on the Aire at Newlay and Kirkstall and inputs from the tributary Oil Mill Beck, which receives significant quantities of metals from industry and sewage from Leeds / Bradford airport and is also a site affected by pollution from agriculture.

In floodplain soils, cadmium was mainly found in exchangeable and surface oxide and carbonate fractions; copper with the organic, residual and Fe and Mn oxides; and lead and zinc both predominantly with the Fe and Mn oxides. Lead was also significantly associated with an operationally defined exchangeable component. In general, subsurface material has a greater proportion of metals bound to the first two extraction steps, but contains lower concentrations of total metals.

8.4 The Use of Sediment Cores

Nine sediment cores were taken at a distance no less than 8 m from the river bank at various locations throughout the Aire catchment in Leeds (figure 5.4). The length of the sediment cores varied between 2.5 and 5.6 m, regulated by the depth to the underlying bedrock, where coring ceased. From these cores a total of 201 samples were collected. Each sample was analysed for total metal concentration and approximately one sample per metre length of the core was determined for chemical speciation, averaging between 4 - 6 samples from each sediment core.

Due to the large number of samples collected, ICP-AES was used for the metal analysis. This enabled other metals, arsenic, chromium and mercury to also be determined. Figures 8.7 - 8.15 show total metal concentrations for each sediment core taken and tables 6 - 14 in Appendix IV show all the results data. Figures 8.16 - 8.24 show the chemical speciation of samples at each site and tables 15 - 23 in Appendix IV show all the results.

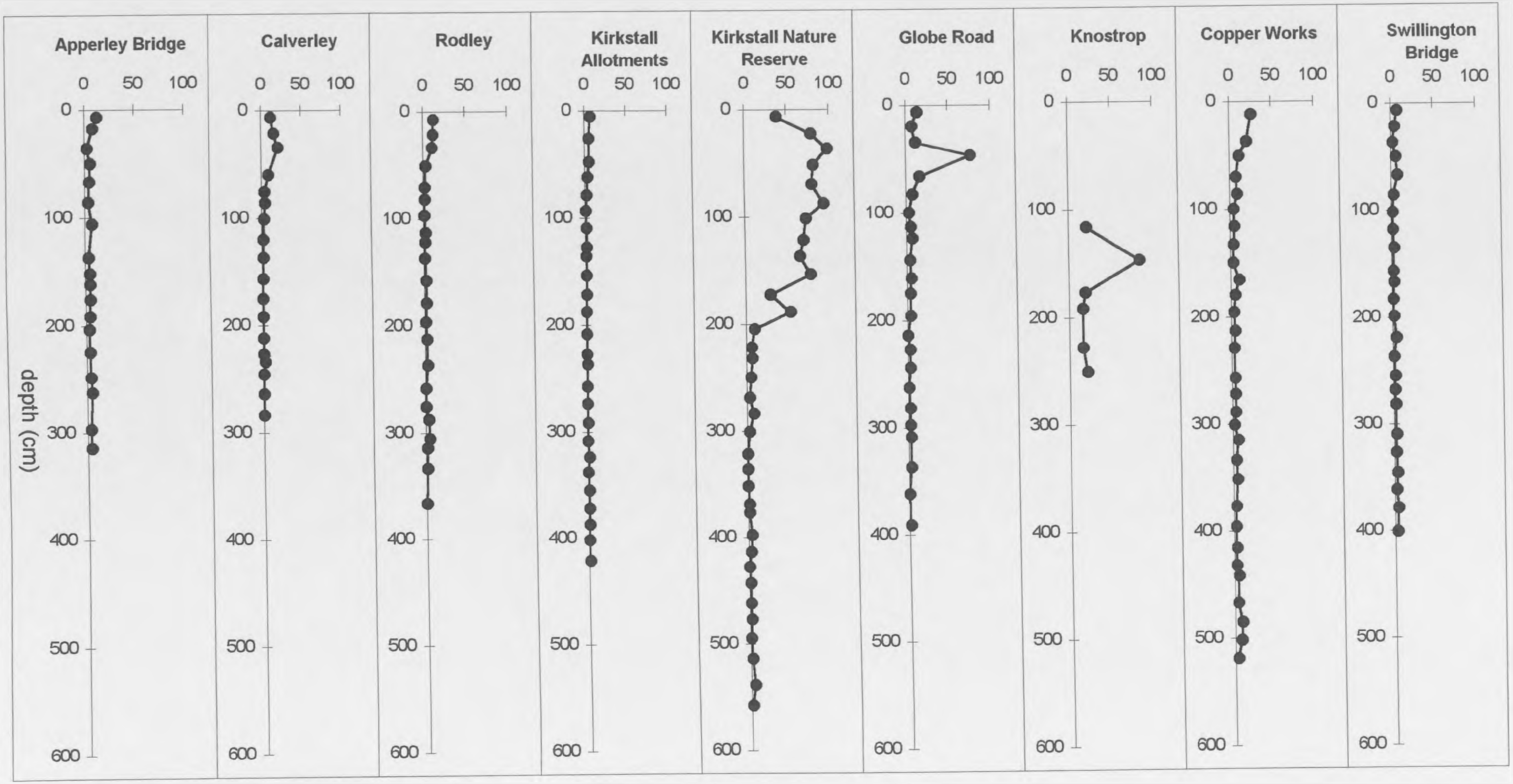
8.4.1 Heavy metal concentrations in sediment cores

Total metal analysis of the core taken at Kirkstall Nature Reserve was hampered up to a depth of 160 cm, by a unit of highly organic pulverised fuel ash, deposited as waste from a previous coal power station near the site. The first sample after this landfill was taken at a depth of 171 - 176 cm. The core taken at Knostrop was also made up of landfill. The site lay on the edge of a waste tip, used to dispose of sewage screenings and building materials. Much of the core was discarded, although some was kept for analysis. However, the results are of little use to the present study.

Total arsenic concentration:

Arsenic concentrations in the majority of sediment cores (figure 8.7) show a general pattern of decreasing concentrations with increasing depth from the surface of the core. By a depth of 50 cm, concentrations are low and remain relatively constant through to the end of the core. Arsenic concentrations at Calverley increase with depth from the surface, reaching a peak concentration at 35 cm. Concentrations decrease sharply from this depth and similar to the other sites, remain low through to the end of the core. Concentrations of arsenic in the Kirkstall Nature Reserve core show high levels in the first 200 cm. This core, until a depth of 160 cm, is made up of landfill. Arsenic concentrations decrease gradually with depth from 170 cm. At Globe Road, the concentration of arsenic initially decreases from the surface and then starts to increase from a depth of 20 cm, reaching a peak in concentration at a depth of 47 cm. Concentrations then decrease, again remaining low through to the end of the core.

Figure 8.7 - Total arsenic concentration (mg/kg), sediment cores



Total cadmium concentration:

In the sediment cores taken from Apperley Bridge, Calverley and the Copper Works, cadmium concentrations increase with depth from the surface of the core (figure 8.8). Peaks in concentration occurring at depths of 67 cm at Apperley Bridge and at 35 cm at Calverley and the Copper Works. From a depth greater than 67 cm at Apperley Bridge, cadmium concentrations fluctuate and are highest overall at a depth between 260 - 300 cm. Following the peaks in concentration, cadmium levels at Calverley and Globe Road generally decrease down the core, smaller peaks occurring at depths of 137 cm and 124 cm respectively. At Rodley, Kirkstall Allotments, Globe Road and Swillington Bridge, concentrations of cadmium decrease with depth from the surface. Peaks in cadmium concentration occur at a depth of 240 cm at Rodley and Kirkstall Allotments and 285 cm at Kirkstall Nature Reserve, 300 cm at the Copper Works and 310 cm at Swillington Bridge. Towards the end of each sediment core, cadmium is generally found at relatively low and consistent levels.

Total chromium concentration:

Chromium concentrations show a very similar pattern with depth in the sediment core to that of cadmium (figure 8.9). Sites where concentrations generally increase with depth from the start of the core include Apperley Bridge, Calverley and the Copper Works. Peaks in concentration occurring at depths of 67 cm for Apperley Bridge and 35 cm for both Calverley and the Copper Works. After these depths, chromium levels decrease to relatively low concentrations, that remain to the end of the core. Chromium concentrations at both Rodley and Kirkstall Allotments decrease from the surface, small peaks in concentration occurring around a depth of 180 - 185 cm in the core. At Globe Road and Swillington Bridge concentrations of chromium also decrease from the surface of the core, but rise and peak in concentration at depths of 67 cm and 37 cm respectively. Small peaks are observed in the deeper cores (Kirkstall Nature Reserve, Globe Road, Copper Works) at a depth just before 300 cm and 400 cm and at approximately 440 cm.

Figure 8.8 - Total cadmium concentration (mg/kg), sediment cores

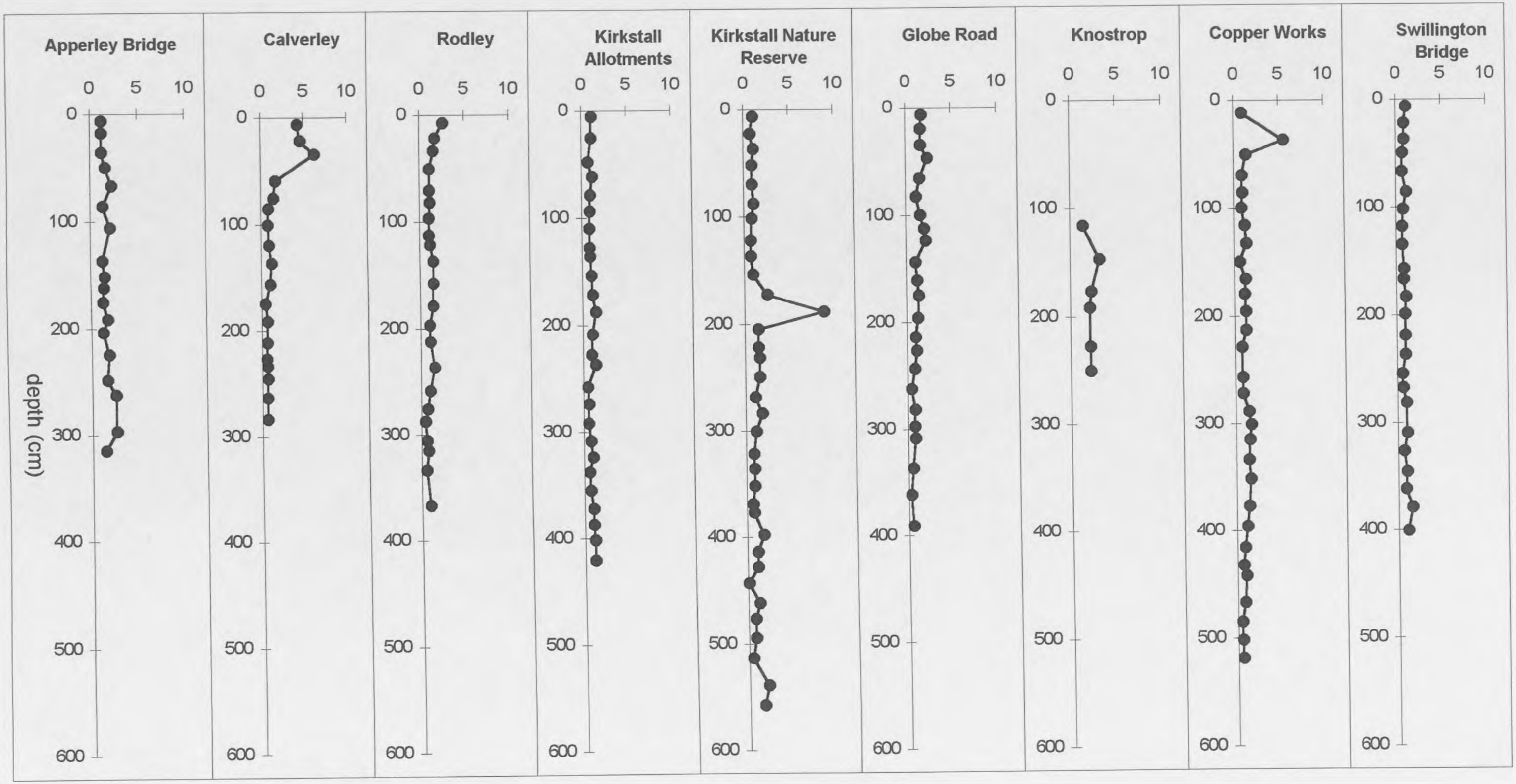
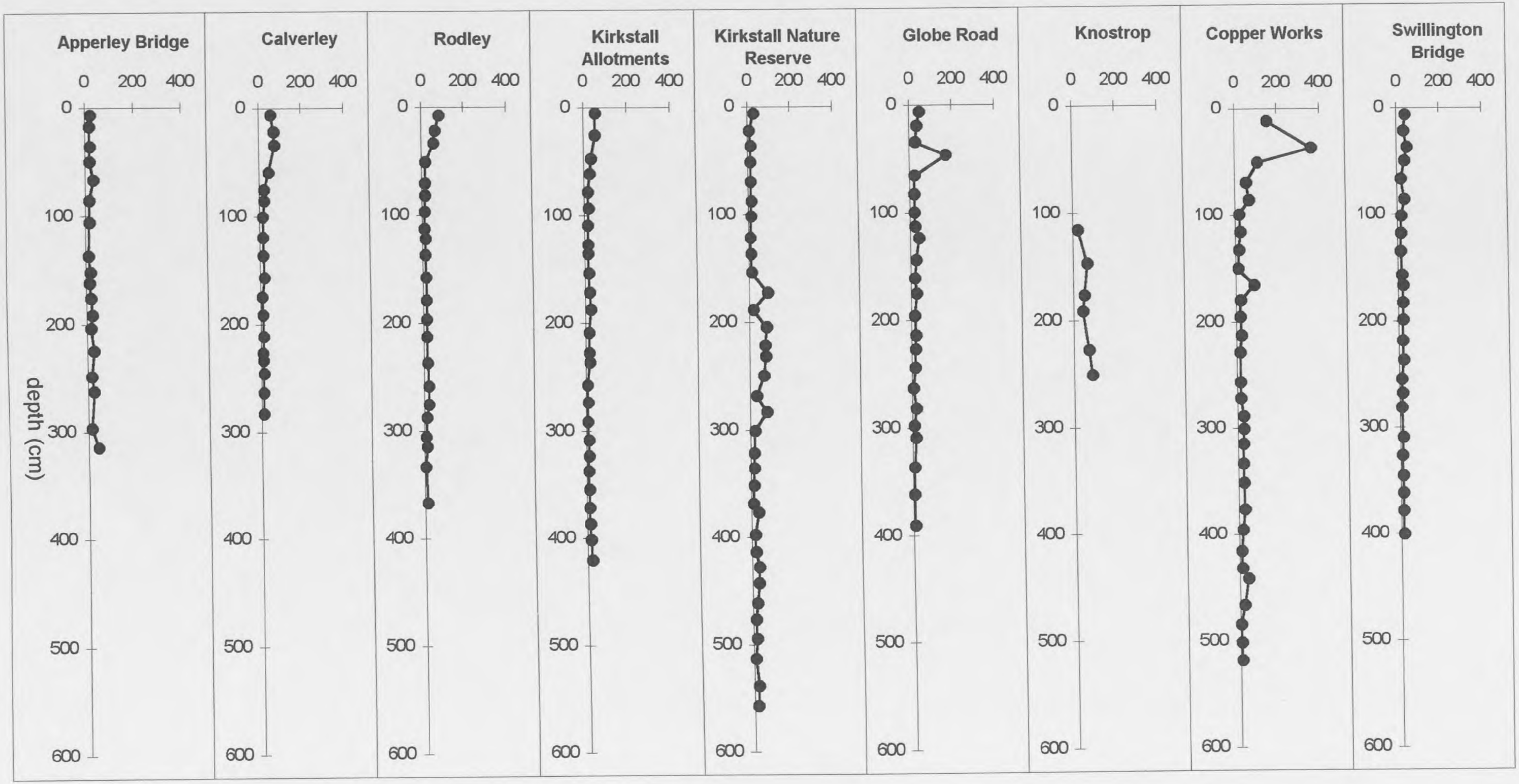


Figure 8.9 - Total chromium concentration (mg/kg), sediment cores



Total copper concentration:

At the majority of sites, copper concentrations decrease with depth from the surface of the core, including those taken from Apperley Bridge, Rodley, Kirkstall Allotments, Globe Road and Swillington Bridge (figure 8.10). Small peaks in concentration occur at depths of 67 cm and 176 cm at Apperley Bridge, concentrations rise between 260 - 275 cm at Rodley and 225 - 240 cm at Kirkstall Allotments. A sharp peak in concentration occurs at Globe Road at a depth of 47 cm, with a high level of total copper (301 mg/kg). Smaller peaks in copper concentration occur at depths of 175 cm and 282 cm at Globe Road and at 67 cm at Swillington Bridge. Concentrations decline after these depths, but rise again towards the end of each core as parent material is reached. At Calverley and the Copper Works, concentrations of copper increase with depth, peaking in concentration at 35 cm and 37 cm respectively, before decreasing relatively sharply. Other peaks in concentration occur at the Copper Works site at depths of 165 cm, 290 cm and 442 cm. Disregarding the first 160 cm of the core taken at Kirkstall Nature Reserve, copper concentrations decrease gradually with depth throughout the core, peaking in concentration at a depth of 285 cm and increasing slightly at 430 cm.

Total lead concentration:

Concentrations of lead in the sediment cores (figure 8.11) show a very similar pattern to that of copper. Lead levels decrease from the surface of the core at Apperley Bridge, Rodley, Kirkstall Allotments, Globe Road and Swillington Bridge. Peaks in concentration occurring at depths of 176 cm at Apperley Bridge, 47 cm, 175 cm and 310 cm at Globe Road and at 67 cm at Swillington Bridge. Lead concentration rises slightly from 260 cm at Apperley Bridge and between 120 - 280 cm and 185 - 240 cm at Rodley and Kirkstall Allotments respectively. Concentrations of lead increase with depth from the surface of the core at Calverley and the Copper Works. Lead concentrations peak at a depth of 35 cm in the core from Calverley, decrease sharply between 35 - 60 cm and then decrease more gradually to the end of the core. Lead concentrations increase with depth from the surface at the Copper Works site, peaking in concentration at 37 cm.

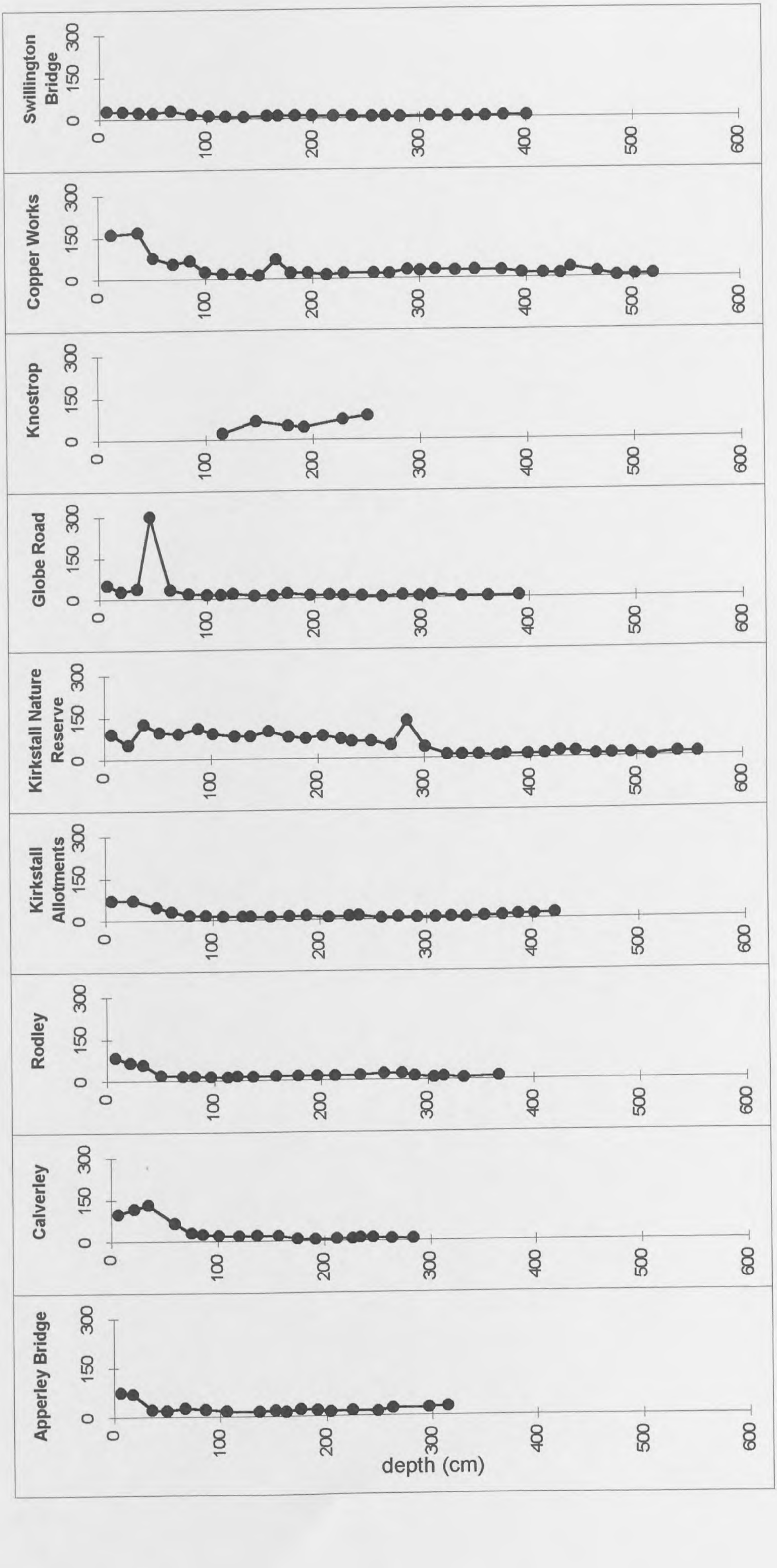
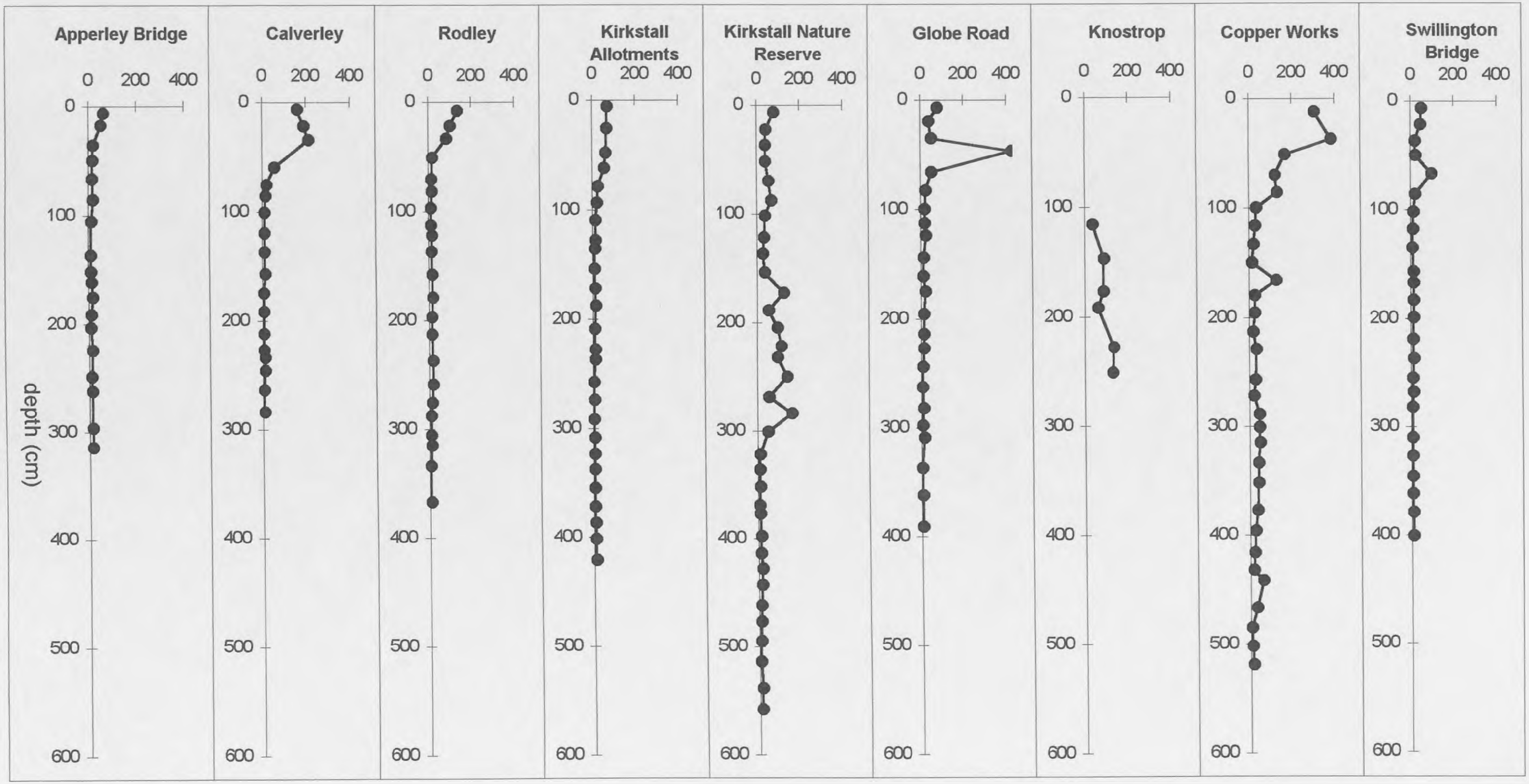


Figure 8.10 - Total copper concentration (mg/kg), sediment cores

Figure 8.11 - Total lead concentration (mg/kg), sediment cores



Concentrations then decrease with depth in the core, however, peaks occur at depths of 166 cm and 442 cm. At Kirkstall Nature Reserve, after a depth of 160 cm, peaks in lead concentration occur at 173 cm, 222 cm, 250 cm and similar to other metals, at 285 cm.

Total mercury concentration:

Mercury was not found in detectable concentrations at all sites (figure 8.12). Of the sites where mercury was measured, the results are very variable, especially at the Copper Works. Concentrations increase with depth from the surface of the core at Apperley Bridge and Calverley, peaking in concentration at a depth of about 35 cm. With increasing depth in the core, mercury concentrations decrease. At Globe Road and the Copper Works, mercury concentration generally decreases with depth from the surface of the core.

Total zinc concentration:

From the surface of the core (figure 8.13), zinc concentrations decrease with depth at Apperley Bridge, Rodley, Kirkstall Allotments, Globe Road and Swillington Bridge. At Apperley Bridge, zinc concentrations decrease and then rise gradually from a depth of 40 cm, peaking in concentration at 150 cm. Concentrations decrease gradually towards the end of the core, peaks occurring at depths of 225 cm and 300 cm. A very similar pattern of zinc concentration is observed between Rodley and Kirkstall Allotments. Concentrations decreasing gradually with depth but increasing between a depth of 120 - 190 cm. Small peaks are found at a depth of 260 cm at Rodley and 237 cm at Kirkstall Allotments. At both sites concentrations rise slightly towards the end of the core as parent material is reached. A sharp peak in zinc concentration occurs at 47 cm at Globe Road and levels generally rise between 85 - 125 cm. Zinc concentrations at Swillington Bridge are relatively low, peaking at a depth of 67 cm. Following peaks in zinc concentration at these two sites, levels decrease through to the end of the core. At Calverley and the Copper Works, zinc levels initially increase with depth in the sediment core. Peaks in concentration occurring at a depth of 22 cm at Calverley and 37 cm at the Copper Works. Concentrations generally decrease from these

Figure 8.12 - Total mercury concentration (mg/kg), sediment cores

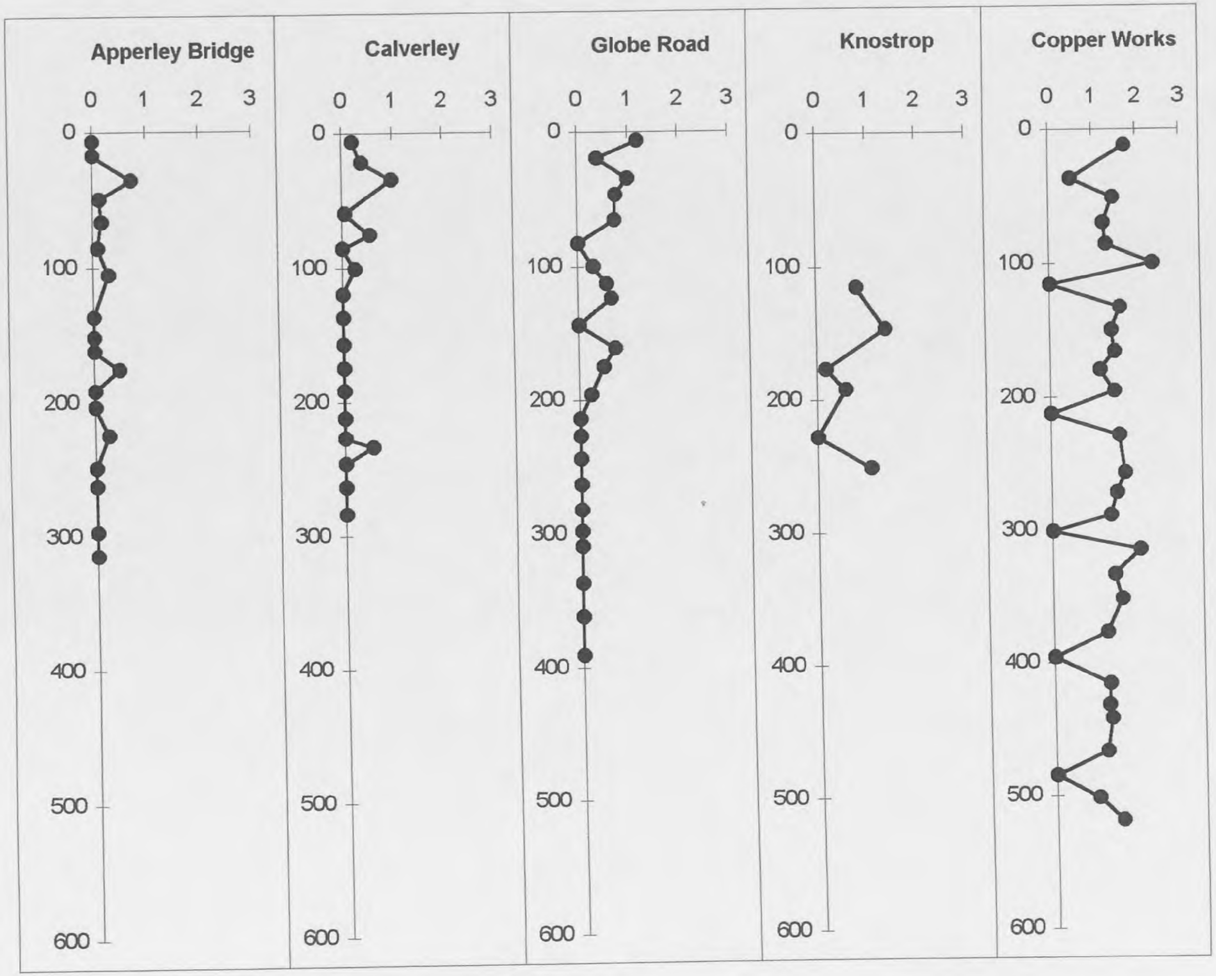
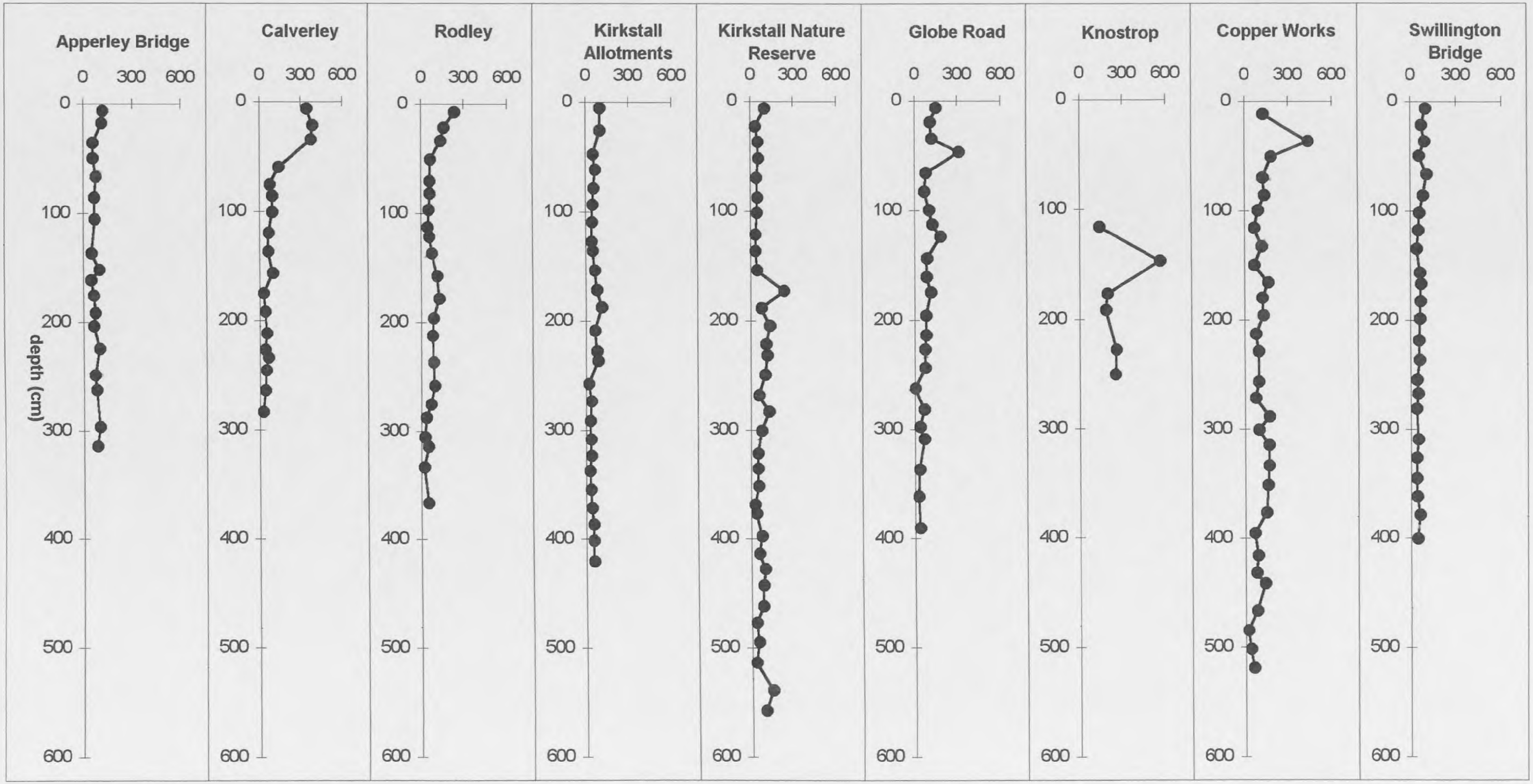


Figure 8.13 - Total zinc concentration (mg/kg), sediment cores



peaks, smaller peaks in concentration occurring at depths of 157 cm and 235 cm at Calverley and 166 cm and 442 cm at the Copper Works. From a depth of 160 cm in the core at Kirkstall Nature Reserve, zinc levels decrease gradually. Peaks in concentration occur at depths of 285 cm and 417 cm. Zinc levels also increase towards the end of the core at this site.

pH:

pH at Rodley, Kirkstall Allotments, Globe Road, Copper Works and Swillington Bridge shows an increase with depth, up until 50 cm, when levels become relatively constant through to the end of the core (figure 8.14). At Apperley Bridge and Calverley, pH initially decreases with depth in the core. pH levels increase gradually from 20 cm at Apperley Bridge and remain relatively constant from a depth of 137 cm. pH at Calverley fluctuates greatly. pH at Kirkstall Nature Reserve generally decreases with depth in the sediment core.

% loss on ignition:

At the majority of sites % LOI (figure 8.15) decreases with depth in the sediment core, the highest % being recorded in the top 15 cm. At Calverley and Globe Road, the largest peak in % LOI occurs at depths of 22 cm and 47 cm respectively.

In the majority of cores, the heavy metals all show elevated levels in the surface sediments and minimum, rather constant values in the deeper horizons of each core. These trends are typical of enrichment profiles described in various publications (Nriagu et al., 1979; Owens and Cornwell, 1995; Ridgway and Price, 1987). Some cores show an increase in metal concentration from the start of the core, reaching a peak, usually within the first 50 cm, before decreasing gradually to background levels with increasing depth. This occurs at Calverley, Knostrop and the Copper Works. Cores taken at Globe Road and Swillington Bridge show declining metal concentrations with depth from the surface, concentrations rising to sharp peaks before decreasing steadily to background concentrations. This occurs at depths of approximately 50 cm at Globe Road and 65 cm at Swillington Bridge. From a depth of 160 cm in the sediment core at Kirkstall Nature Reserve,

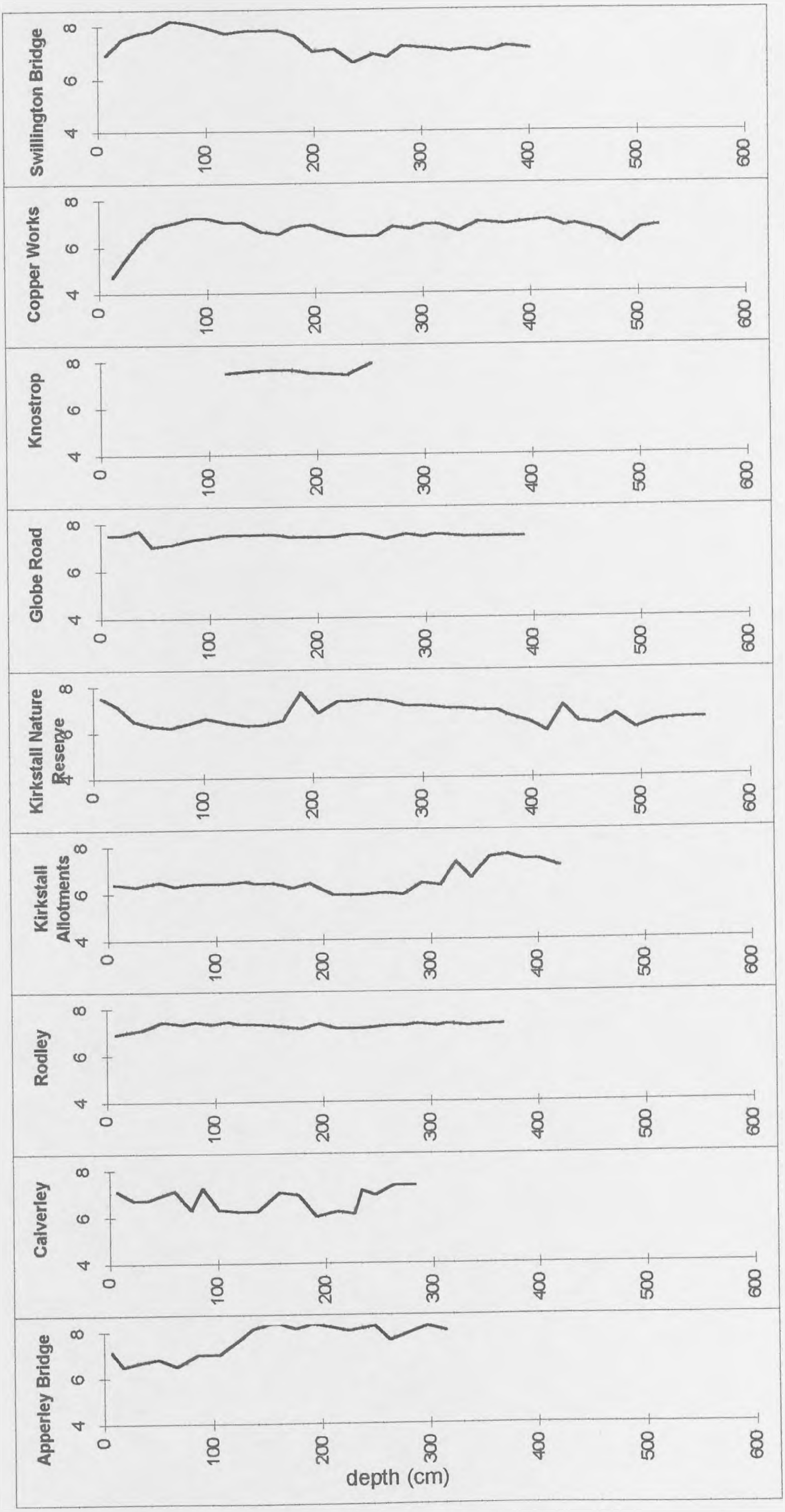


Figure 8.14 - pH, sediment cores

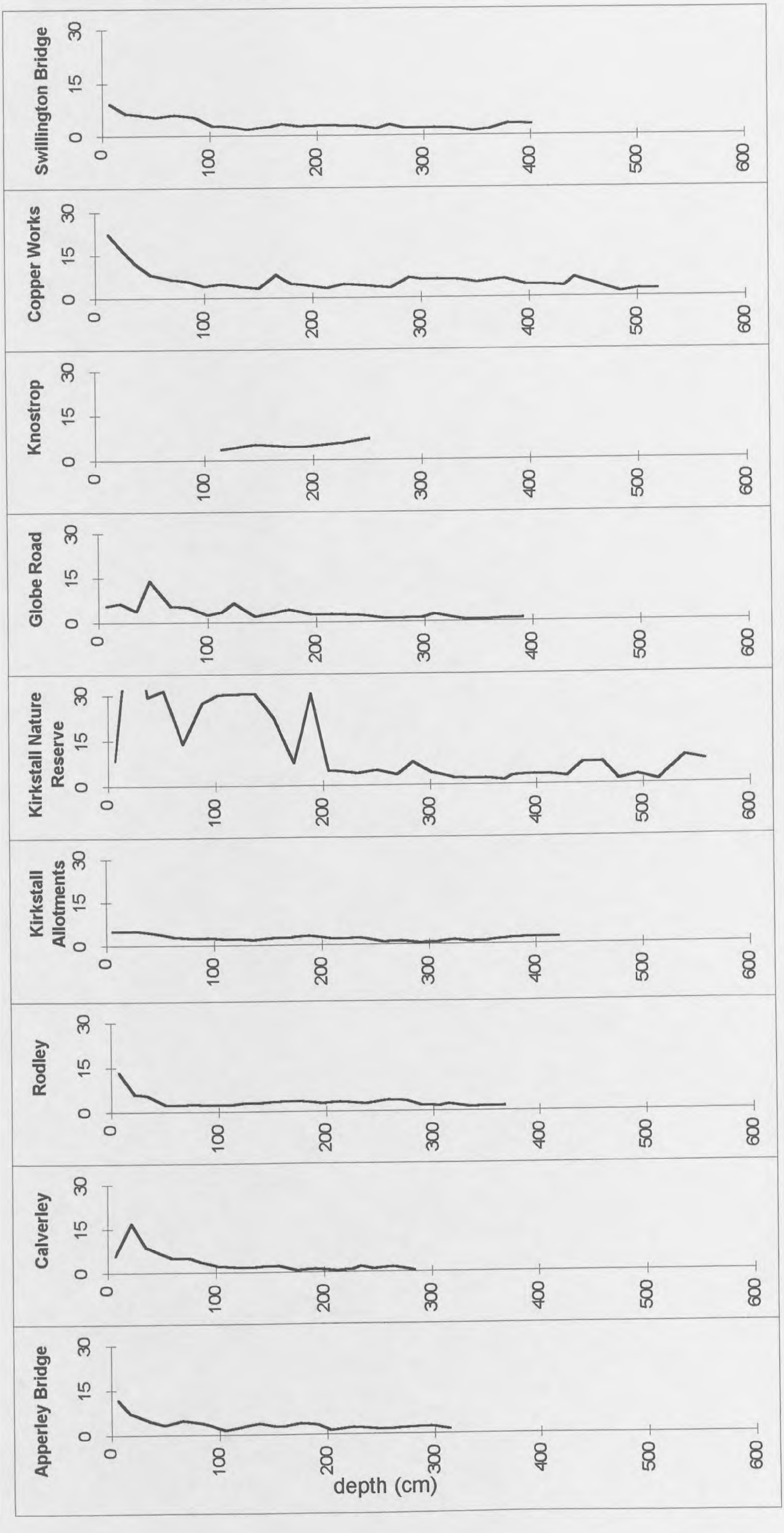


Figure 8.15 - % loss on ignition, sediment cores

taken as the surface of the core, metal concentrations increase. The likely result of surface enrichment from anthropogenic inputs before the addition of landfill in the late 1980s and leaching of metals from the landfill of pulverised fuel ash.

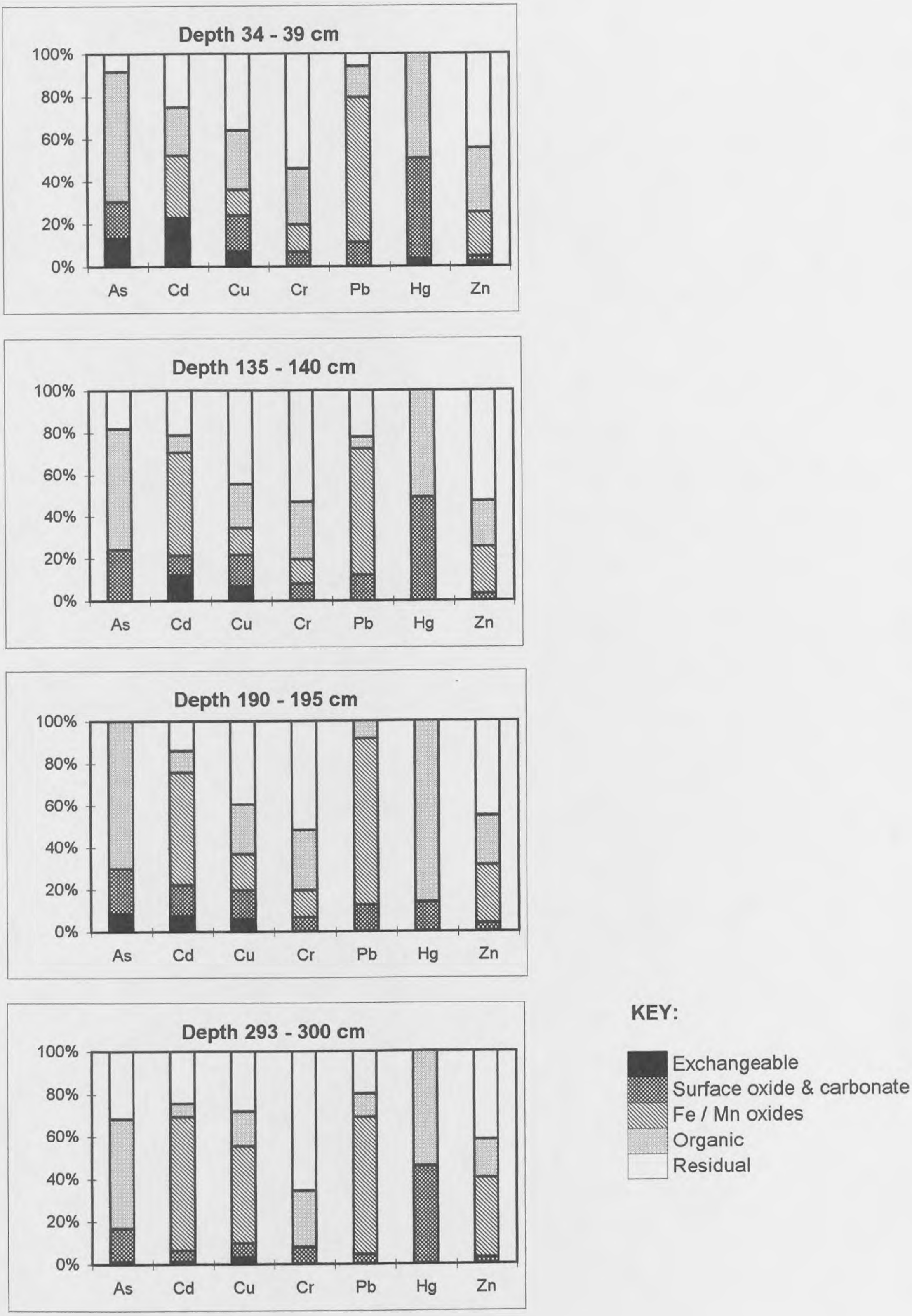
Several sites show an increase in metal concentration towards the end of the core, including cores taken at Apperley Bridge, Rodley, Kirkstall Allotments, Kirkstall Nature Reserve, Knostrop and Swillington Bridge. The core from Knostrop can be disregarded as it consisted mainly of landfill material. For the others, slight increases may be due to natural concentrations of metals in parent material, reached at the end of the core. Other reasons may be due to experimental error and possible contamination with sediment from higher up the core, being pushed down with the corer and mixing with samples at greater depth or due to post-depositional mobility. Metal concentration trends are closely followed by % LOI results, particularly in cores from Calverley, Rodley, Kirkstall Allotments, Kirkstall Nature Reserve, Globe Road and Swillington Bridge. In these cores, a rise in % LOI is often met by an increase in the total concentration of a metal.

8.4.2 The chemical speciation of sediment cores

Apperley Bridge 1.0 km downstream:

With depth in the sediment core the general speciation pattern remained very similar at this site (figure 8.16 and table 15, Appendix IV). Arsenic is largely associated with the organic fraction (> 50 %), cadmium and lead with the Fe and Mn oxides, chromium, copper and zinc with the residual component and mercury almost entirely with the organic and surface oxide and carbonate fractions. For arsenic, the residual fraction increases in importance with depth as the exchangeable component decreases. The Fe and Mn oxide fraction accounts for an increasing percentage of cadmium with depth as the exchangeable component accounts for less. The chemical speciation of chromium is very consistent up to a depth of 190 - 195 cm, however, in the last sample analysed the residual fraction becomes significantly more important. With depth in the sediment core, copper becomes less associated with the exchangeable and surface oxide and carbonate

Figure 8.16 - Chemical speciation, sediment cores - Apperley Bridge 1.0 km downstream



fractions and more with the Fe and Mn oxides. The Fe and Mn oxides predominate over all other forms of lead, accounting for more than 60 % of total sediment lead concentration at all depths. Zinc speciation is also relatively consistent with depth, the exchangeable fraction only accounting for a very small percentage of the total zinc in the sample closest to the surface. Generally the last 3 fractions account for more than 95 % of total sediment zinc.

Calverley 3.0 km downstream:

At this site (figure 8.17 and table 16, Appendix IV), arsenic was mainly associated with the organic fraction, cadmium with the first 3 extraction steps, chromium and copper with the organic and residual components, lead with the Fe and Mn oxides, mercury with the organic and surface oxide and carbonate fractions and zinc with the last 3 sequential extraction components. Within this sediment core there was more variation in chemical speciation with depth than at Apperley Bridge. For arsenic, the Fe and Mn oxide fraction disappears, with the surface oxide and carbonate and organic fractions increasing in importance with depth. The exchangeable fraction decreases its proportion of total sediment cadmium with depth down the core as the organic component increases. For chromium and copper, the residual fraction increases with depth as the organic fraction decreases its percentage of total sediment chromium and copper. The Fe and Mn oxides in particular and also the surface oxide and carbonates dominate over all other forms of lead. As depth increases, the percentage of mercury bound to the Fe and Mn oxides decreases as more is associated with the organic and surface oxide and carbonate fractions. The majority of the zinc in the top half of the core is associated with the Fe and Mn oxides, the proportion decreasing with depth, whereas the percentage bound to the residual and organic fractions increase.

Rodley 4.0 km downstream:

As at previous sites, arsenic is mainly associated with the organic fraction, cadmium with the exchangeable and Fe and Mn oxides, chromium and copper with the organic and residual components, lead the Fe and Mn oxides, mercury with the organic and surface oxide and carbonates and zinc, almost entirely within the last

Figure 8.17 - Chemical speciation, sediment cores - Calverley 3.0 km downstream

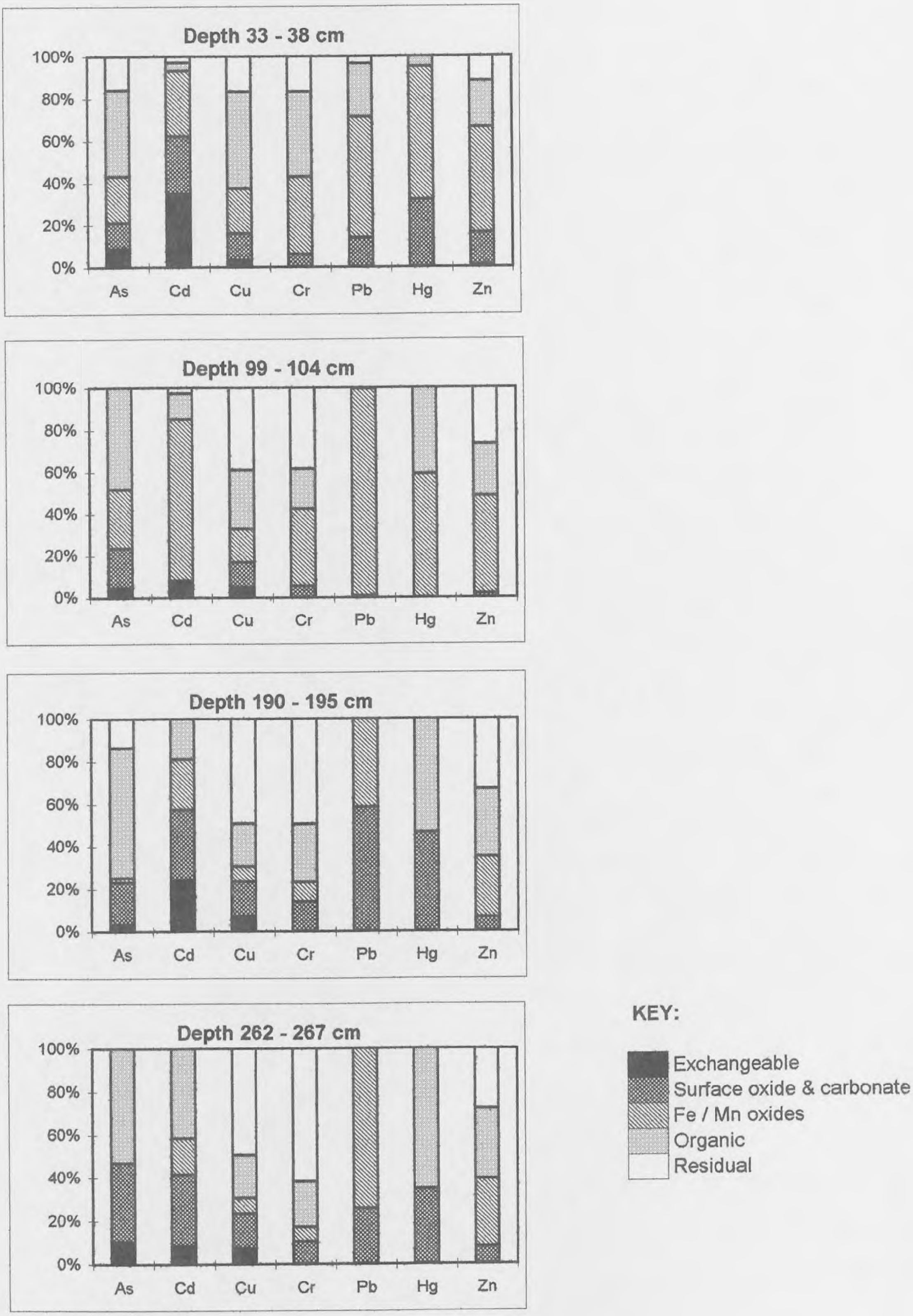
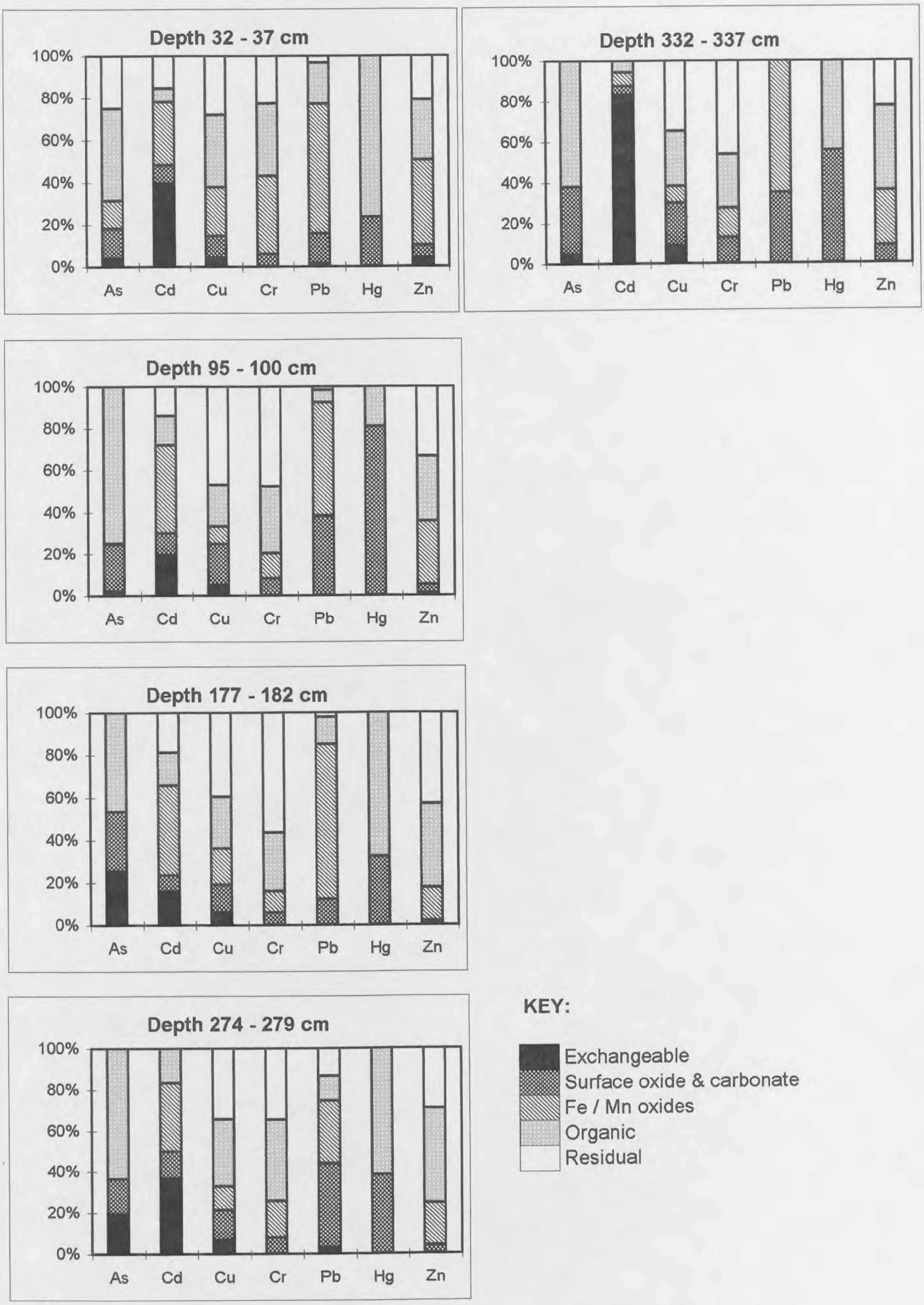


Figure 8.18 - Chemical speciation, sediment cores - Rodley 4.0 km downstream



Depth 32 - 37 cm

Depth 332 - 337 cm

Depth 95 - 100 cm

Depth 177 - 182 cm

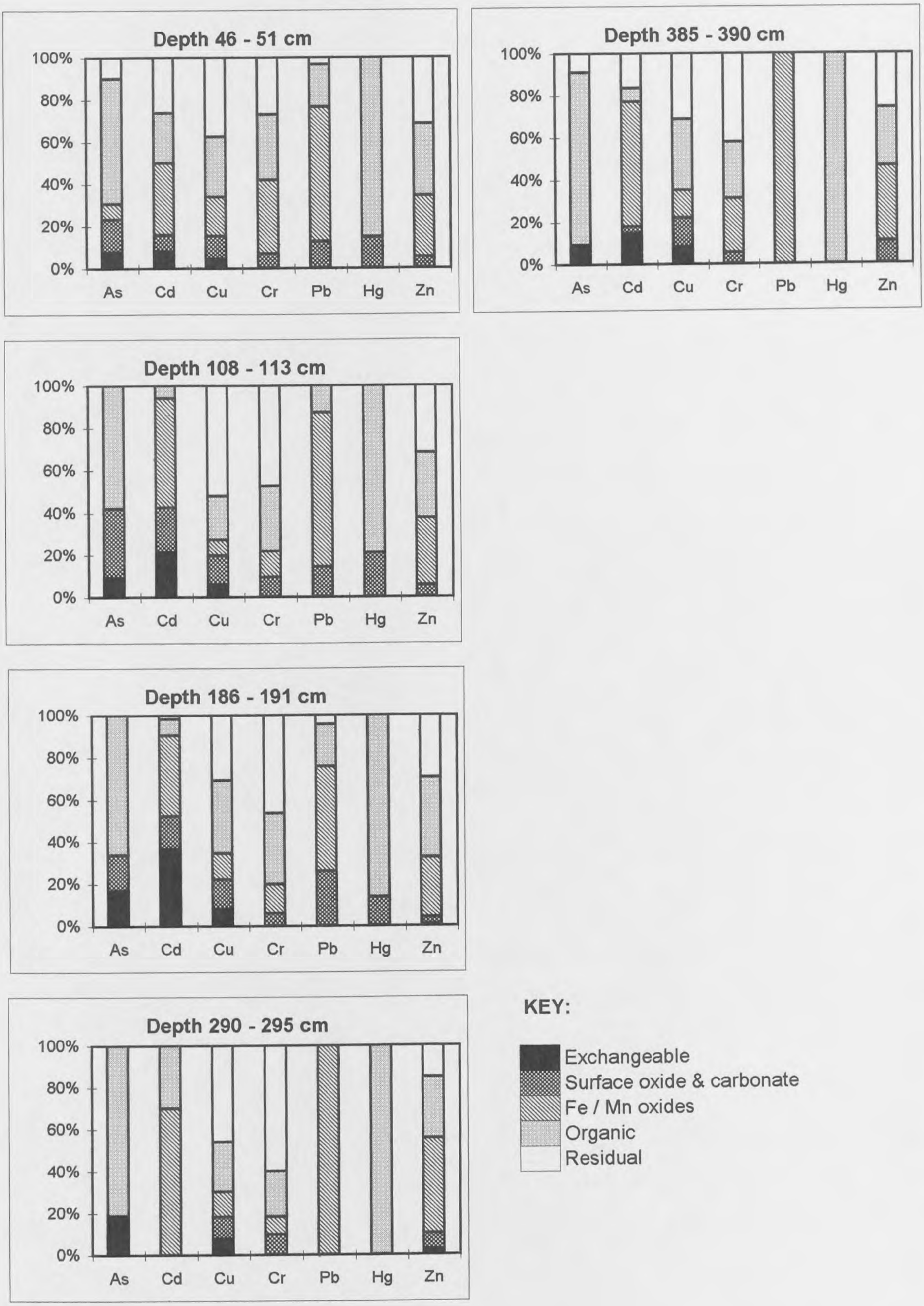
Depth 274 - 279 cm

three sequential extraction fractions (figure 8.18 and table 17, Appendix IV). With depth in the sediment core, arsenic is increasingly associated with the organic and surface oxide and carbonate fractions and cadmium with the exchangeable fraction. For chromium, the percentage bound to the surface oxide and carbonates also increases with depth. The majority is associated with the residual and organic fractions throughout the core. The percentage of copper also bound to the exchangeable and surface oxide and carbonate fractions increases with depth, accounting for a maximum 30 % total sediment copper in the last sample analysed for chemical speciation. The residual in particular, but also the organic fraction account for the remaining copper. The chemical speciation of lead fluctuates down the sediment profile, the majority associated with the Fe and Mn oxides and the surface oxide and carbonate fractions. Mercury is only bound to the organic and surface oxide and carbonate fractions, the latter increasing in percentage with depth. The proportion of zinc associated with the residual fraction increases up to a depth of 177 - 182 cm, then decreases, the Fe and Mn oxides showing the opposite to this trend. The organic fraction generally increasing its percentage of total sediment zinc with depth.

Kirkstall Allotments 8.5 km downstream:

The general pattern of speciation is the same at this site as for the previous sites (figure 8.19 and table 18, Appendix IV). A greater percentage of arsenic is associated with the organic fraction as depth increases, accounting for more than 80 % in the last two samples. Cadmium speciation is highly variable throughout the sediment core. The proportion in the Fe and Mn oxides generally increasing down the profile. For chromium, the last three sequential extraction steps are most significant at all depths, accounting for more than 90 % total sediment chromium. Copper is relatively consistent in speciation with depth, the percentage associated to the organic fraction is slightly greater at depth in the core. Lead and mercury are predominantly bound to the Fe and Mn oxides and organic fractions respectively, both these fractions increasing in importance with depth. The pattern of zinc speciation remains relatively consistent with depth, the last three extraction steps important throughout.

Figure 8.19 - Chemical speciation, sediment cores - Kirkstall Allotments 8.5 km downstream



Kirkstall Nature Reserve 10.0 km downstream:

Arsenic, as with previous sites is predominantly associated with the organic fraction, cadmium with the exchangeable and Fe and Mn oxides, chromium and copper with the organic and residual fractions, lead with the Fe and Mn oxides and zinc with the last three sequential extraction fractions (figure 8.20 and table 19, Appendix IV). The first two samples were part of landfill, so interpretation will start at 230 - 235 cm depth. The proportion of arsenic bound to the organic fraction increases with depth. A significant amount (up to 25 %) was also associated with the exchangeable component throughout. The percentage of cadmium associated with the exchangeable fraction is significant throughout the core, as is the percentage bound to the Fe and Mn oxides, both fractions accounting for 68 - 89 % of total sediment cadmium. The amount of chromium, copper and lead bound to the residual fraction increases with depth. For zinc, the percentage associated with the organic and residual fractions increases with depth up until the last sample where it decreases. The amount bound to the Fe and Mn oxides increases in this sample.

Globe Road 14.0 km downstream:

The general chemical speciation pattern of the sediment core at Globe Road is very similar to that at other sites (figure 8.21 and table 20, Appendix IV). Arsenic is mainly associated with the organic fraction, which becomes increasingly important with depth, along with the exchangeable component. At the start of the core cadmium was largely found within the first three extraction steps. With increasing depth the residual fraction becomes more important, accounting for more than 55 % of total sediment cadmium at the end of the core. The majority of chromium is associated with the Fe and Mn oxides and copper with the organic fraction at the surface, with depth the residual fraction becomes more important for both metals. Throughout the core most of the sediment lead is bound with the Fe and Mn oxides, its proportion increasing slightly with depth. Zinc is mainly found within the last three sequential extractions. A small percentage is also associated with the exchangeable and surface oxide and carbonate fractions, which decrease with depth.

Figure 8.20 - Chemical speciation, sediment cores - Kirkstall Nature Reserve 10.0 km downstream

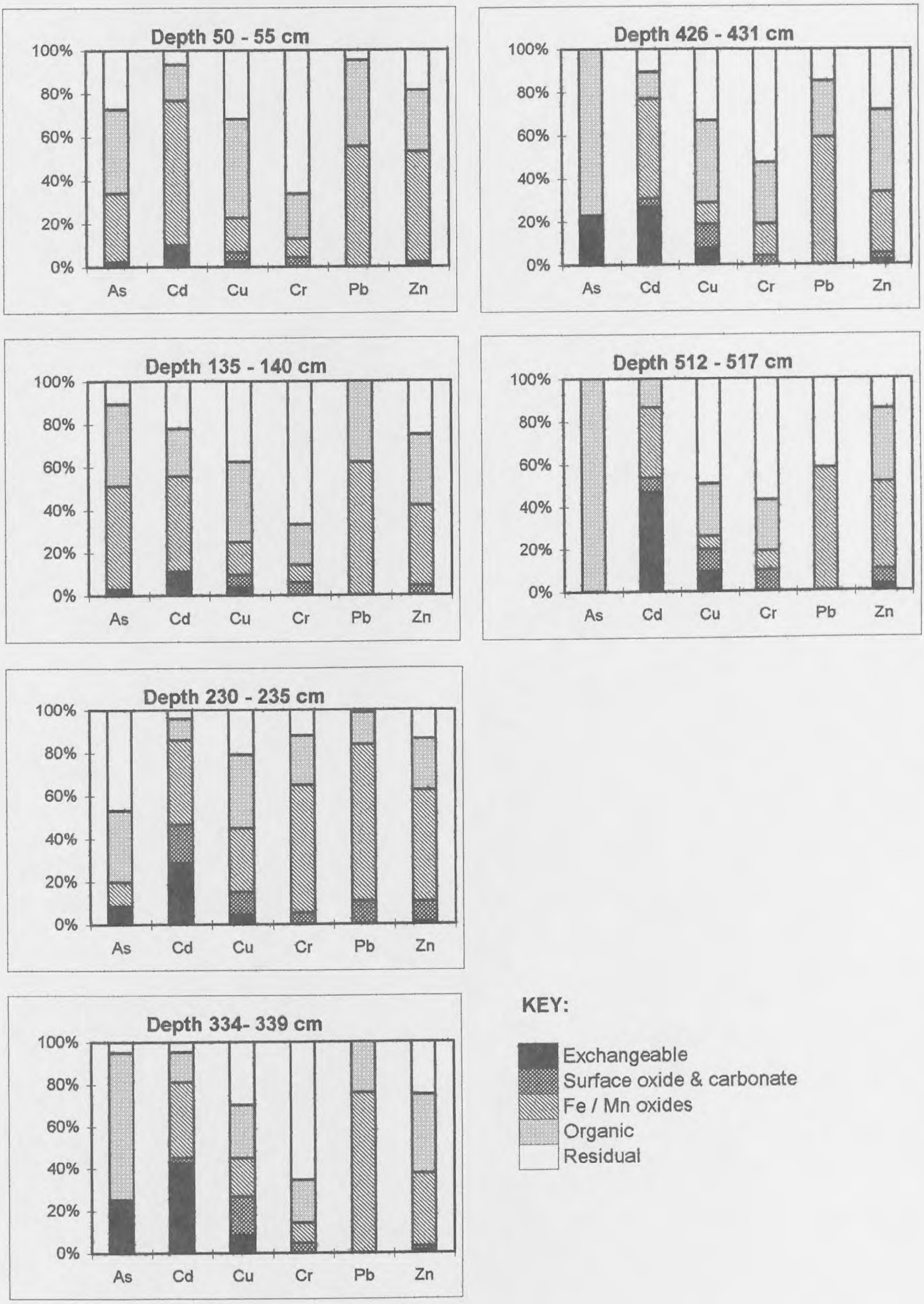
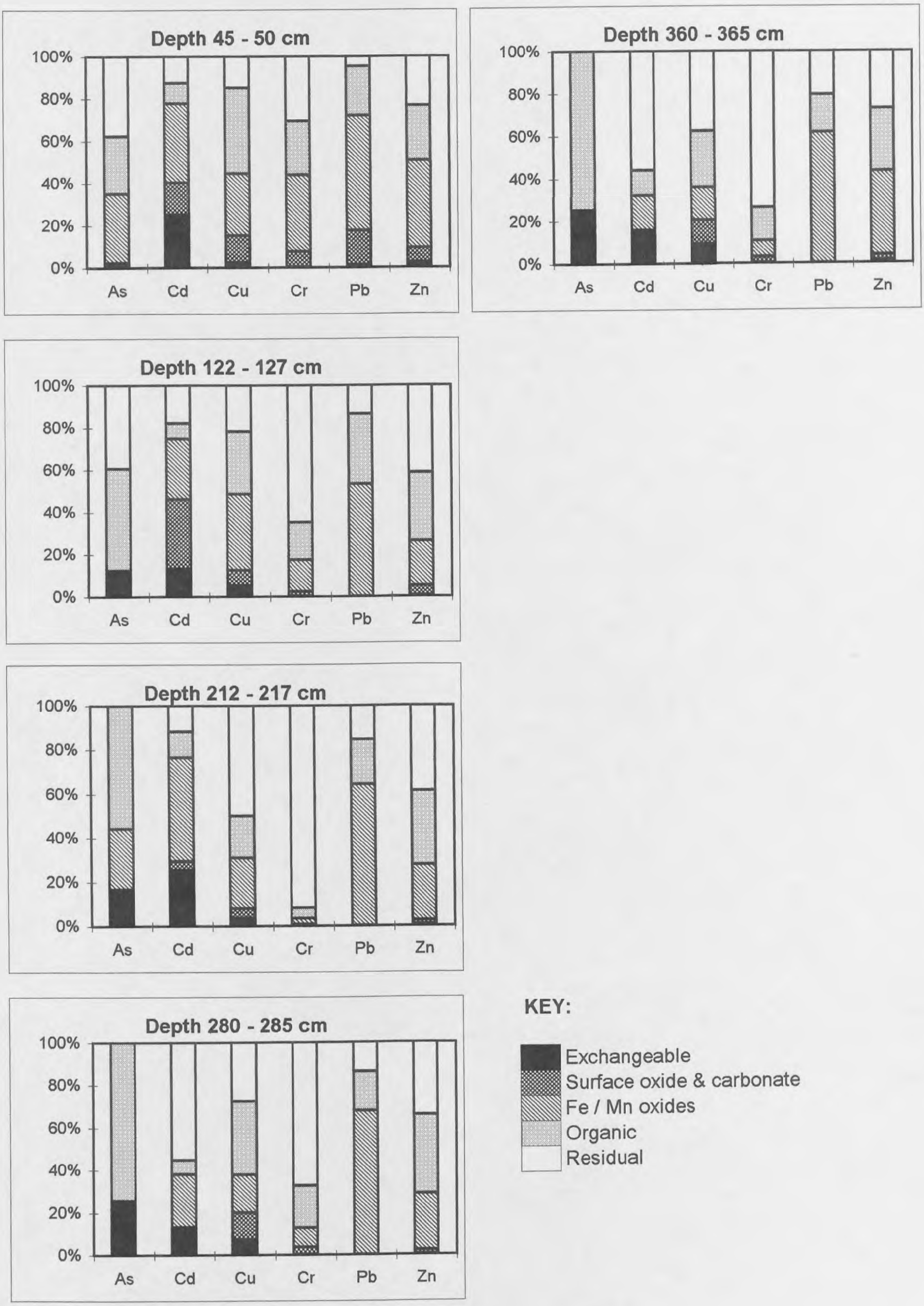


Figure 8.21 - Chemical speciation, sediment cores - Globe Road 14.0 km downstream



Knostrop 19.0 km downstream:

The pattern of speciation was very similar with depth for chromium, copper, lead and zinc (figure 8.22 and table 21, Appendix IV). Chromium is associated mainly with the Fe and Mn oxides, copper with the organic fraction, lead and zinc with the Fe and Mn oxides, but also with the surface oxide and carbonate fraction. For arsenic, the organic fraction increased with depth at the expense of the Fe and Mn oxides, whereas for cadmium, the residual component increased and the surface oxide and carbonate fraction and Fe and Mn oxides decreased.

Copper Works 23.0 km downstream:

The pattern of speciation differs at this site (figure 8.23 and table 22, Appendix IV). Arsenic is associated mainly with the residual fraction. A significant and increasing proportion with depth is also bound to the Fe and Mn oxides. At the start of the core cadmium is mainly found within the exchangeable fraction, the percentage associated to this fraction generally decreasing with depth. The proportion of cadmium in the organic fraction, however, increases throughout the core. In the first sample analysed for chemical speciation, the majority of chromium is associated with the Fe and Mn oxides. With increasing depth all fractions decrease, with the exception of the residual component which accounts for between 69 - 96 % of total sediment chromium. The percentage of copper bound to the first two sequential extraction steps generally increases with depth, whereas the proportion associated with the organic fraction decreased. Lead and zinc are mainly associated with the Fe and Mn oxides, the exchangeable component increases with depth for lead and the residual fraction for zinc. In the first half of the core, mercury was predominantly bound to the Fe and Mn oxides, but with increasing depth, the residual fraction increases in importance.

Swillington Bridge 26.0 km downstream:

At Swillington Bridge (figure 8.24 and table 23, Appendix IV) arsenic was mainly associated with the organic fraction, cadmium, lead and zinc with the Fe and Mn oxides, chromium and copper with the residual component. A large percentage (57 %) of arsenic was associated with the residual fraction near the surface of the core.

Figure 8.22 - Chemical speciation, sediment cores - Knostrop 19.0 km downstream

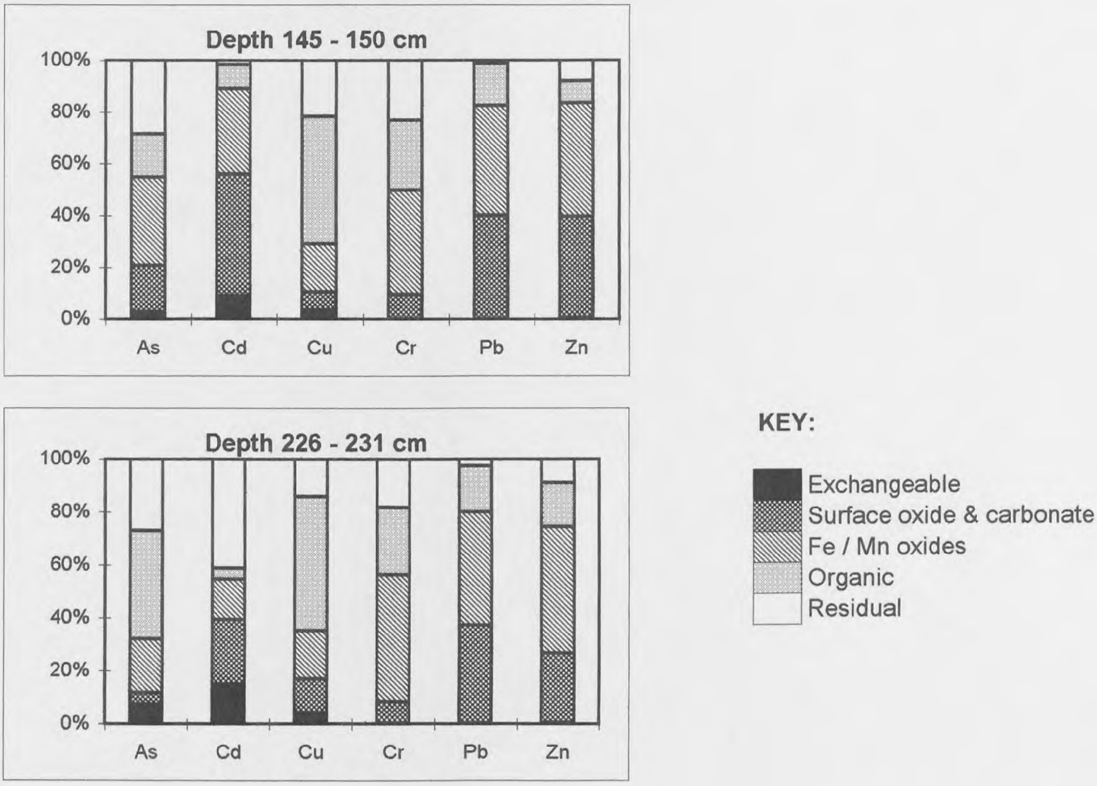


Figure 8.23 - Chemical speciation, sediment cores - Copper Works 23.0 km downstream

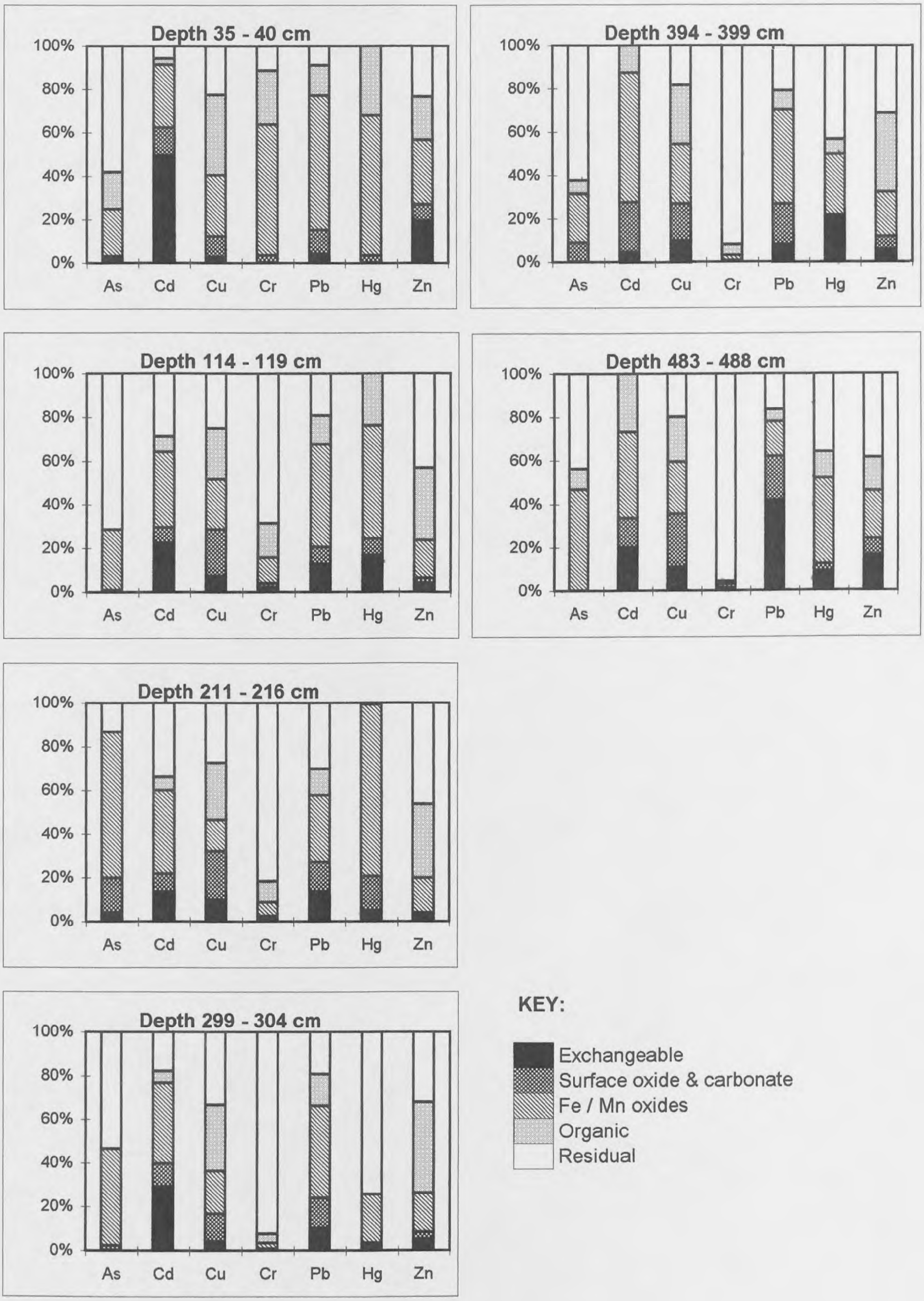
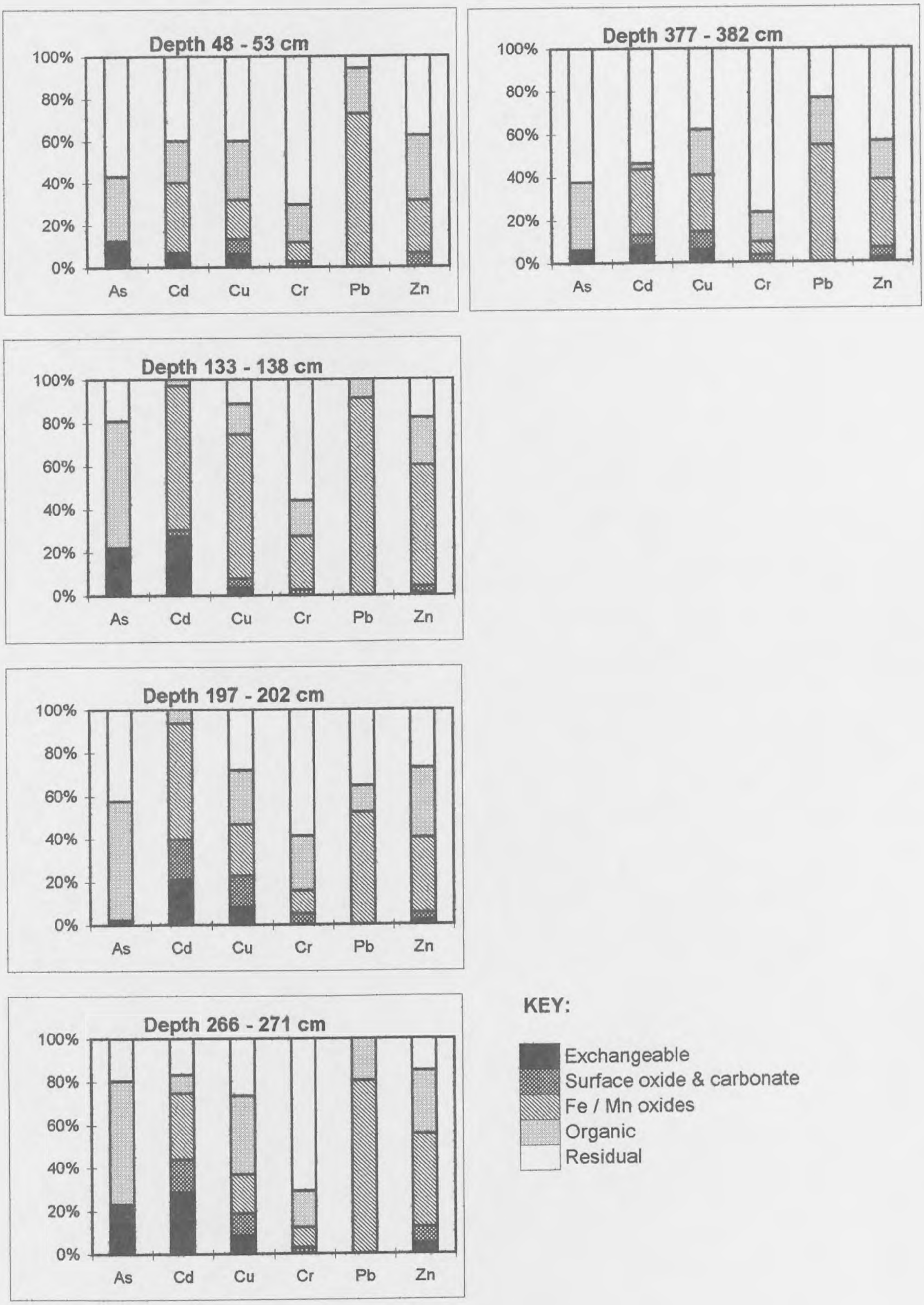


Figure 8.24 - Chemical speciation, sediment cores - Swillington Bridge 26.0 km downstream



With depth the organic fraction became increasingly important. However, in the sample analysed at greatest depth, the residual fraction contained the majority of sediment arsenic. The residual fraction was also important for cadmium and copper towards the start and end of the core. In samples in between, the Fe and Mn oxides and exchangeable component became increasingly important for cadmium and the Fe and Mn oxides and organic fractions for copper. Throughout the core the residual fraction maintains the majority of total sediment chromium. For lead and zinc the residual component generally increased with depth, at the expense of the Fe and Mn oxides and the organic fraction.

To summarise, taking into consideration the speciation patterns from all the sediment cores, arsenic is mainly associated with the organic fraction, cadmium with the exchangeable and Fe and Mn oxides, chromium and copper both with the organic and residual fractions, lead with the Fe and Mn oxides, mercury with the organic and surface oxide and carbonate fractions and zinc with the last three sequential extraction steps. With depth, the percentage of arsenic and mercury bound to the organic fraction tends to increase, for cadmium and zinc the residual and organic fractions become more important, the residual fraction increases with depth for chromium and copper and for lead, the Fe and Mn oxides or the residual fraction increases in importance with depth.

Generally for all metals, both the exchangeable and surface oxide and carbonate fractions decrease with depth, whereas the Fe and Mn oxides, organic and residual fractions all increase. In the majority of the sediment cores, soil pH increases down the profile, increasing the number of sorption sites available on hydrous oxides or organic matter (Ritchie and Sposito, 1995), hence an increase in these fractions with depth. pH in the surface is generally lower, corresponding to higher % LOI where the breakdown of organic matter may have produced the lower pH values. At lower pH values, the amount of a metal bound to the exchangeable and surface oxide and carbonate fractions can increase, because of a lack of adsorption sites on hydrous oxides and organic matter.

These processes are observed at Apperley Bridge, Kirkstall Allotments, Globe Road, Knostrop and Swillington Bridge. However, at Calverley, significant proportions of all metals are associated with the surface oxide and carbonate fraction at depth and also arsenic, cadmium and copper with the exchangeable fraction in the lower part of the profile. Metal levels associated with the Fe and Mn oxides (except for lead) decrease down the profile. The Fe and Mn oxides are particularly susceptible to alterations in redox potential and are soluble under reducing conditions that occur when ground water level is reached or rises during flood conditions. This can release heavy metals which are then taken up by the exchangeable and surface oxide and carbonate bound fractions, hence an increase in these fractions with depth in the sediment core.

A similar situation also occurs at Rodley, where large proportions of each metal are associated with the exchangeable and surface oxide and carbonate fractions and less with the Fe and Mn oxides with depth. From a depth of 270 cm in the sediment core, the soil was gleyed, in a reduced state, the Fe and Mn oxides solubilised. At Kirkstall Allotments, following an increase in pH and % LOI from a depth of 275 cm, the proportion bound to the organic and Fe and Mn oxide fractions rise for arsenic, cadmium, lead, mercury and zinc, because of the increasing number of sorption sites available on these fractions. At Globe Road, concentrations of arsenic and copper in the exchangeable and organic fractions increase with depth, particularly in the sample taken from a depth of 280 - 285 cm, likewise the percentage associated with the Fe and Mn oxides decrease. All other metals at this site conform to the general patterns observed. The reasons for this are not obvious and are not easily explained. At the site called copper works, concentrations of metals in the first two sequential extraction steps are relatively high throughout for cadmium, copper, lead and zinc, particularly in the sample at greatest depth analysed for chemical speciation. This could be the result of the decrease in pH which occurred at this depth, leading to the lack of adsorption sites on the Fe and Mn oxides and organic matter.

It was found that the pattern of chemical speciation was very similar between different sediment core sites, arsenic mainly associating with the organic fraction, cadmium with the exchangeable and Fe and Mn oxides, chromium and copper with the organic and residual fractions, lead with the Fe and Mn oxides, mercury almost entirely with the organic and surface oxide and carbonate fractions and zinc with the last three sequential extraction steps. The results show that changes in chemical properties such as pH and redox conditions are accompanied by a release or sorption of metals from the sediment and a significant amount of each metal is associated with the most mobile and easily exchangeable fractions in all cores.

8.4.3 Radiocarbon dates for sediment cores

Carbon-14 is formed in the upper atmosphere by cosmic ray bombardment of nitrogen atoms. The resulting carbon isotope is rapidly oxidised to form CO_2 and is then mixed uniformly through the atmosphere. Photosynthesis leads to ^{14}C being taken up by plants, which in turn is passed on to higher organisms. When organisms die their ^{14}C content is no longer replenished and the isotopic clock is set in motion, ^{14}C decaying at a fixed rate. The time elapsed can be gauged from how far the decay process has proceeded since then, as indicated by the amount of radioactivity left in the element (Roberts, 1989). ^{14}C dating can be used to determine the age of any material containing carbon, including wood. Dates were determined from wood samples in sediment cores at Kirkstall Nature Reserve and the Copper Works. The results are indicated in the table below.

Table 8.2 - Radiocarbon dates

Site	**Interval (cm)**	**^{14}C date**
Kirkstall Nature Reserve	460 - 465	995 - 1265 AD *
Copper Works	480 - 500	1435 - 1680 AD *

* 2 sigma calibration, 95 % probability

These dated sections can be used to interpret the chronology of contamination in the River Aire in Leeds.

8.4.4 History of heavy metal pollution in the River Aire

The dated cores are shown in figures 8.25 and 8.26 for Kirkstall Nature Reserve and the Copper Works respectively, calibrated from the ^{14}C wood horizon (table 8.2). This was done using the two sigma calibrated dates (95 % probability) and the depth at which the wood sample was found. The sedimentation rate was calculated from the amount above the sample (cm), divided by the difference (years) between present time and the dated horizon. A constant annual sedimentation rate was assumed. Sedimentation rates of 0.35 cm/yr at Kirkstall Nature Reserve and 1.12 cm/yr at the Copper works, were divided into the depths where the samples were collected, to calculate the year, for that particular depth. For the Kirkstall Nature Reserve core, a depth of 160 cm was taken to represent the time before landfill of the core took place (i.e. 1990), the first 160 cm were therefore disregarded.

The core at Kirkstall Nature Reserve (figure 8.25) goes back to 900 AD (±162 years), (to be written from here on as ±162). The most recent sample was dated as 1953 (±6). Metal concentrations at Kirkstall Nature Reserve start to elevate from a very early time period, levels beginning to rise in concentration around 900. Chromium, copper, lead and zinc concentrations start to rise slowly from 1100 (±132), arsenic and cadmium levels increasing from approximately 1200 (±117), but metal levels decreasing up until 1400 (±87). After 1400 concentrations start to rise significantly to 1640 (±52), where peaks in metal levels were observed, the highest concentrations determined throughout the core for chromium, copper and lead. Metal concentrations gradually start to increase from about 1690 (±45). For arsenic and cadmium from 1880 (±16) onwards, the increase is very sharp, reaching maximum levels in 1900 (±14) and then declining through to present day. Chromium concentrations increase relatively sharply between 1690 - 1740 (±45, ±37 respectively) and then more gradually up to 1880. By 1900 concentrations had decreased significantly only to increase again after this time, showing the highest

Figure 8.25 - Metal contamination history, dated sediment core - Kirkstall Nature Reserve 10.0 km downstream

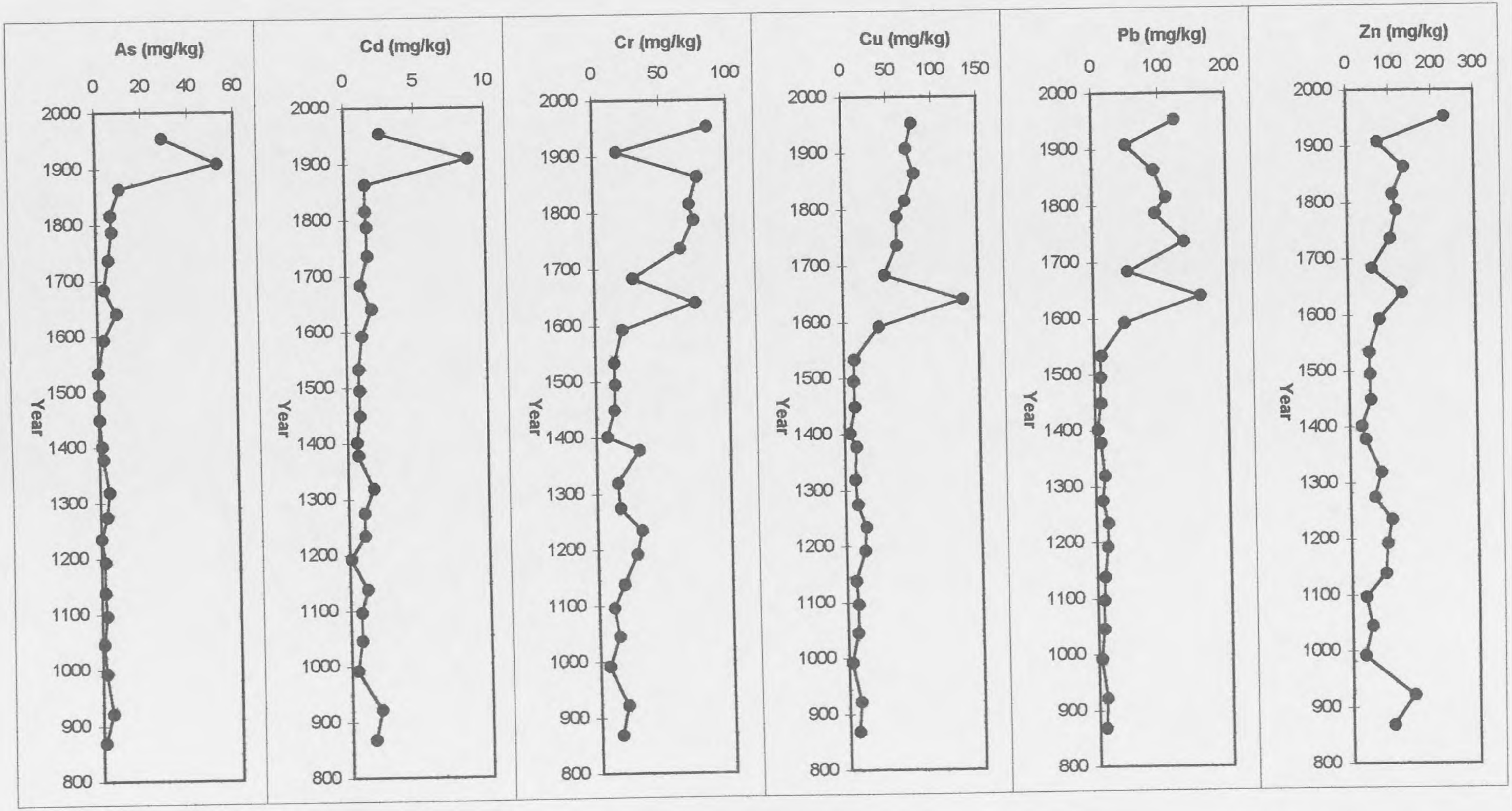
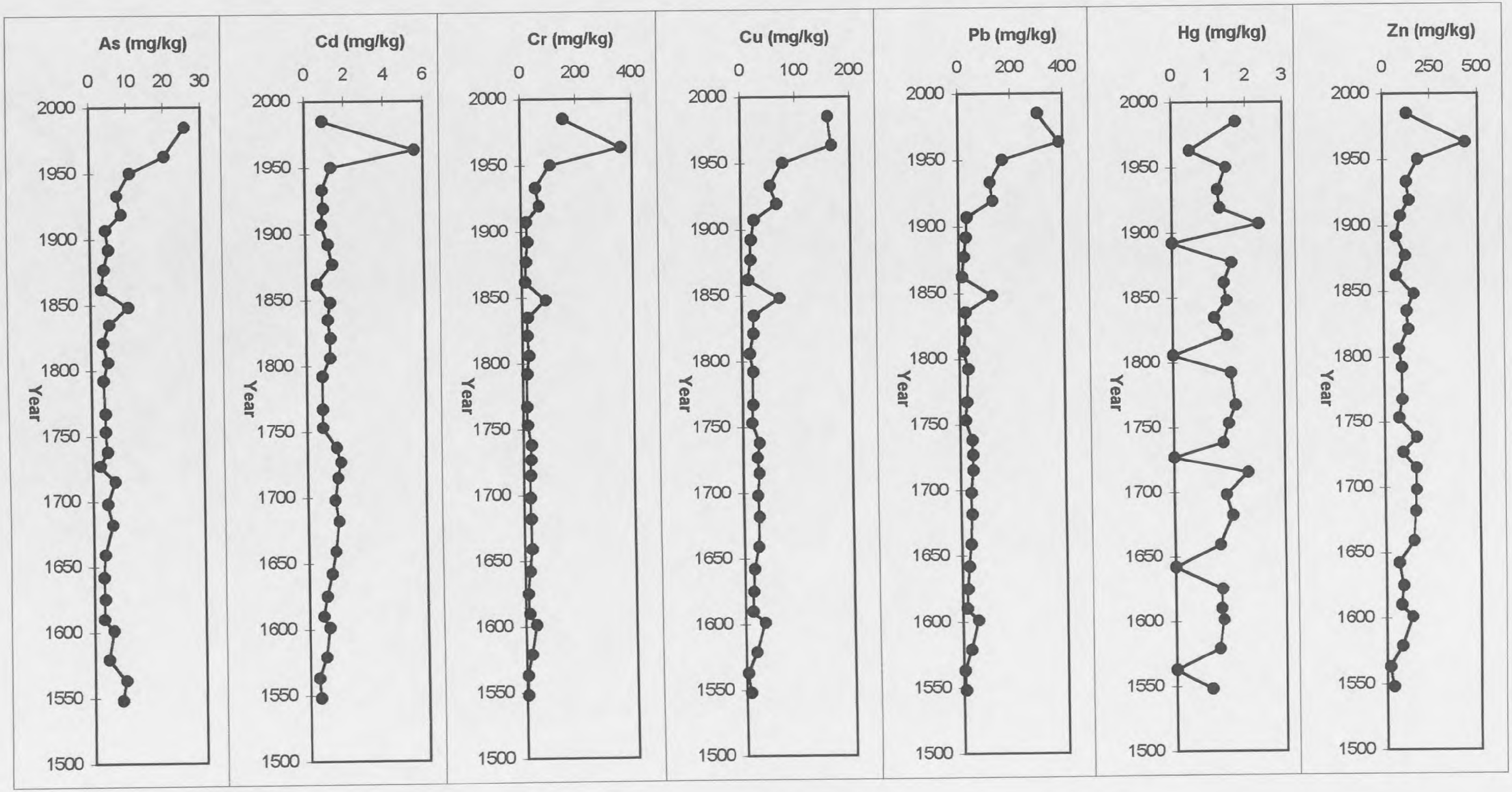


Figure 8.26 - Metal contamination history, dated sediment core - Copper Works 23.0 km downstream



concentrations observed in the core at 173 cm, occurring in 1953. For copper and zinc, concentrations increase between 1690 and 1880, decrease to 1900 and then increase up to 1953. Likewise lead concentrations increase from 1690 - 1740, decrease up to 1900 and increase from this time.

The distributions of arsenic, cadmium, chromium, copper, lead and zinc in the core at the Copper Works site (figure 8.26), resemble each other to a large extent, suggesting similarities in sources. Mercury is the exception, however, and shows a very random pattern with little relationship to the other metals. The core has been dated from 1550 (±126) up until 1985 (±3), which represents the last and most recent sample taken. Concentration maxima are observed at two depths occurring around 1950 (±13) and 1970 (±7). A major decrease of heavy metal pollution is apparent for most metals in the 1980s. Profiles of all the metals show an increase in metal concentration from approximately 1560 (±123) up until 1720 (±78), when a slight decrease occurs. Levels then increase gradually, peaking in concentration just before 1850 (±42) and continuing to increase up to 1950, from when concentrations rise sharply until 1970. Peak concentrations are reached for all metals except arsenic during the 1970s. Arsenic and mercury continue to increase in concentration up to 1985, whilst all other metal levels decrease.

The general pattern is much clearer and easier to interpret at the Copper Works site. For Kirkstall Nature Reserve, it is difficult to know how much effect and site disturbance the landfill caused. The deepest zones of both cores correspond to periods before industrialisation and small scale local activity. The very early increases in metal concentration at Kirkstall Nature Reserve, may be due to higher % LOI results at these depths. Metal concentrations start to pick up in the fifteenth and sixteenth centuries in both cores, corresponding to the rise of the textile industry. The period up until 1850 represents a period of intense industrial activity, during which industrial and domestic wastes were discharged directly to the river (section 4.2). After 1850, the importance of manufacturing industry to Leeds declined slightly, and the region saw the construction of the first sewerage system, reflected by a decrease in metal concentration. Contamination rapidly accelerated in the early 1900s, through the increase in burning of fossil fuels, and developments in the metal, chemical and leather industries. A sharp increase occurred in the 1950s and the climax of contamination appears in sediments deposited around the 1970s. Pollution levels of metals in sediments have decreased drastically since the 1970s, presumably due to the improvement in wastewater treatment and decline in the use of leaded petrol. An increase in concentration was observed for arsenic at the Copper Works site from the 1970s through to 1985. This is also true for chromium, copper, lead and zinc from the Kirkstall Nature Reserve core, although this is probably due to contamination from the above landfill. The reason for high surface arsenic levels at the Copper Works site may be due to atmospheric deposition from copper smelting (the largest single anthropogenic input of arsenic to the atmosphere, O'Neill, 1995) carried out in the past by IMI Yorkshire Imperial Ltd.

The results are comparable to those found in other studies. Owens and Cornwell (1995) and Zwolsman et al. (1993) reported sediment profiles showing an increase in metal concentration from the beginning of the century to the early 1970s. A major decrease in heavy metal pollution was apparent in these studies in the 1980s. Both studies were largely concerned with lead. Coal combustion and the use of lead in petrol were the main reasons for increased levels of lead in sediment profiles. The sediment cores showed a direct response to the phasing out of leaded petrol and to legislation, passed in the 1970s to improve air and water quality. The reduction in metal loadings is represented by a very pronounced decrease of these metals, in sediments deposited after 1970. The authors suggested that present day loadings of lead, copper and zinc have been reduced to approximately 1930s levels. Spliethoff and Hemond (1996) studied sediment cores in the Abejona watershed, Massachusetts, finding that metal concentration decreased sharply in the mid-1930s, when much of the watershed was sewered.

Dated sediment cores have proven to be an effective tool for reconstructing the chronology of contaminant inputs to sediment systems. However, the estimation of sediment age is complicated by sampling errors, biological or physical mixing of sediments and migration of radiotracers. In addition to problems such as mixing, the diagenetic remobilisation and migration of heavy metals in pore water can result in post-depositional mobility (Owens and Cornwell, 1995). Interpretation of contaminant profiles must consider such potential complications. Profiles of metals in the sediment cores show increase in concentrations from the beginning of the fifteenth or sixteenth century. However, the twentieth century in particular has been characterised by a large increase in depositional fluxes of heavy metal inputs at small spatial scales, the combustion of coal in power plants and the use of lead in petrol have led to contamination over relatively larger spatial scales. The results show that significant progress has been made in decreasing heavy metal contamination in the River Aire.

8.5 Conclusions

Metal contamination in the River Aire catchment in Leeds is higher in floodplain soils than in contemporary sediment indicating that pollution of the system is now less than in the past. Floodplain soils are most severely polluted between 6.0 - 9.2 km downstream, with metal levels increasing laterally across the floodplain and a relatively high frequency of flooding. The chemical speciation of floodplain soils is consistent with other sediment forms, cadmium being mainly associated with the exchangeable and surface oxide and carbonate fractions, copper with the remaining three sequential extraction steps and lead and zinc predominantly with the Fe and Mn oxides. Heavy metal concentrations in sediment cores show elevated levels in the surface sediments, concentrations usually peaking within the first 50 cm, before declining to minimum concentrations with depth in the profile. Sediment cores follow the general speciation trend of arsenic being primarily associated with the organic fraction, cadmium with the exchangeable and Fe and Mn oxides, chromium and copper with the organic and residual fractions, lead with the Fe and Mn oxides, mercury almost entirely with the organic and surface oxide and carbonate fractions and zinc with the last three sequential extraction steps. Sedimentary records from the river system show that the twentieth century has been characterised by large increase in depositional fluxes of heavy metals. Elimination of alkyl lead in petrol and the treatment of domestic and industrial wastes have resulted in a decrease in heavy metal inputs to the environment since the 1970s.

CHAPTER 9

HEAVY METAL BUDGETS FOR THE RIVER AIRE

9.1 Introduction

The routing of sediment through watershed systems has long been of interest to geomorphologists (Macklin and Lewin, 1989; Walling and Webb, 1988). Sediment budgets have often been used in the past to estimate sediment yield from river basins (Trimble, 1983; Walling, 1974). The recognition of associations between heavy metals and fluvial sediment has added to the practical significance of sediment budgets (Renwick and Ashley, 1984). The main objective of this study is to investigate quantitatively the dispersal, storage and remobilisation of heavy metals in the River Aire in Leeds. A multi-scale approach is used to evaluate the spatial patterns of metal pollution in this fluvial environment and to compile mass balances of sediment and associated heavy metals. Once compiled, a mean annual heavy metal budget provides an accounting of the amounts of heavy metals moving into and out of the River Aire in Leeds, during a typical year. Such a budget is a basis for assessing the rates of heavy metal transport and the location of storage along the river.

The budget as calculated here, follows that used by Leenaers (1989) for the River Geul. It requires data concerning sediment and associated heavy metal concentrations in the sediment. The discharge and suspended sediment data that are available from Environment Agency gauging sites, define the overall framework for budget construction. Data collected and described in earlier chapters of this thesis, provide heavy metal concentrations for contemporary river bed sediment, suspended sediment and floodplain soil. The calculations in this study used mean values of heavy metal concentration from all measurements at or near the site. In some cases, described in the following sections, data is missing and best estimates are used. Whatever short comings are imposed by the lack of, or small number of samples, time constraints and expensive chemical processing and analysis, have always precluded the acquisition of additional data.

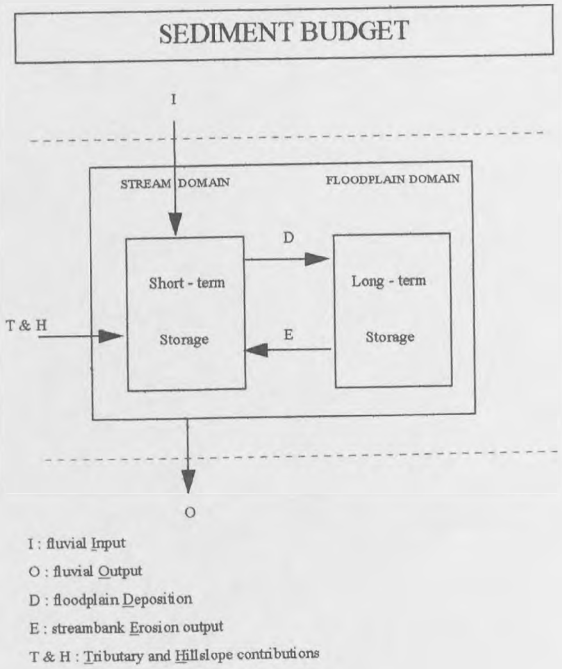
In this chapter an attempt will be made to construct a tentative sediment budget for the alluvial area of the River Aire in Leeds. From the data presented in the previous chapters, this budget will provide the basis for the construction of budgets for cadmium, copper, lead and zinc, whose cycling in the fluvial environment is to a large extent associated with the routing of sediments. Metal budgets for arsenic, chromium and mercury are not possible. Data for these metals were not obtained for the majority of terms used in the compilation of these budgets.

9.2 The Sediment Budget

In constructing a sediment budget (figure 9.1), the following terms are taken into account:

- fluvial input
- fluvial output
- short-term storage in the stream domain
- long-term storage in the floodplain domain
- sediment deposition in the floodplain
- tributary and hillslope contributions
- streambank erosion.

Figure 9.1 - The sediment budget *(after Leenaers, 1989)*



The fluvial input term was quantified using discharge data and suspended sediment concentrations for the year 1996 (table 1, Appendix V). As no discharge data is available for Apperley Bridge, the start of the study reach, it was calculated from discharge data from a site upstream at Kildwick and a site downstream at Armley. The fluvial output term was estimated using the method described above at Swillington Bridge, the end of the study reach. Because no discharge data is available for the point where the River Aire leaves Leeds, discharge data from a nearby gauging station (Fleet Weir) is used. Fleet weir is located approximately 1 km downstream of Swillington Bridge. The total mass transport of suspended sediment through the catchment is shown in table 9.1. However, because no data is available on the magnitude of bedload transport, the calculated transport rate provides an underestimation of the true transport rate.

Table 9.1 - Total mass transport of suspended sediment past Apperley Bridge & Swillington Bridge in 1996

	Total tonnes
Apperley Bridge	5229.6
Swillington Bridge	8451.2

Once the input and output of sediment through the river channel have been estimated, the sediment yield from the Leeds part of the catchment can be derived from their difference. The magnitude of the other budget terms now need to be estimated and these have to account for the annual sediment production. However, the available data do not always allow precise and independent estimates of the various terms. The storage of fine-grained sediments in the river channel is an important part of the budget, as contemporary river bed sediments (section 6.3) were found to contain some of the highest concentrations of heavy metals in this study. However, this term is not easily quantified. To calculate the short-term storage of sediment in the stream domain only contemporary river bed material was used, as the quantity of visible within channel sediment varied greatly downstream. River bed material was mainly gravel, however no data was collected on the complete grain size spectrum of the river bed. As metal concentrations are generally highest in the finest fractions (< 63 μm) and this size was used in total metal analysis, the amount of fine grained sediment as a percentage of the total < 2 mm, was calculated from data provided by Hill et al., (1995) and used in the budget. In considering only the finest river bed sediment, the storage calculated is going to be an under approximation of the true storage amount. Floodplains are the main storage sites for sediment and associated metals (section 8.2). In this section the quantitative aspects of sediment storage was derived from the volume of alluvial soils (table 4, Appendix V). Floodplain metal storage calculations are important as they provide a measure of efficiency for storing contaminated sediments. The magnitude of tributary and hillslope contributions were unknown. However, because a large percentage of the River Aire in Leeds is unnatural, the contribution from Knostrop sewage treatment works is taken into consideration. It is represented in the budget by the term sewage effluent. Effluent from Esholt is not considered in the budget calculations, as most is discharged upstream of the study reach. Because of the nature of the river, large quantities of surface water are abstracted each year for potable water supply and industrial use. This amounts to a total of 27511000 TCMA (thousand cubic metres per annum). Therefore, this term is also considered in the budget. River abstractions are calculated using an average concentration of suspended sediment for the River Aire. For sediment deposition in the floodplain, two dated sections were available that provide an indication of long-term sediment deposition rates. The reported rates (section 8.43) vary from 0.35 - 1.55 cm/yr. It is likely that sediment deposition is much lower than this at present time. These data, therefore, can not be interpreted as overall deposition rates. The deposition term is based on an estimated average sediment deposition rate. With regard to streambank erosion, detailed field sampling would have been necessary. Thus, in addition to the deposition term this cannot be estimated with a high degree of precision.

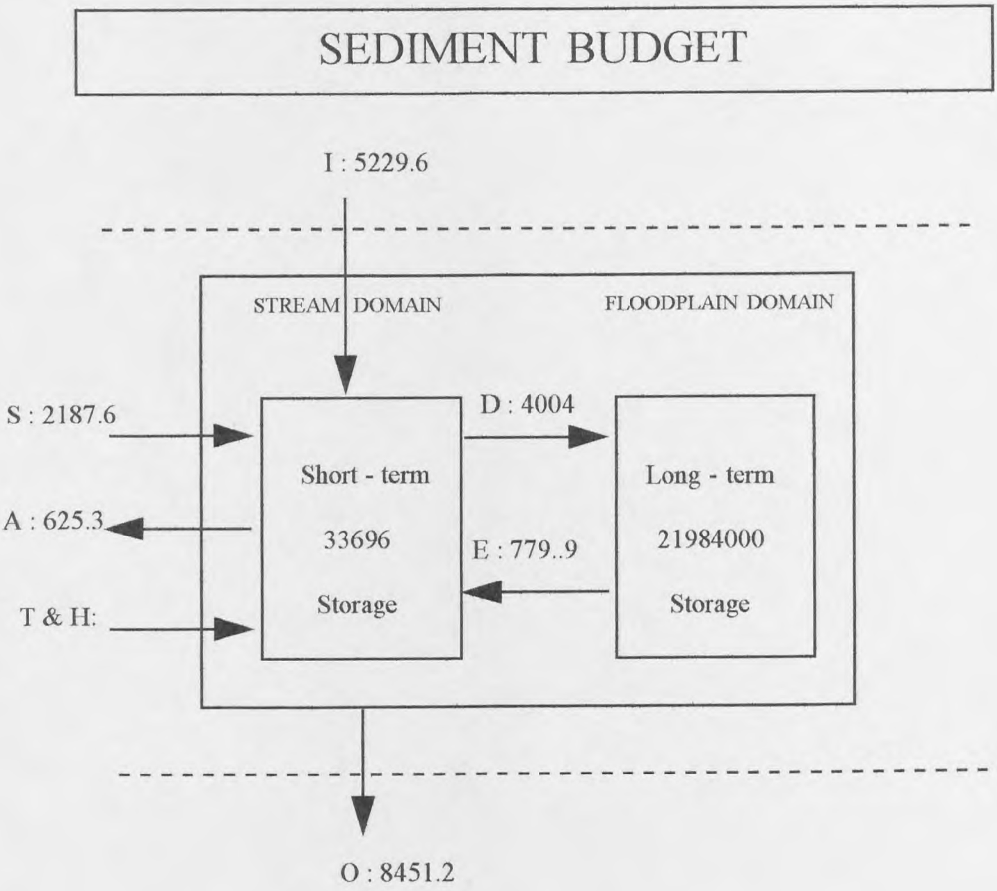
Nevertheless, given the fact that the metal concentrations of all studied sediments are known, it is possible, once an estimate is made on one of the unknown terms, say the deposition rate - to derive the others from the fact that only one possible mixture of the other types of sediment can account for the fluvial output of both suspended sediment and associated heavy metals. The area of floodplains most likely to be flooded was estimated, as it is unlikely that the entire area will be inundated during a flood. This was calculated with an estimated sediment deposition rate of 1 mm/yr to give the floodplain deposition term. The streambank erosion term was given by the difference in the budget to make it balance. Because the available data do not allow a more accurate approach, the presented budgets of sediments and heavy metals should be regarded as tentative. The results of each budget term are outlined in the table below and in figure 9.2, the sediment budget for the River Aire.

Table 9.2 - Total amounts of sediment for each budget term

Budget term	**tonnes**
fluvial input	5229.6
fluvial output	8451.2
storage in floodplain domain	21984000
storage in stream domain	33696
sewage effluent	2187.6
abstraction	625.3
floodplain depostion	4004.0
tributary & hillslope contributions	*
streambank erosion	779.9

* magnitude unknown

Figure 9.2 - A sediment budget for the River Aire in Leeds (values in tonnes)



I : fluvial Input

O : fluvial Output

S : Sewage effluent

D : floodplain Deposition

T & H: Tributary & Hillslope contributions

E : streambank Erosion output

A : Abstraction

9.3 The Budgets of Heavy Metals

The sediment budget and the budget of sediment-associated metals were calculated together in the way described in section 9.2. The estimated fluvial input and output terms are given from the total mass transport of suspended sediment and solid-bound metals and dissolved metal concentrations at the top and end of the study reach (table 9.3 and Appendix V). Heavy metal concentrations bound to suspended sediment was not measured at these sites. For the purpose of the budget, average sediment-associated metal concentrations for the River Aire are used (Chapter 7 and table 2, Appendix V).

Table 9.3 - Total mass transport of solid-bound & dissolved metals past Apperley Bridge & Swillington Bridge in 1996

Apperley Bridge	**total transport (kg)**	**solid (kg)**	**dissolved (kg)**	**solid (%)**	**dissolved (%)**
cadmium	79	53.4	25.6	68	32
copper	6983	5516	1467	79	21
lead	969	674	295	70	30
zinc	32588	27024	5564	83	17

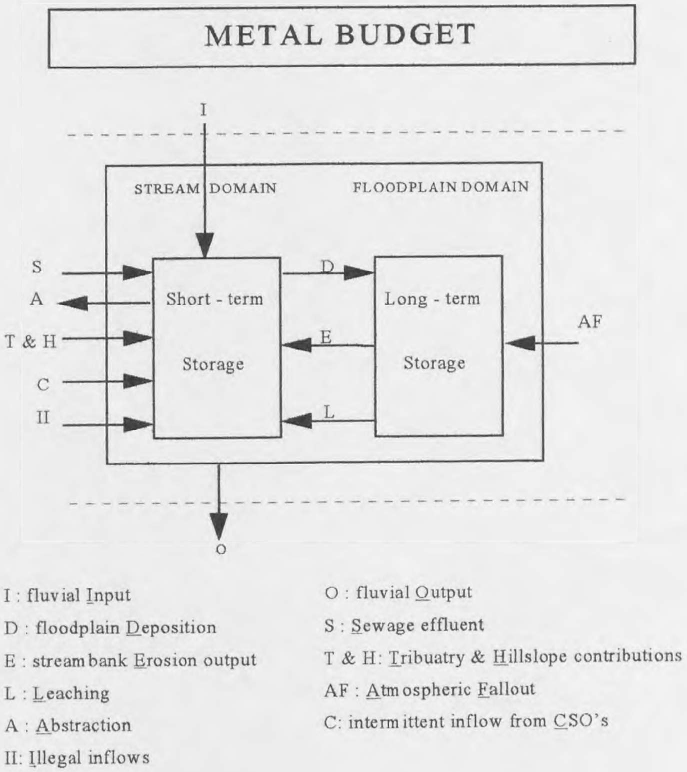
Swillington Bridge	**total transport (kg)**	**solid (kg)**	**dissolved (kg)**	**solid (%)**	**dissolved (%)**
cadmium	174.4	86.4	88.0	49	51
copper	11722	8915	2807	76	24
lead	1990	1089	901	55	45
zinc	54913	43671	11242	80	20

Given the known metal concentrations of floodplain soils, flood deposits, contemporary river bed and within channel sediments and the quantities derived from the sewage treatment works, the budgets of sediment-associated metals could be calculated. For metals deposited on the floodplain, levels determined in flood sediments at Apperley Bridge were used (Table 5, Appendix V). To calculate the amount of metals in eroded sediment, average concentrations in contemporary within channel sediment were used, as these sediments are the most likely to be eroded with an increase in flow (Table 5, Appendix V). Where no information exists on metal concentrations, either dissolved or with the sediment, average figures found for the River Aire are used. This applies to the budget term abstraction. In addition to the above terms, the magnitude of the following flows of other than sediment-associated heavy metals were estimated (figure 9.3):

- leaching of heavy metals from the alluvial soils
- atmospheric fallout.

There are also several other likely sources of heavy metals to the channel. These include heavy metal inputs from tributary and hillslope contributions, intermittent inflows from combined sewer overflows and any possible illegal inflows that may exist. It was not possible to quantify these sources but because they exist it is necessary to include these terms within the metal budget.

Figure 9.3 - The heavy metal budget



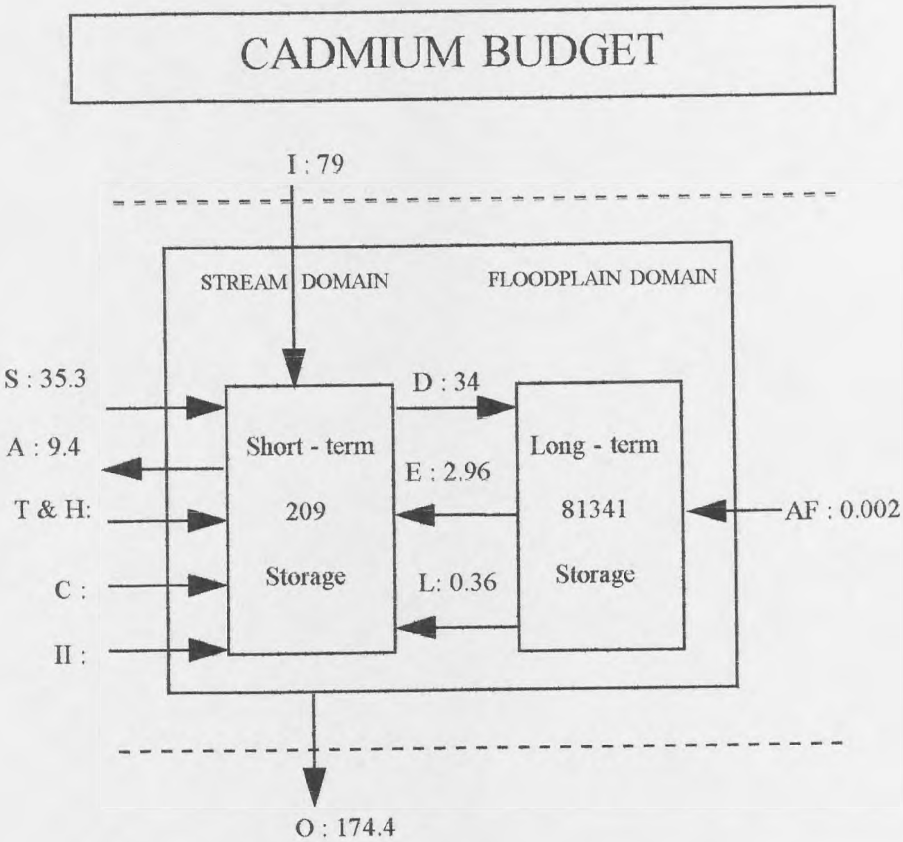
The amount of leached heavy metals that enter the river via the alluvial aquifer from floodplain soils was estimated from the effective precipitation surplus (240 mm/yr) and the average concentration of dissolved heavy metals in the Leeds reach of the Aire (table 3, Appendix V). The latter figures are assumed to have the same order of magnitude as the metal concentration in the alluvial aquifer (Leenaers, 1989). The contribution of atmospheric fallout was derived from data provided by Leeds Environment Department (1994). The data used is metal concentrations in the Leeds atmosphere for the year 1993 (figure 3.1 and table 5, Appendix V). After reviewing literature on atmospheric fallout of heavy metals in urban areas (Galloway et al., 1982; Jaffrezo and Colin, 1988; Kane et al., 1994; Pattenden, 1974), such wide ranging metal levels were given for various sites across the UK. Hence, it was decided to use the above data which actually related to Leeds. Metal levels contained in the atmosphere or in atmospheric fallout were assumed to not be significantly different. Leenaers (1989) also used a contribution from agricultural additives, such as fertilisers, manure and sewage sludge. Because much of the Aire catchment in Leeds is not agricultural, this term is not considered in constructing metal budgets for the Leeds reach of the river.

The tentative budget of cadmium, copper, lead and zinc are presented in figures 9.4, 9.5, 9.6 and 9.7 respectively. The calculated budget terms are shown in the table below.

Table 9.4 - Total amounts of heavy metals for each budget term

heavy metal budget terms	cadmium (kg)	copper (kg)	lead (kg)	zinc (kg)
storage in floodplain domain	81341	2506176	2857920	4352832
storage in stream domain	209	2426	5358	9064
sewage effluent	35.3	2841	466	13136
abstraction	9.4	792	121	3820
deposition	34.0	426.4	589	2972.2
erosion	2.96	56.1	83.6	184.8
leaching	0.36	15.8	4.6	70.6
atmospheric fallout	0.002	0.036	0.307	0.277
unexplained error	84.7	6433	866	28924.5

Figure 9.4 - A cadmium budget for the River Aire in Leeds (values in kg)



Error = 84.7

I : fluvial Input

D : floodplain Deposition

E : streambank Erosion output

L : Leaching

A : Abstraction

II: Illegal inflows

O : fluvial Output

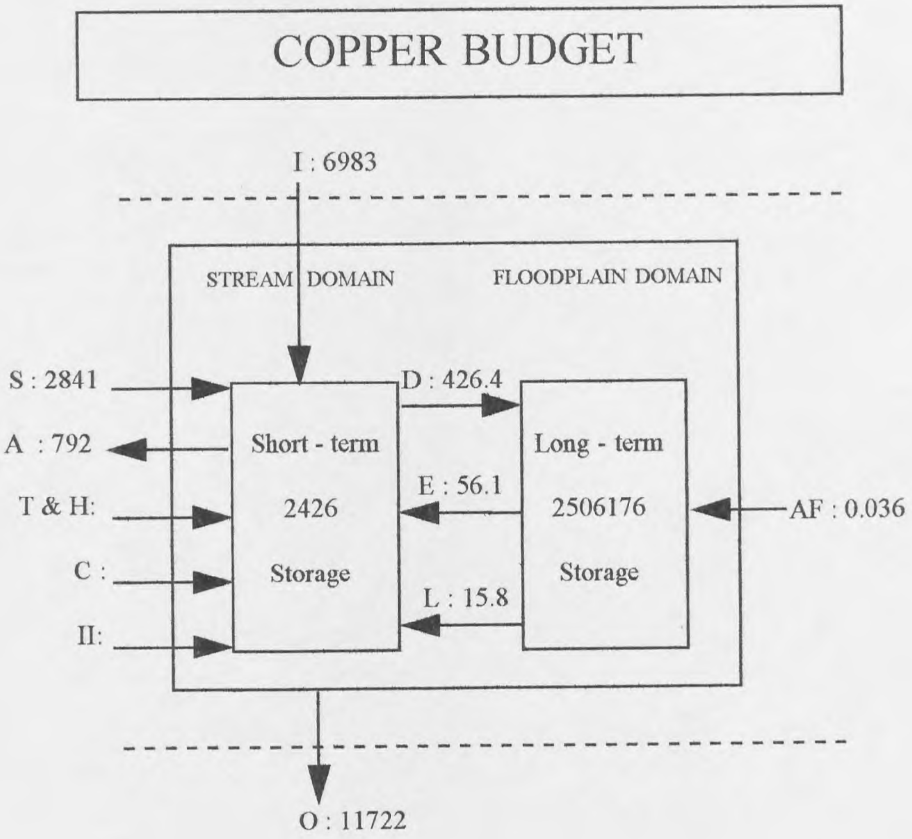
S : Sewage effluent

T & H: Tributary & Hillslope contributions

AF : Atmospheric Fallout

C: intermittent inflow from CSO's

Figure 9.5 - A copper budget for the River Aire in Leeds (values in kg)



Error = 6433

I : fluvial Input

D : floodplain Deposition

E : streambank Erosion output

L : Leaching

A : Abstraction

Il: Illegal inflows

O : fluvial Output

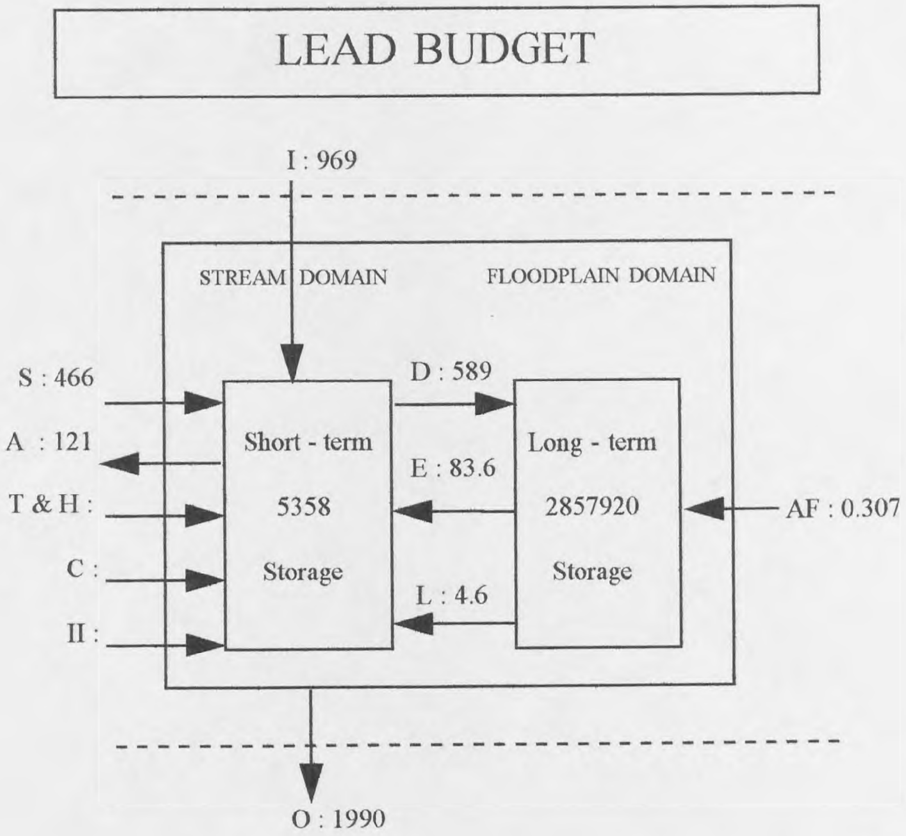
S : Sewage effluent

T & H: Tributary & Hillslope contribtuons

AF : Atmospheric Fallout

C: intermittent inflows from CSO's

Figure 9.6 - A lead budget for the River Aire in Leeds (values in kg)



Error = 866

I : fluvial Input

D : floodplain Deposition

E : streambank Erosion output

L : Leaching

A : Abstraction

II: Illegal inflows

O : fluvial Output

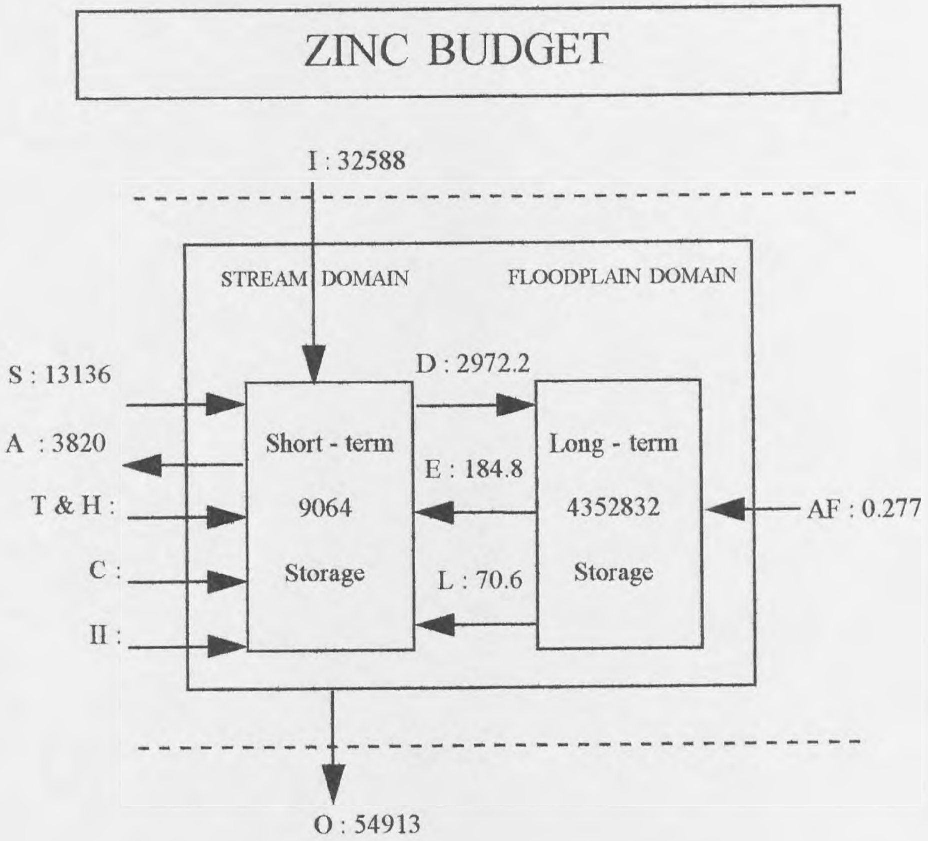
S : Sewage effluent

T & H: Tributary & Hillslope contributions

AF : Atmospheric Fallout

C: intermittent inflows from CSO's

Figure 9.7 - A zinc budget for the River Aire in Leeds (values in kg)



Error = 28924.5

I : fluvial Input	O : fluvial Output
D : floodplain Deposition	S : Sewage effluent
E : streambank Erosion output	T & H: Tributary & Hillslope contributions
L : Leaching	AF : Atmospheric Fallout
A : Abstraction	C: intermittent inflow from CSO's
II: Illegal inflows	

As a consequence of the procedure followed, the catchment output of the metals can not be explained completely by the flows of sediment. The procedure yielded unexplained output of approximately 50 % for each of the metals. The annual heavy metal budgets calculated for the Aire in Leeds are only first approximations and should be regarded as tentative. Although the calculations use the best available data, substantial errors arise in the results. Sources of these errors are likely to include measurement, sampling and estimation errors. The term causing the budgets to have unexplained catchment output of metals, is that from sewage effluent, which forms a highly significant source of metals to the channel.

9.4 The Significance of the River Aire in Leeds as a Source of Heavy Metals

The significance of the Aire in Leeds as a source of heavy metals can now be assessed. The mass transport of suspended sediment and heavy metals past Swillington Bridge at the end of the study reach (table 9.3), is compared to the loads determined from the River Aire to the Humber catchment and out into the North Sea (Robson and Neal, 1997). The results are presented in the table below.

Table 9.5 - Total loads transported

	River Aire entering the North Sea (kg/yr)	**River Aire in Leeds (kg/yr)**	**% of that entering the North Sea (%)**
sediment	58960000	8451200	14.3
cadmium	140	174.4	124.6
copper	18560	11722	63.2
lead	14500	1990	13.7
zinc	57600	54913	95.3

It is clear that, in terms of the transport of sediment, the catchment output of the Aire in Leeds is relatively small compared to the output from the Aire to the North Sea. The mass of sediment transported in Leeds is only 14 % of the load entering the North Sea. However, the possible contribution of metals from the Leeds reach of the Aire, as a percentage of that reaching the North Sea is much more significant. These values suggest that the Aire in Leeds may play a significant role in terms of total emissions of heavy metals entering the North Sea. Particularly for cadmium, zinc and copper. The results suggest that a relatively large amount of cadmium is 'lost' on the way, as that passing through the end of the Leeds reach, is greater than that calculated to be going through to the North Sea. The Leeds reach of the Aire transports relatively low total levels of lead compared to the other metals. Therefore, the results of the budgets are consistent with those found in previous chapters, where lead concentrations in floodplain soils also exceed guidelines set by the ICRCL and Dutch Soil Protection Policy the least. Furthermore, if the contributions of the Aire in Leeds are considered in relation to discharges of heavy metal contaminants through sewage effluent, it becomes clear that they are of major importance. Of equal importance are the amounts of heavy metals currently stored in the river channel and in floodplain soils.

9.5 Conclusions

Tentative budgets of sediment and associated metals have been calculated for the River Aire in Leeds. The budgets are very much first approximations in which large unexplained errors occur. However, they do suggest that the Leeds reach of the Aire contributes high metal loads to the river downstream, with significant inputs to the channel coming from sewage effluent. The results also suggest that improvements in the discharge of contaminated effluent need to be made, although the mass of metals stored in floodplain soils and channel sediments are likely to contribute a diffuse source of metals to the river system for many years to come.

CHAPTER 10

CONCLUSIONS & IMPLICATIONS

This chapter summarises the results of the research. It highlights the main findings of each chapter and examines what has been achieved with respect to the aims and objectives of the research outlined in Chapter 1. The research is placed in a wider context to assess the environmental implications for sustainability. Finally a discussion is presented on future research, suggesting how the work can be developed further.

10.1 Summary of Findings

To achieve the main objectives of this study, to compile mass budgets of sediment and associated heavy metals for the Leeds reach of the River Aire, a wide variety of data were collected and analysed. Heavy metals in the River Aire system are derived from a variety of past and present sources, both natural and anthropogenic. As present day river water quality is influenced by past activities, it must be analysed within a historical context. Identifying the past and present sources of metals is crucial to characterising a river's past and present water and sediment quality and also for predicting future trends.

In the past, the influence of water on industrial location meant that activity or manufacturing was concentrated along the Aire and Meanwood valleys in Leeds, which are considered to be the main historical sources of heavy metal pollutants. The river was used by these industries as a convenient means of effluent disposal and as a sewer. Industries located along the river included iron and steel forges and foundries (sources of lead and zinc), textile factories, leather works, chemical and other manufacturing industries (sources of cadmium, chromium, copper and zinc). Until the 1850s, little provision was made for the disposal of animal and human excreta which contains quantities of cadmium, copper, lead and zinc. Coal, the standard fuel, was used in vast quantities and contributed to heavy metal pollution, via the atmosphere and through the disposal of ash residues to the water course.

The main present source of heavy metals to the River Aire in Leeds comes from sewage effluent, highlighting the urban and industrial nature of the river. Esholt and Knostrop sewage works treat significant quantities of both domestic and industrial effluent. Small quantities of metals pass through sewage treatment system and into the river. Effluents discharged from sewage treatment works represent a significant proportion of the flow of the River Aire in Leeds. Combined sewer overflows (CSO's), during periods of heavy rain, may operate prematurely, discharging undiluted sewage to the river. At these times CSO's are a significant point source of heavy metals to the river.

The dispersal of heavy metals in sediment and soils in the study reach is a highly variable and complicated phenomenon. Metal concentrations in contemporary within channel and river bed sediment are highest between 0 - 1 km and at 25 km downstream of the study reach. This is the result of the close proximity to Esholt and Knostrop sewage treatment works respectively. Between 12 - 15 km downstream, through the city centre of Leeds, where traffic and industrial density is the greatest, metal concentrations in contemporary sediment are also high. Floodplain soils are the most severely polluted between 6.0 - 9.2 km downstream, with metal levels increasing laterally across the floodplain with distance from the river. This area of floodplains has a relatively high frequency of flooding and has consequently been inundated more often with metal polluted floodwaters. It was found for the river channel, that contemporary river bed sediments have the highest concentrations of heavy metals. These sediments therefore provide the main store and sink for metals in the Aire channel in Leeds. Metal concentrations are found to be higher in floodplain soils than in either contemporary within channel sediment or contemporary river bed sediment, possibly indicating that pollution of the fluvial system is now less than it was in the past. Historical records provided by sediment cores taken from the River Aire floodplain, show elevated metal levels within the first 50 cm. This illustrates that the twentieth century has been characterised by a large increase in depositional fluxes of heavy metals. However, the elimination of alkyl lead in petrol and the treatment of domestic and industrial wastes have resulted in a decrease of heavy metal inputs to the environment and hence in sedimentary metal accumulation since the 1970s.

Sequential extraction procedures provide an insight into the partitioning of metals on sediments, enabling the 'bioavailability' of metals to be estimated. The partitioning of metals on contemporary within channel sediment, suspended sediment and in floodplain soils has been studied for the River Aire in Leeds. The chemical speciation found between the different sediment forms through the study is relatively consistent. Cadmium is mainly associated with the exchangeable and surface oxide and carbonate fractions, copper with the remaining three sequential extraction steps and lead and zinc predominantly with the Fe and Mn oxides. Cadmium is therefore likely to be more easily exchangeable and has a greater potential for remobilisation. Of all the metal fractions, the residual may be considered as of no immediate environmental concern, as release from this fraction is unlikely. The form in which metals were bound to suspended sediment varies during the flood event studied and is specific to each metal, but appears to be largely controlled by changes in pH and influenced by adsorption and coprecipitation processes. During flood events, the Fe and Mn oxide fraction appeared to be the most important component for transporting sediment-associated metals.

In floodplain soils, the percentage of metals released during the first four extraction steps varies from 46 - 99 %. These fractions, which may be considered 'potentially mobile', form a very large part of the total concentration. A significant proportion of both cadmium and lead were associated with the exchangeable fractions and are therefore the most potentially mobile. Organic matter content, pH and redox conditions are important factors controlling the solubility, mobility and bioavailability of sediment-associated metals. It appears that in floodplain surface soils higher loss on ignition percentages may be associated with the relatively low pH values, through the breakdown of organic matter. This has lead to the partial leaching of metals associated with the exchangeable and surface oxide and carbonate fractions. The exchangeable fraction contains metals which are most easily mobilised and carbonates become increasingly soluble at lower pH values. In floodplain subsurface soils, rising groundwater tables give rise to reducing conditions which are solubilising Fe and Mn oxides and hydroxides. Heavy metals are released from this fraction and taken up by the exchangeable and surface oxide and carbonate fractions. Hence, these fractions account for a greater proportion of metals at a greater depth in the soil profile.

Discharge, suspended sediment and dissolved metal concentration data were collected for the year 1996 to quantify transport rates of sediment and sediment-associated and dissolved heavy metals. The flood event occurring on the Aire at Thwaite Mills in February of the same year was studied in detail. It was found that, for the Aire in Leeds, sediment concentration exhibited a general positive relationship with discharge. Most of the suspended sediment transported by the river is during floods. During peak flow, suspended sediment levels increase and the concentration of sediment-associated metals decrease, as a result of dilution. However, although metal concentrations are lower at the peak of the flood, the mass flow of solid-bound metals is the highest. For example, 8.6 kg of cadmium and 111 kg of lead were transported past Swillington Bridge in 1996 compared to a total of 17 kg cadmium and 155 kg lead for the entire flood event which lasted for 71 hours.

Sediment and associated heavy metal budgets were calculated using data for 1996 for the Leeds reach of the River Aire. The budget had to allow for the urban and industrial nature of the river, by taking into account the discharge of effluents from sewage treatment works and water abstracted for domestic and industrial use. However, it was not possible to directly measure all budget terms employed, hence, they should be regarded as tentative. The budgets illustrated the influence of sewage effluents on heavy metal inputs to the channel, Furthermore, the large storage capacity of metals in the floodplains was highlighted. The Leeds reach of the Aire, as compared to the total for the River Aire, contributes very high metal loads, to the Humber catchment and ultimately to the North Sea, particularly cadmium and zinc.

10.2 Environmental Implications for Sustainability

Due to the urban and industrial nature of the River Aire in Leeds, demands on the fluvial system are wide ranging, often conflicting and they can have an effect on the environment. The river provides a habitat for plants and animals, water for public supply, industry and agriculture, opportunities for sport and recreation and acts as a receptacle for wastewater. The enhanced levels of heavy metals in the river, sediment and soil of this fluvial system may affect the health of plants and animals that naturally inhabit the riparian area and are of great importance with regard to both human toxicology and agricultural productivity.

Average dissolved concentrations of metals in the River Aire are generally well below environmental quality standards (EQS) set for the protection of freshwater fish and other aquatic life (DOE, 1989). However, copper does give some cause for concern. The EQS adopted for the average dissolved concentration for the protection of aquatic life is 10 μg/l copper. Although the average concentration determined for the River Aire in Leeds is 4.8 μg/l, recent studies have shown that some species of invertebrates are often more sensitive than expected to concentrations of copper as low as 2.5 - 5.0 μg/l (Mallett et al., 1992). It appears that dissolved concentrations of metals, in themselves, are likely to have little impact on aquatic life in the River Aire in Leeds. However, it has been established that, for a given sampling station monitored over a long period of time, the metal values of the collected samples tend to vary by several orders of magnitude, although the samples may have been collected at short-time intervals (Salomons and Förstner, 1984). Such fluctuations are attributable to a large number of variables such as daily and seasonal variations in water flow, local discharges of effluent, changing pH and redox conditions, the input of treated secondary sewage, detergent levels, salinity and temperature.

Hence, pollutant concentrations in sediment often provide a more convenient means of obtaining an indication of the state and effects of associated waters. In addition, the main pathways of metal uptake in aquatic organisms are considered to be from the sediment and below ground species tend to have higher concentrations of metals (Mallett et al., 1992). Contemporary river bed sediments in the River Aire in Leeds were found to contain significant amounts of metals. Although these sediments were not analysed for chemical speciation, in keeping with other sediment forms, it can be anticipated that a significant proportion of each metal is held in a potentially mobile and bioavailable form. Improvements in water and sediment quality through reductions in polluting loads discharged from sewerage and sewage treatment systems and industry need to continue to help prevent the accumulation of contaminants in contemporary river sediment.

Elevated levels of heavy metals in floodplain soils is an issue of considerable importance wherever they impinge directly on human health. This may occur where food is grown on contaminated land or when metal polluted soil is inadvertently ingested by young children. Soil pollution also has major planning implications especially when new industry is sited on a historically metal contaminated area. As soil is a major influence on the chemistry of surface waters and the major threat is likely to occur during site redevelopment.

Throughout the River Aire catchment in Leeds the highest metal concentrations have been found in floodplain soils. The chemical analysis showed that they are appreciably contaminated with cadmium, copper, lead and zinc. ICRCL and Dutch soil protection policy guidelines, which provide a set of values for heavy metals in the soil, are used to assess the level of contamination. These may be interpreted as concentrations that when exceeded, may cause a reduction of crop yield or may affect human health when contaminated agricultural products are consumed.

For all floodplain samples taken, 54 % exceed the ICRCL guideline set for cadmium in domestic gardens and allotments, 28 % and 12 % of samples exceed the guidelines set for copper and zinc respectively, for any use where plants are to be grown. Using the Dutch system, 1.5 % and 14 % of the samples exceed cadmium and copper values respectively where cleanup of the site is considered necessary. The exceedance percentages suggest that enhanced concentrations of cadmium, copper and zinc in the soil, mean that it is unwise to grow crops for human consumption in parts of the Aire valley in Leeds, or to utilise the land for domestic gardens.

10 % of floodplain soils were classified by the pollution index as being severely polluted. The majority of these soils were found to be between 6.0 - 9.2 km downstream and have a relatively high frequency of flooding. To prevent further contamination and erosion of these polluted soils, there is a need to maintain and construct flood defences. These are now in place at Kirkstall and currently under construction at several other sites in the Aire valley in Leeds.

Sustainability in the use of soil requires effective measures to prevent serious or irreversible damage to sites on which industrial, urban or agricultural activities are currently taking place. The soil is a primary recipient, intended or otherwise, for many waste products containing heavy metals. Once these metals enter the soil they become part of a cycle that affects all forms of life. Environmental policies to date, have largely taken soil for granted. In recent years, however, there has been increased recognition of the need to protect and conserve soils. Although this has been more marked in some other European countries than in the UK. It is suggested that soil pollution to be given the same priority as pollution of air and water.

For the Aire catchment in Leeds, it is unlikely in the future that development will take place on land currently forming floodplains. These floodplains have a role to allow the storage and free flow of flood waters. Whilst the development of such land would cause enhanced concentrations of metals in the water column, continued flooding is likely to increase the overall metal burden of the floodplain and the potential for metals to be remobilised through changes in redox conditions. However, the demand for land, both for residential and commercial use, coupled with planning controls on the development of floodplains, is likely to lead to an increase in the redevelopment of derelict land. This may occur to the detriment of the aquatic environment. As cleaning up of contaminated sites is costly both to the environment and financially, future policy should ensure that further contamination is avoided.

With regard to the future quality of the river catchment, it is dependent on reconciling all of the uses demanded by the community at large whether it be for water supply, effluent disposal, fisheries, conservation, recreation or protection from flooding. To make optimal sustainable use of soil it must be: conserved as an essential part of life-support systems; accorded the same priority in environmental protection as air or water; recovered for beneficial use, wherever practicable, if contaminated; and protected from further contamination from any source. A balanced approach to all activities is to be aimed at within the catchment to achieve a sustainable use of the river environment.

10.3 Research Recommendations

The original research aims of this project were to investigate quantitatively the dispersal, storage and remobilisation of heavy metals in the River Aire. These have all been achieved. However, the project has suggested topics which require further work. Research has focused on an urban and industrial river since limited studies exist in the UK, as compared to rivers draining metal mining catchments. However, a small lead mine, the only ore body on the River Aire occurs upstream at Cononley, near Skipton. River sediment downstream of Cononley has been shown to contain elevated concentrations of heavy metals (Hill et al., 1997). Further research is needed to investigate the impacts of the mine on water and sediment quality and how far these effects continue downstream. In particular, information will be required on the storage and speciation of heavy metals in floodplain soils to assess their potential for being secondary non-point sources of heavy metal contaminants. In the light of recent political commitment to reduce inputs of pollutants such as heavy metals to the North Sea, the potential for these metals to be transported further downstream will be an important parameter in estimating fluxes of metals to the North Sea from the River Aire. Further research on the partitioning of metals on sediments could be studied to establish the speciation under the influence of a lead mine, as compared to that observed downstream, where the river is affected by urban and industrial wastes. This offers the potential to observe speciation changes downstream through different influences on river water and sediment quality.

Using macroinvertebrates as an indicator of river metal pollution lies outside the scope of the present study. Further investigation of the macroinvertebrate community in the river will facilitate sediment data obtained to date. It may also assist in pin-pointing sources of metals to the channel through the observed effect on species. Species being either sensitive or tolerant to metal pollution (Mance, 1987).

In terms of the metal budgets, the results obtained suggest further improvement could be made by measuring those parameters only estimated in the budget. For example, measuring rates of bedload transport, floodplain deposition and streambank erosion. Once all these terms are defined it may be possible to develop a method which enables the model to be easily transported and applied to other river catchments, with a much more limited amount of sampling.

As discussed in Chapter 7, tributaries of the River Ouse discharge sediments and contaminants to the Humber Estuary. From the results, the role of hydrological processes was identified as being highly important, but the determination of the exact mechanisms lies outside the scope of the present study. Further investigation is warranted on suspended sediment in the Ouse tributaries specifically to assess the influence of hydrological process on speciation, so differences can be established between rural, urban and industrial catchments, with and without mining activity.

Lead isotopes can be used to provenance sources of lead and distinguish types of lead in river sediment from different time periods, as each type has its own distinct isotopic signature. By examining the lead isotopic compositions of river sediment it is possible to quantify the lead input into these sediments from natural and anthropogenic sources over time. Initial lead isotope work by Barreiro and Grant (1996) showed that there are at least 3 sources of lead in the Humber Estuary;

natural (background), Yorkshire Dales ores and industrial. Samples from the River Aire have been found to contain a high proportion of non-radiogenic 'industrial' lead. Samples from the dated copper works core are currently undergoing analysis for lead isotopes. These should give better understanding on the industrial or atmospheric sediment signatures, which at present are relatively poorly characterised. This combined with information on mineralogical and geochemical properties on the speciation of lead in river alluvium will provide information on heavy metal contaminant and sediment sources and their fate and bioavailability in the River Aire. This in turn will aid in future predictive modelling of remobilisation of pollutants stored in sediment reservoirs and in developing long-term river basin sediment and metal budgets. As the present day river water quality is still influenced by the changing patterns of industry, urbanisation and agriculture over the past two centuries, the present state of river water quality must be considered within an historical context of environmental change.

Further research is required with regard to possible climate change and its effects on river environments. Despite great uncertainty over how the climate may change in the future, several papers demonstrate a move towards drier summers and wetter winters, with an associated increase in hydrological extremes (Knox, 1993; Newson and Lewin, 1991; Rumsby and Macklin, 1994). Several key questions need to be addressed by future research. Firstly, what are the impacts of summer dry periods on heavy metals? It is during these times that concentrations of pollutants are at their highest because of diminished dilution of effluents. Secondly, what are the effects of larger and more frequent floods on river environments? It can be anticipated that more heavy metals will be eroded from the river channel and floodplains and transported further downstream, where they may have adverse effects on water and sediment quality.

Detailed studies should be considered within a multi-disciplinary framework: this study has demonstrated that a wide variety of chemical and physical processes need to be analysed, to understand the fate of sediment-bound heavy metals in a fluvial system.

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APPENDIX I

GRAIN-SIZE EFFECTS & BACKGROUND CONCENTRATIONS

Grain-size effects

From the examples of contemporary river sediment shown below, it is apparent that little difference occurs between the < 63 μm and the < 2 mm fractions in terms of chemical speciation.

Contemporary river sediment, 0.1 km downstream

< 63 μm	Cd	Cu	Pb	Zn	< 2 mm	Cd	Cu	Pb	Zn
A	36	1	11	0	**A**	24	1	7	0
B	36	3	8	14	**B**	40	7	8	16
C	5	7	72	76	**C**	8	12	74	56
D	0	79	5	4	**D**	5	64	8	7
E	23	10	4	6	**E**	23	16	3	21

Contemporary river sediment, 0.25 km downstream

< 63 μm	Cd	Cu	Pb	Zn	< 2 mm	Cd	Cu	Pb	Zn
A	39	2	20	1	**A**	34	2	9	1
B	43	5	20	14	**B**	40	7	12	21
C	5	40	50	75	**C**	9	18	72	50
D	4	36	3	1	**D**	3	55	7	6
E	9	17	7	9	**E**	14	18	0	22

A = exchangeable metal ions

B = surface oxide and carbonate metal ions

C = metals bound to Fe and Mn oxides

D = organic metal ions

E = residual metal ions

Background concentrations

Average Shale Concentrations (ppm)

Arsenic	13
Cadmium	0.3
Chromium	90
Copper	45
Lead	20
Mercury	0.2
Zinc	95

(after Förstner and Wittmann, 1981; Salomons and Förstner, 1984)

APPENDIX II

RESULTS DATA, CONTEMPORARY RIVER SEDIMENT

Table 1 - Total metal concentration, contemporary within channel sediment, north of the river

km downstream	Cadmium (mg/kg)	Copper (mg/kg)	Lead (mg/kg)	Zinc (mg/kg)	pH	% Loss on ignition
0.0	1.5	45.0	49.0	242.0	6.4	1.9
0.5	2.5	155.0	271.0	1079.0	5.8	1.3
1.0	2.5	97.0	133.0	421.0	6.5	6.0
2.0	3.0	49.0	75.0	152.0	4.7	3.0
2.5	2.5	21.0	19.0	58.0	5.6	4.6
2.8	2.0	36.0	35.0	121.0	5.5	7.0
3.0	3.4	54.0	102.0	211.0	6.6	1.8
3.4	4.0	42.0	64.0	130.0	6.7	1.5
3.8	6.2	80.0	162.0	254.0	6.9	6.6
4.1	3.9	37.0	58.0	145.0	6.9	2.9
4.4	3.6	50.0	80.0	172.0	6.6	11.8
4.7	5.0	45.0	68.0	148.0	6.6	1.8
5.1	3.8	63.0	124.0	206.0	6.2	2.1
5.5	4.3	75.0	85.0	244.0	6.8	7.7
5.7	4.4	45.0	61.0	132.0	7.0	2.4
6.0	4.1	62.0	88.0	190.0	6.9	5.6
6.3	4.7	85.0	63.0	142.0	6.8	2.9
6.7	3.7	89.0	54.0	137.0	6.9	0.8
6.9	3.3	104.0	54.0	163.0	6.7	2.1
8.0	3.9	51.0	64.0	168.0	6.7	8.5
8.1	3.2	41.0	53.0	135.0	6.8	2.0
8.3	4.9	63.0	90.0	218.0	6.6	14.0
8.5	5.9	55.0	55.0	151.0	6.7	5.0
8.7	4.7	73.0	73.0	189.0	6.6	7.8
8.8	3.7	70.0	87.0	226.0	6.7	6.3
9.0	7.2	117.0	180.0	338.0	6.6	10.6
10.0	2.5	45.0	74.0	174.0	6.1	5.7
10.5	3.0	107.0	223.0	330.0	6.5	7.6
11.5	0.5	47.0	36.0	95.0	5.8	1.6
12.0	2.5	56.0	89.0	183.0	5.2	0.9
12.5	4.5	149.0	331.0	288.0	5.9	3.4
16.5	3.5	63.0	134.0	211.0	6.8	3.5
17.0	3.5	70.0	114.0	223.0	6.5	10.0
17.5	4.0	88.0	141.0	396.0	6.4	3.5
18.0	4.5	107.0	211.0	354.0	6.9	10.9
19.0	4.5	134.0	71.0	144.0	6.8	4.2
19.5	2.5	43.0	203.0	388.0	6.7	2.6
22.0	2.0	34.0	42.0	109.0	5.0	15.5
23.0	3.5	201.0	234.0	417.0	5.3	3.1
23.5	2.5	61.0	117.0	207.0	7.2	7.2
24.0	2.0	38.0	36.0	116.0	7.9	14.2
25.5	4.0	110.0	178.0	412.0	4.9	7.8
26.0	1.5	27.0	30.0	84.0	6.9	7.5

Table 2 - Total metal concentration, contemporary within channel sediment, south of the river

km downstream	Cadmium (mg/kg)	Copper (mg/kg)	Lead (mg/kg)	Zinc (mg/kg)	pH	% Loss on ignition
0.0	1.5	37.0	58.0	140.0	6.6	4.7
0.5	3.0	94.0	208.0	705.0	6.6	1.5
1.0	3.5	49.0	28.0	109.0	6.9	5.3
1.5	2.5	88.0	100.0	314.0	6.9	3.6
2.5	2.5	71.0	78.0	154.0	6.5	7.7
3.4	15.0	140.0	290.0	463.0	6.0	27.6
3.8	4.0	71.0	124.0	280.0	7.2	13.4
5.1	6.8	57.0	136.0	211.0	6.5	4.1
5.5	3.1	51.0	61.0	146.0	6.6	2.8
5.7	4.0	84.0	65.0	174.0	6.4	4.0
6.0	4.2	99.0	97.0	204.0	6.9	5.0
6.9	1.9	71.0	137.0	299.0	6.8	8.1
7.7	4.7	47.0	46.0	122.0	6.8	1.5
8.0	5.1	66.0	82.0	191.0	6.9	4.4
8.1	4.2	40.0	72.0	154.0	6.9	3.0
8.3	4.9	57.0	59.0	152.0	6.5	6.2
8.5	7.6	104.0	180.0	403.0	7.0	19.6
8.7	4.8	51.0	117.0	248.0	6.7	10.0
9.0	6.5	107.0	187.0	423.0	7.0	14.1
9.2	4.0	50.0	91.0	183.0	6.6	3.7
13.0	4.0	118.0	143.0	287.0	5.5	9.8
14.0	2.0	56.0	34.0	148.0	6.3	1.2
14.5	2.5	78.0	112.0	280.0	5.9	12.7
16.0	3.0	48.0	68.0	132.0	6.3	2.0
17.0	3.0	60.0	111.0	229.0	6.8	9.6
19.0	4.0	63.0	123.0	202.0	6.8	5.0
19.5	4.5	117.0	204.0	323.0	6.9	10.7
20.0	2.5	68.0	97.0	201.0	6.8	6.0
20.5	2.0	49.0	101.0	273.0	7.4	10.3

Table 3 - Total metal concentration, contemporary river bed sediment

km downstream	Cadmium (mg/kg)	Copper (mg/kg)	Lead (mg/kg)	Zinc (mg/kg)	pH
0.0	14.0	162.0	267.0	1038.0	7.4
1.0	9.5	95.0	180.0	422.0	7.4
2.0	9.5	89.0	261.0	316.0	7.4
3.0	5.0	52.0	181.0	218.0	7.2
4.0	4.0	35.0	128.0	154.0	7.3
6.0	5.0	46.0	140.0	178.0	7.3
8.0	5.0	54.0	136.0	120.0	7.9
9.0	6.0	48.0	118.0	222.0	7.2
10.0	4.5	35.0	110.0	166.0	7.4
11.0	5.0	39.0	91.0	170.0	7.6
12.0	4.5	68.0	96.0	169.0	7.6
13.0	7.0	121.0	159.0	227.0	7.5
14.0	5.0	53.0	117.0	213.0	7.3
15.0	11.5	188.0	485.0	695.0	7.0
16.0	6.0	46.0	138.0	210.0	7.8
17.0	6.0	52.0	154.0	228.0	7.3
18.0	4.5	40.0	118.0	165.0	6.9
19.0	5.5	52.0	146.0	208.0	7.3
20.0	6.0	68.0	192.0	274.0	7.2
23.0	3.5	34.0	78.0	79.0	7.3
24.0	4.0	72.0	71.0	143.0	7.2
25.0	7.5	139.0	181.0	356.0	7.6
26.0	5.0	66.0	101.0	214.0	6.9

Table 4 - Correlation coefficients between contemporary river sediment, pH and % loss on ignition

Contemporary within channel sediment, north of the river

	km downstream 0 - 12.0 & 18.0 - 22.0 km	km downstream 12.5 - 17.5 & 23.0 - 26.0 km
	pH	pH
Cadmium	0.562	-0.698
Copper	0.247	-0.783
Lead	0.131	-0.698
Zinc	-0.013	-0.837

	km downstream 9.0 - 19.5 km
	pH
% LOI	0.554

Contemporary within channel sediment, south of the river

	km downstream 5.7 - 9.2 km	km downstream 0 - 5.5 & 13.0 - 20.5 km
	pH	pH
Cadmium	0.424	-0.039
Copper	0.370	-0.329
Lead	0.586	-0.041
Zinc	0.555	-0.139

Contemporary river bed sediment

	km downstream 0 - 6.0 & 17.0 - 26.0 km	km downstream 8.0 - 16.0 km
	pH	pH
Cadmium	0.489	-0.603
Copper	0.542	-0.537
Lead	0.500	-0.586
Zinc	0.372	-0.707

Correlated at 95 % confidence level

Table 5 - % of samples with metal concentrations higher than UK and Dutch policy guidelines

UK policy, ICRCL

	Contemporary river sediment		
	Within channel sediment		River bed sediment
Trigger concentration	North	South	
Cadmium 3 mg/kg	70%	69%	100%
Cadmium 15 mg/kg	0	3%	0
Copper 130 mg/kg	9%	3%	13%
Lead 500 mg/kg	0	0	0
Zinc 300 mg/kg	21%	21%	22%

Dutch policy

	Contemporary river sediment		
	Within channel sediment		River bed sediment
A-values	North	South	
Cadmium 0.8 mg/kg	98%	100%	100%
Copper 36 mg/kg	91%	100%	100%
Lead 85 mg/kg	47%	62%	69%
Zinc 140 mg/kg	77%	80%	91%

	Contemporary river sediment		
	Within channel sediment		River bed sediment
C-values	North	South	
Cadmium 12 mg/kg	0	3%	4%
Copper 190 mg/kg	2%	0	0
Zinc 720 mg/kg	2%	0	4%

Table 6 - Chemical speciation, contemporary within channel sediment

Date sampled Distance downstream	Oct-94 0.1 km	Oct-94 0.25 km	Oct-94 1.0 km	Feb-95 0.1 km	Feb-95 0.25 km
Cadmium % in each fraction	%	%	%	%	%
Exchangeable	5.0	22.0	28.0	39.0	36.0
Surface oxide & carbonate	35.0	31.0	35.0	43.0	36.0
Fe/Mn oxide & hydroxide	6.0	4.0	24.0	5.0	5.0
Organic	15.0	22.0	13.0	3.0	neg
Residual	39.0	21.0	neg	10.0	23.0
Total (mg/kg)	12.3	9.6	6.8	8.2	8.8
Copper % in each fraction	%	%	%	%	%
Exchangeable	5.0	6.0	3.0	2.0	2.0
Surface oxide & carbonate	9.0	13.0	22.0	5.0	3.0
Fe/Mn oxide & hydroxide	12.0	9.0	28.0	40.0	7.0
Organic	40.0	23.0	47.0	36.0	79.0
Residual	34.0	49.0	neg	17.0	9.0
Total (mg/kg)	87.5	53.2	63.6	64.5	148.5
Lead % in each fraction	%	%	%	%	%
Exchangeable	19.0	51.0	30.0	20.0	11.0
Surface oxide & carbonate	20.0	11.0	16.0	20.0	8.0
Fe/Mn oxide & hydroxide	43.0	23.0	48.0	50.0	71.0
Organic	9.0	3.0	6.0	4.0	5.0
Residual	9.0	12.0	neg	6.0	5.0
Total (mg/kg)	105.0	55.0	95.4	84.9	209.3
Zinc % in each fraction	%	%	%	%	%
Exchangeable	3.0	5.0	3.0	1.0	neg
Surface oxide & carbonate	25.0	6.0	27.0	14.0	14.0
Fe/Mn oxide & hydroxide	61.0	55.0	55.0	75.0	76.0
Organic	8.0	14.0	8.0	1.0	4.0
Residual	3.0	20.0	7.0	9.0	6.0
Total (mg/kg)	285.7	108.0	202.7	438.5	1046.1
pH	5.8	5.9	6.0	6.4	6.3
Loss on ignition (%)	2.6	4.0	3.8	1.2	2.9

APPENDIX III

RESULTS DATA, SUSPENDED SEDIMENT

Table 1 - Raw data, Thwaite Mills

date sampled	time sampled	discharge (m^3/s)	filter & sediment (g)	filter (g)	sediment (g)	bottle & sample	bottle	sample volume	concentration (mg/l)
10/02/96	09:30	14.989	0.3351	0.3286	0.0065	495	176	319	20.4
10/02/96	11:30	17.449	0.3481	0.3375	0.0106	453	177	276	38.4
10/02/96	13:30	19.838	0.3455	0.3323	0.0132	457	173	284	46.5
10/02/96	15:30	22.295	0.3500	0.3279	0.0221	445	177	268	82.5
10/02/96	17:30	24.719	0.3526	0.3275	0.0251	468	176	292	86.0
10/02/96	21:30	32.077	0.3909	0.3378	0.0531	441	171	270	196.7
11/02/96	00:30	38.274	0.4281	0.3363	0.0918	460	176	284	323.2
11/02/96	03:30	42.821	0.4289	0.3311	0.0978	447	177	270	362.2
11/02/96	06:30	45.213	0.4544	0.3285	0.1259	458	177	281	448.0
11/02/96	09:30	47.074	0.4431	0.3341	0.1090	479	201	278	392.1
11/02/96	12:30	47.768	0.4395	0.3375	0.1020	452	176	276	369.6
11/02/96	15:30	45.836	0.4211	0.3337	0.0874	474	176	298	293.3
11/02/96	18:30	43.275	0.4006	0.3312	0.0694	496	176	320	216.9
11/02/96	21:30	40.382	0.3775	0.3290	0.0485	517	192	325	149.2
12/02/96	00:30	37.090	0.3661	0.3328	0.0333	485	176	309	107.8
12/02/96	04:30	51.019	0.3716	0.3296	0.0420	499	176	323	130.0
12/02/96	08:30	70.015	0.4241	0.3281	0.0960	492	176	316	303.8
12/02/96	12:30	64.260	0.4191	0.3308	0.0883	480	176	304	290.5
12/02/96	16:30	72.015	0.3954	0.3360	0.0594	424	177	247	240.5
12/02/96	20:30	63.711	0.3809	0.3318	0.0491	441	171	270	181.9
13/02/96	00:30	56.973	0.3660	0.3309	0.0351	474	180	294	119.4
13/02/96	04:30	52.204	0.3588	0.3288	0.0300	459	163	296	101.4
13/02/96	08:30	47.363	0.3595	0.3318	0.0277	503	187	316	87.7

Table 2 - Day, time, discharge, sediment & total metal concentration, Thwaite Mills

day	time	discharge (m^3/s)	sediment (g)	cadmium (mg/kg)	copper (mg/kg)	lead (mg/kg)	zinc (mg/kg)
10/02/96	09:30	14.989	0.0065	1383.1	804.7	5869.3	8269.0
10/02/96	11:30	17.449	0.0106	290.5	567.9	4701.9	3511.4
10/02/96	13:30	19.838	0.0132	284.1	605.4	2809.5	3761.4
10/02/96	15:30	22.295	0.0221	222.1	422.5	2825.4	2457.4
10/02/96	17:30	24.719	0.0251	197.3	408.7	1900.4	1782.9
10/02/96	21:30	32.077	0.0531	110.0	188.9	979.8	962.5
11/02/96	00:30	38.274	0.0918	99.4	370.2	1026.2	741.9
11/02/96	03:30	42.821	0.0978	34.2	201.8	571.3	454.0
11/02/96	06:30	45.213	0.1259	16.8	198.7	356.2	423.2
11/02/96	09:30	47.074	0.1090	57.3	224.4	711.5	547.3
11/02/96	12:30	47.768	0.1020	48.1	163.4	607.0	528.7
11/02/96	15:30	45.836	0.0874	39.6	240.1	590.4	609.5
11/02/96	18:30	43.275	0.0694	58.3	219.8	691.4	649.8
11/02/96	21:30	40.382	0.0485	60.7	172.8	783.6	932.9
12/02/96	00:30	37.090	0.0333	102.6	228.8	1061.0	1538.4
12/02/96	04:30	51.019	0.0420	80.8	203.1	992.4	1317.9
12/02/96	08:30	70.015	0.0960	51.6	146.3	698.2	433.8
12/02/96	12:30	64.260	0.0883	45.6	157.1	659.0	441.1
12/02/96	16:30	72.015	0.0594	66.5	166.1	735.4	905.8
12/02/96	20:30	63.711	0.0491	69.9	210.8	771.8	1034.1
13/02/96	00:30	56.973	0.0351	146.8	274.3	1382.9	1652.5
13/02/96	04:30	52.204	0.0300	123.7	227.1	1268.0	1721.0
13/02/96	08:30	47.363	0.0277	139.6	221.6	1919.9	1894.3

Table 3 - Dissolved metal concentration & pH, Thwaite Mills

day	time	pH	cadmium ug/l	copper ug/l	lead ug/l	zinc ug/l
10/02/96	09:30	8.06	0.05	9.0	0.6	39.0
10/02/96	11:30	8.04	0.20	8.0	0.7	39.0
10/02/96	13:30	7.92	0.10	7.0	1.2	34.0
10/02/96	15:30	7.88	0.20	6.0	0.7	37.0
10/02/96	17:30	7.88	0.20	6.0	0.8	35.0
10/02/96	21:30	7.86	0.05	3.0	0.5	27.0
11/02/96	00:30	7.79	0.05	3.0	0.5	17.0
11/02/96	03:30	7.67	0.05	6.0	1.4	16.0
11/02/96	06:30	7.61	0.05	3.0	1.0	12.0
11/02/96	09:30	7.60	0.05	3.0	0.8	13.0
11/02/96	12:30	7.60	0.10	3.0	1.1	15.0
11/02/96	15:30	7.61	0.05	3.0	0.4	13.0
11/02/96	18:30	7.60	0.05	3.0	1.0	12.0
11/02/96	21:30	7.59	0.05	6.0	1.0	20.0
12/02/96	00:30	7.61	0.05	3.0	0.7	14.0
12/02/96	04:30	7.65	0.05	3.0	0.3	19.0
12/02/96	08:30	7.59	0.50	34.0	44.5	148.0
12/02/96	12:30	7.60	0.05	6.0	1.3	17.0
12/02/96	16:30	7.60	0.10	5.0	0.7	17.0
12/02/96	20:30	7.59	0.05	3.0	0.8	18.0
13/02/96	00:30	7.61	0.10	3.0	1.2	16.0
13/02/96	04:30	7.60	0.05	3.0	0.7	27.0
13/02/96	08:30	7.60	0.05	3.0	0.7	14.0

Table 4 - Chemical speciation, Thwaite Mills (% in each fraction)

day	10/02/96						11/02/96								12/02/96						13/02/96		
time	09:30 %	11:30 %	13:30 %	15:30 %	17:30 %	21:30 %	00:30 %	03:30 %	06:30 %	09:30 %	12:30 %	15:30 %	18:30 %	21:30 %	00:30 %	04:30 %	08:30 %	12:30 %	16:30 %	20:30 %	00:30 %	04:30 %	08:30 %
CADMIUM																							
Exchangeable	14.3	44.2	36.3	27.7	40.4	21.9	14.9	36.0	34.0	21.8	26.0	39.4	31.6	40.7	35.1	33.0	25.8	35.7	24.4	32.6	32.6	32.3	28.9
Surface oxide & carbonate	6.2	23.4	27.7	24.4	16.2	16.5	21.0	36.0	30.4	20.4	17.9	34.6	27.6	27.2	32.7	21.2	30.6	15.8	12.2	39.7	29.5	36.7	31.0
Fe/Mn oxide & hydroxide	73.4	19.5	32.0	40.7	36.3	58.2	50.4	17.8	19.0	41.7	40.7	11.6	24.7	13.5	11.7	35.4	36.4	39.7	35.5	23.3	31.1	21.6	25.9
Organic	1.7	neg	4.0	3.1	3.0	neg	4.9	4.4	7.1	9.6	3.1	8.6	11.1	5.1	8.8	4.5	3.1	3.7	7.6	4.4	2.9	4.0	3.9
Residual	4.4	12.9	neg	4.1	4.1	3.4	8.8	5.8	9.5	6.5	12.3	5.8	5.0	13.5	11.7	5.9	4.1	5.1	20.3	neg	3.9	5.4	10.3
COPPER																							
Exchangeable	13.8	5.3	8.0	6.0	3.1	8.8	4.2	4.8	3.8	4.9	1.5	3.8	4.6	9.5	7.3	13.1	6.3	6.4	8.1	7.7	15.8	10.5	26.1
Surface oxide & carbonate	18.3	19.9	15.0	18.0	17.9	20.0	12.9	16.6	11.8	12.1	16.3	11.8	12.1	15.3	17.8	20.6	18.3	15.0	19.4	15.5	14.1	15.3	16.9
Fe/Mn oxide & hydroxide	26.8	49.9	32.5	21.4	23.4	23.9	18.8	22.3	19.2	15.6	20.4	14.3	19.7	26.3	23.6	18.8	25.6	20.2	18.2	19.3	18.7	29.4	22.8
Organic	25.8	14.9	16.9	22.5	26.3	25.4	42.9	28.9	37.2	45.4	37.8	47.2	37.4	25.1	35.6	19.4	25.6	36.8	32.0	36.2	26.5	15.4	14.7
Residual	15.3	10.0	27.6	32.1	29.3	21.9	21.2	27.4	28.0	22.0	24.0	22.9	26.2	23.8	15.7	28.1	24.2	21.6	22.3	21.3	24.9	29.4	19.5
LEAD																							
Exchangeable	15.5	17.2	14.9	11.4	23.0	13.1	4.3	8.3	14.5	12.2	11.5	13.5	11.8	16.6	15.2	21.1	13.7	9.8	12.6	15.2	11.9	14.4	10.0
Surface oxide & carbonate	11.8	19.3	18.1	14.0	19.8	7.8	16.0	16.9	14.6	12.1	10.3	18.6	19.2	13.9	15.6	15.9	14.2	13.3	15.9	17.5	10.9	20.2	10.4
Fe/Mn oxide & hydroxide	33.0	23.3	29.7	24.0	23.1	34.2	32.4	34.7	37.0	36.9	33.7	22.5	25.4	26.8	20.4	33.1	30.7	37.1	25.7	33.3	39.1	20.0	24.1
Organic	16.1	20.5	14.1	28.8	6.8	29.1	19.1	18.3	10.7	21.9	24.2	21.8	18.2	19.0	23.3	16.9	33.6	21.9	13.7	18.2	15.5	25.2	26.5
Residual	23.6	19.7	23.2	21.8	27.3	15.8	28.2	21.8	23.2	16.9	20.3	23.6	25.4	23.7	25.5	13.0	7.8	17.9	32.1	15.8	22.6	20.5	29.0
ZINC																							
Exchangeable	15.6	12.7		14.3	14.3	16.7			20.4	18.8	19.4	20.1	29.8	10.2	15.8	21.0			17.1	18.3	19.3	13.3	15.8
Surface oxide & carbonate	4.4	6.9		4.0	5.7	7.7			10.8	11.0	9.7	9.4	8.8	6.0	5.9	6.0			6.4	5.0	4.5	4.4	4.0
Fe/Mn oxide & hydroxide	33.0	31.4		35.4	29.4	26.5			25.6	24.4	36.0	29.7	12.2	34.7	27.5	29.3			31.6	30.8	30.0	31.7	31.2
Organic	17.6	27.1		24.4	27.3	21.0			26.7	25.8	22.2	23.1	28.8	23.9	25.1	21.0			24.3	28.6	23.8	24.4	24.2
Residual	29.4	21.9		21.9	23.3	28.1			16.5	20.0	12.7	17.7	20.4	25.2	25.7	22.7			20.6	17.3	22.4	26.2	24.8

Table 5 - Raw data, Ouse tributaries

site	river	date sampled	time sampled	sample volume (ml)	filter (g)	filter & sample	sample (g)	concentration (mg/l)
Allerton Bywater	Aire	05/11/96	13:05	1014	0.3460	0.3977	0.0517	51
Beal	Aire	05/11/96	10:05	1014	0.3457	0.3699	0.0242	24
Beal	Aire	05/11/96	18:25	975	0.3459	0.4182	0.0723	74
Beal	Aire	06/11/96	10:45	330	0.3396	0.4137	0.0741	224
Beal	Aire	07/11/96	10:50	636	0.3396	0.4256	0.0860	135
Methley Bridge	Calder	05/11/96	12:35	980	0.3454	0.4101	0.0647	66
Methley Bridge	Calder	06/11/96	11:30	290	0.3389	0.5007	0.1618	558
Skip Bridge	Nidd	05/11/96	11:45	957	0.3489	0.3881	0.0392	41
Acaster	Ouse	28/10/96	10:10	977	0.3450	0.3848	0.0398	41
Acaster	Ouse	05/11/96	11:17	1027	0.3451	0.3632	0.0181	18
Acaster	Ouse	06/11/96	12:20	1009	0.3388	0.3730	0.0342	34
Acaster	Ouse	07/11/96	11:45	620	0.3399	0.4241	0.0842	136
Clifton	Ouse	27/10/96	11:30	1003	0.3443	0.3972	0.0529	53
Clifton	Ouse	28/10/96	11:00	1002	0.3469	0.4190	0.0721	72
Clifton	Ouse	05/11/96	12:30	1002	0.3463	0.3715	0.0252	25
Clifton	Ouse	07/11/96	11:25	486	0.3388	0.4241	0.0853	176
Catterick	Swale	05/11/96	09:25	1039	0.3487	0.3747	0.0260	25
Thornton Manor	Swale	30/09/96	10:50	1016	0.3450	0.4369	0.0919	90
Thornton Manor	Swale	28/10/96	10:50	997	0.3485	0.4448	0.0963	97
Thornton Manor	Swale	05/11/96	10:30	1001	0.3488	0.3856	0.0368	37
Thornton Manor	Swale	07/11/96	10:45	821	0.3367	0.3956	0.0589	72
Boroughbridge	Ure	28/10/96	09:40	994	0.3460	0.3824	0.0364	37
Boroughbridge	Ure	05/11/96	11:10	976	0.3459	0.3889	0.0430	44
Tadcaster	Wharfe	30/09/96	09:00	1001	0.3459	0.3891	0.0432	43
Tadcaster	Wharfe	05/11/96	19:10	990	0.3474	0.4009	0.0535	54

Table 6 - Site, river & total metal concentration, Ouse tributaries

site	river	date sampled	time sampled	arsenic (mg/kg)	cadmium (mg/kg)	chromium (mg/kg)	copper (mg/kg)	lead (mg/kg)	zinc (mg/kg)
Allerton Bywater	Aire	05/11/96	13:05	122.14	13.10	141.47	1379.90	107.38	8383.77
Beal	Aire	05/11/96	10:05	239.57	10.97	194.55	1586.24	128.41	11602.09
Beal	Aire	05/11/96	18:25	27.75	10.43	188.08	1161.44	87.66	2988.63
Beal	Aire	06/11/96	10:45	9.86	9.23	177.29	388.31	132.75	4057.96
Beal	Aire	07/11/96	10:50	63.11	10.23	114.48	1083.42	175.34	2021.16
Methley Bridge	Calder	05/11/96	12:35	112.80	9.74	321.34	1023.25	163.12	24.73
Methley Bridge	Calder	06/11/96	11:30	22.05	6.38	306.99	553.83	172.39	142.69
Skip Bridge	Nidd	05/11/96	11:45	145.68	4.79	36.89	1673.44	400.94	17267.79
Acaster	Ouse	28/10/96	10:10	186.88	5.30	24.26	72.01	467.49	7451.23
Acaster	Ouse	05/11/96	11:17	188.26	29.62	8.81	2561.31	280.62	27920.00
Acaster	Ouse	06/11/96	12:20	40.30	17.58	37.26	2427.53	329.12	14659.06
Acaster	Ouse	07/11/96	11:45	17.43	10.12	10.71	18.00	262.30	80.89
Clifton	Ouse	27/10/96	11:30	143.90	4.64	53.29	6171.01	425.40	17026.78
Clifton	Ouse	28/10/96	11:00	75.03	4.00	18.67	1943.41	409.71	17653.72
Clifton	Ouse	05/11/96	12:30	363.92	7.61	34.39	2399.49	453.87	11854.18
Clifton	Ouse	07/11/96	11:25	65.24	12.52	9.65	324.50	760.61	755.27
Catterick	Swale	05/11/96	09:25	347.48	9.36	46.36	1819.62	518.65	18148.90
Thornton Manor	Swale	30/09/96	10:50	24.12	6.81	11.16	136.31	675.42	1225.38
Thornton Manor	Swale	28/10/96	10:50	89.16	9.02	16.98	1114.84	875.45	2292.54
Thornton Manor	Swale	05/11/96	10:30	81.52	7.56	3.07	1743.75	687.05	5631.34
Thornton Manor	Swale	07/11/96	10:45	110.12	18.04	9.54	1126.47	834.75	178.15
Boroughbridge	Ure	28/10/96	09:40	179.64	7.28	2.63	325.72	154.07	6694.61
Boroughbridge	Ure	05/11/96	11:10	124.99	3.89	10.07	94.66	77.79	5696.58
Tadcaster	Wharfe	30/09/96	09:00	280.46	5.52	5.17	200.21	579.31	2546.25
Tadcaster	Wharfe	05/11/96	19:10	19.85	11.84	70.85	3917.59	323.16	11766.79

Table 7 - Chemical speciation, Ouse tributaries (% in each fraction)

river	AIRE	AIRE				CALDER		NIDD	OUSE				OUSE				SWALE	SWALE				URE		WHARFE	
site	A.B.	BEAL	BEAL	BEAL	BEAL	M.B.	M.B.	S.B.	ACASTER	ACASTER	ACASTER	ACASTER	CLIFTON	CLIFTON	CLIFTON	CLIFTON	C.K.	T.M.	T.M.	T.M.	T.M.	B.B.	B.B.	T.D.	T.D.
date	05/11/96	05/11/96	05/11/96	06/11/96	07/11/96	05/11/96	06/11/96	05/11/96	28/10/96	05/11/96	06/11/96	07/11/96	27/10/96	28/10/96	05/11/96	07/11/96	05/11/96	30/09/96	28/10/96	05/11/96	07/11/96	28/10/96	05/11/96	30/09/96	05/11/96
	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
ARSENIC																									
Exchangeable	neg	neg	neg	neg	36.5	neg	neg	neg	neg	neg	neg	69.0	neg	neg	50.0	45.2	neg	neg	neg	neg	42.7	neg	neg	neg	neg
Surface oxide & carbonate	neg	0.6	neg	neg	neg	neg	neg	8.4	neg	neg	neg	neg	6.8	4.7	1.0	neg	9.1	28.7	11.0	21.4	neg	7.8	neg	1.3	neg
Fe/Mn oxide & hydroxide	6.8	24.5	19.5	62.4	35.5	5.3	50.4	7.2	4.2	neg	78.8	31.0	neg	5.9	1.1	14.3	29.9	neg	neg	12.5	10.3	2.1	22.4	1.7	99.2
Organic	75.1	74.9	neg	37.6	neg	58.8	6.4	84.4	77.5	100.0	28.2	neg	93.2	89.4	47.9	neg	61.0	neg	89.0	66.1	neg	90.1	50.0	67.0	neg
Residual	18.1	neg	80.5	neg	28.0	35.9	43.2	neg	18.3	neg	neg	neg	neg	neg	neg	40.5	neg	71.3	neg	neg	47.0	neg	27.6	30.0	0.8
CADMIUM																									
Exchangeable	17.5	51.5	20.0	14.4	22.6	2.1	7.4	40.5	35.3	13.6	15.4	24.3	34.7	21.8	38.0	22.1	52.4	27.9	12.1	41.8	21.8	51.0	35.7	38.8	6.3
Surface oxide & carbonate	57.6	neg	53.2	60.2	52.2	61.7	50.3	neg	neg	66.0	64.8	52.0	neg	neg	neg	49.7	neg	15.9	44.4	neg	56.9	neg	neg	neg	66.9
Fe/Mn oxide & hydroxide	24.9	48.5	26.5	25.4	25.2	36.2	42.3	59.5	64.7	20.4	19.8	23.7	65.3	78.2	62.0	28.2	47.6	56.2	43.5	58.2	21.3	49.0	64.3	61.2	26.8
Organic	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg
Residual	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg
CHROMIUM																									
Exchangeable	neg	neg	neg	neg	1.9	neg	neg	neg	neg	neg	neg	13.2	neg	neg	neg	27.4	neg	neg	neg	neg	52.4	neg	neg	neg	neg
Surface oxide & carbonate	0.3	11.2	1.1	1.1	1.0	0.8	0.7	neg	9.5	neg	0.7	neg	4.1	10.0	18.8	neg	8.4	11.9	7.2	100.0	neg	100.0	21.5	63.2	neg
Fe/Mn oxide & hydroxide	42.7	62.2	40.5	46.2	42.7	43.1	32.2	45.8	neg	neg	neg	12.3	26.7	neg	33.2	8.3	65.6	18.9	7.4	neg	neg	neg	neg	neg	12.4
Organic	30.4	17.4	36.6	36.6	34.6	38.8	44.5	1.2	neg	100.0	34.8	48.3	16.9	neg	neg	35.9	neg	neg	neg	neg	6.1	neg	neg	neg	17.9
Residual	26.6	9.2	21.8	16.1	19.8	17.3	22.6	53.0	90.5	neg	64.5	26.2	52.3	90.0	48.0	28.4	26.0	69.2	85.4	neg	41.5	neg	78.5	36.8	69.7
COPPER																									
Exchangeable	0.6	0.2	0.7	0.4	neg	neg	0.1	neg	13.4	1.0	0.4	neg	neg	0.1	neg	neg	0.5	1.7	neg	0.2	neg	neg	5.3	neg	0.2
Surface oxide & carbonate	neg	neg	neg	3.3	neg	neg	neg	neg	4.4	neg	neg	neg	neg	1.0	neg	neg	1.4	1.1	neg	neg	0.5	6.0	neg	2.4	neg
Fe/Mn oxide & hydroxide	neg	neg	neg	neg	neg	neg	neg	7.4	neg	neg	neg	neg	neg	neg	neg	neg	44.3	31.5	36.1	neg	neg	3.5	neg	neg	0.6
Organic	21.3	neg	22.1	50.9	24.8	45.1	60.0	31.7	82.2	neg	12.9	100.0	44.4	0.2	neg	neg	42.1	65.7	29.0	51.8	7.8	69.0	neg	97.6	13.0
Residual	78.1	99.8	77.2	45.4	75.2	54.9	39.9	60.9	neg	99.0	86.7	neg	55.6	98.7	100.0	100.0	11.7	neg	34.9	48.0	91.7	21.5	94.7	neg	86.2
LEAD																									
Exchangeable	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	1.6
Surface oxide & carbonate	12.2	68.9	10.3	13.7	18.3	neg	8.3	20.7	31.1	31.5	35.7	40.9	19.6	12.0	47.0	32.7	46.6	19.3	19.8	37.0	42.3	26.6	46.9	23.3	24.7
Fe/Mn oxide & hydroxide	87.8	31.1	73.9	73.0	69.5	91.4	63.9	75.4	66.9	68.5	59.1	53.9	80.4	82.8	53.0	59.0	53.4	78.3	75.8	58.0	50.6	73.4	53.1	76.7	65.3
Organic	neg	neg	15.8	13.3	12.2	8.6	14.2	3.9	2.0	neg	5.2	5.2	neg	5.2	neg	8.3	neg	2.4	4.4	5.0	7.1	neg	neg	neg	8.4
Residual	neg	neg	neg	neg	neg	neg	13.6	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg
ZINC																									
Exchangeable	0.5	0.7	1.7	1.1	0.6	neg	6.0	neg	0.3	0.3	0.2	20.7	0.1	0.1	0.3	3.2	1.0	3.4	2.0	0.6	22.2	0.9	0.5	2.0	0.3
Surface oxide & carbonate	1.1	1.3	4.7	2.5	6.1	100.0	94.0	0.4	neg	neg	0.6	79.3	0.5	0.1	0.2	13.9	0.5	2.1	4.9	0.8	77.8	0.6	neg	7.2	0.8
Fe/Mn oxide & hydroxide	7.1	neg	neg	neg	neg	neg	neg	neg	8.0	13.2	neg	neg	10.6	6.6	neg	neg	neg	57.9	24.8	neg	neg	52.9	neg	79.1	13.5
Organic	neg	neg	neg	12.3	72.4	neg	neg	neg	neg	neg	neg	neg	neg	neg	neg	82.9	neg	neg	neg	neg	neg	neg	neg	neg	neg
Residual	91.3	98.0	93.6	84.1	20.9	neg	neg	99.6	91.7	86.5	99.2	neg	88.8	93.2	99.5	neg	98.5	36.6	68.3	98.6	neg	45.6	99.5	11.7	85.4

A.B. - Allerton Bywater
M.B. - Methley Bridge
S.B. - Skip Bridge
C.K. - Catterick
T.M. - Thornton Manor
B.B. - Boroughbridge
T.D. - Tadcaster

APPENDIX IV

RESULTS DATA, FLOODPLAIN SOILS & SEDIMENT CORES

Table 21 Sediment cores, chemical speciation, Knostrop, 19.0 km

Table 22 Sediment cores, chemical speciation, Copper Works, 23.0 km

Table 23 Sediment cores, chemical speciation, Swillington Bridge, 26.0 km

Table 1 - Total metal concentrations, floodplain soil, north of the river

	distance from river									
km downstream	2 m 0-20cm	2 m 20-50cm	25 m 0-20cm	25 m 20-50cm	50 m 0-20cm	50 m 20-50cm	75 m 0-20cm	75 m 20-50cm	100 m 0-20cm	100 m 20-50cm
0.0 km										
Cadmium	3.0	2.0	2.5	3.0	3.5	x	3.0	4.0	3.5	3.0
Copper	19.0	23.0	35.0	37.0	158.0	x	85.0	44.0	55.0	30.0
Lead	20.0	17.0	68.0	57.0	269.0	x	111.0	73.0	64.0	60.0
Zinc	392.0	331.0	100.0	101.0	250.0	x	138.0	121.0	126.0	102.0
pH	6.3	5.2	5.9	6.8	6.4	x	6.4	6.3	6.1	6.6
% LOI	2.6	2.0	7.1	5.6	14.3	x	7.5	6.8	9.5	6.7
1.0 km										
Cadmium	2.5	3.0	2.5	2.5	3.0	4.0	1.0	2.5	2.5	2.5
Copper	62.0	69.0	62.0	36.0	54.0	48.0	42.0	52.0	49.0	56.0
Lead	119.0	94.0	71.0	47.0	63.0	20.0	66.0	57.0	75.0	60.0
Zinc	156.0	136.0	123.0	101.0	114.0	110.0	104.0	119.0	101.0	106.0
pH	6.5	6.6	6.4	6.3	6.2	6.6	6.9	7.0	6.7	7.0
% LOI	7.7	6.7	6.8	7.6	7.7	6.3	8.9	7.1	9.4	8.3
2.5 km										
Cadmium	2.0	1.5	4.5	3.5	3.0	3.0				
Copper	32.0	28.0	78.0	44.0	113.0	92.0				
Lead	17.0	12.0	90.0	52.0	147.0	121.0				
Zinc	71.0	43.0	608.0	670.0	374.0	359.0				
pH	5.9	6.5	6.4	6.4	6.3	6.1				
% LOI	1.6	1.2	11.2	6.9	18.5	13.4				
3.0 km										
Cadmium	3.9	x	3.2	x	4.0	x				
Copper	98.0	x	112.0	x	174.0	x				
Lead	204.0	x	136.0	x	355.0	x				
Zinc	163.0	x	180.0	x	231.0	x				
pH	6.7	x	6.8	x	6.7	x				
% LOI	15.0	x	9.7	x	10.2	x				
3.4 km										
Cadmium	4.8	4.7								
Copper	72.0	82.0								
Lead	124.0	115.0								
Zinc	222.0	239.0								
pH	6.7	7.1								
% LOI	7.0	5.7								
3.8 km										
Cadmium	4.0	5.5								
Copper	61.0	66.0								
Lead	107.0	119.0								
Zinc	188.0	217.0								
pH	6.8	6.8								
% LOI	4.2	5.0								
4.4 km										
Cadmium	6.1	6.4	3.7	2.9						
Copper	70.0	71.0	61.0	82.0						
Lead	140.0	140.0	76.0	42.0						
Zinc	241.0	222.0	138.0	107.0						
pH	7.0	6.4	6.6	6.8						
% LOI	8.8	8.8	5.6	3.8						
5.5 km										
Cadmium	6.7	5.4								
Copper	97.0	116.0								
Lead	190.0	218.0								
Zinc	338.0	363.0								
pH	6.9	6.8								
% LOI	6.6	9.4								
6.0 km										
Cadmium	5.6	5.4	13.8	13.7						
Copper	118.0	115.0	494.0	500.0						
Lead	185.0	142.0	196.0	201.0						
Zinc	182.0	232.0	269.0	248.0						
pH	5.8	6.5	5.4	5.3						
% LOI	13.2	11.7	x	x						
6.7 km										
Cadmium	3.7	1.0	4.9	1.4						
Copper	56.0	51.0	179.0	163.0						
Lead	46.0	73.0	212.0	143.0						
Zinc	134.0	158.0	296.0	218.0						
pH	6.2	6.3	6.3	6.6						
% LOI	1.4	3.3	9.2	7.0						

Table 1 - continued....

	distance from river									
km downstream	2 m 0-20cm	2 m 20-50cm	25 m 0-20cm	25 m 20-50cm	50 m 0-20cm	50 m 20-50cm	75 m 0-20cm	75 m 20-50cm	100 m 0-20cm	100 m 20-50cm
8.1 km										
Cadmium	5.3	6.0	5.2	4.6	5.1	5.2				
Copper	80.0	112.0	133.0	138.0	141.0	210.0				
Lead	135.0	220.0	179.0	190.0	368.0	442.0				
Zinc	269.0	343.0	423.0	293.0	344.0	422.0				
pH	6.6	6.8	6.7	6.5	6.9	7.1				
% LOI	9.2	8.2	14.3	9.6	19.0	18.4				
8.5 km										
Cadmium	4.5	1.9	2.8	2.1	2.4	2.5				
Copper	60.0	92.0	87.0	145.0	100.0	52.0				
Lead	113.0	171.0	158.0	173.0	154.0	121.0				
Zinc	202.0	258.0	163.0	177.0	153.0	131.0				
pH	6.9	6.6	6.4	6.5	6.2	6.3				
% LOI	5.3	6.0	8.8	7.1	7.0	6.8				
8.8 km										
Cadmium	5.2	5.7	6.0	x	4.6	4.4				
Copper	298.0	289.0	116.0	x	152.0	84.0				
Lead	193.0	185.0	362.0	x	382.0	369.0				
Zinc	240.0	233.0	142.0	x	226.0	153.0				
pH	6.9	6.7	6.4	x	6.7	6.9				
% LOI	12.0	8.0	9.2	x	8.8	8.1				
21.0 km										
Cadmium	2.0	x	2.0	x	3.0	x				
Copper	79.0	x	60.0	x	76.0	x				
Lead	79.0	x	62.0	x	70.0	x				
Zinc	146.0	x	124.0	x	111.0	x				
pH	4.9	x	5.5	x	5.9	x				
% LOI	12.3	x	12.9	x	17.1	x				
22.0 km										
Cadmium	2.0	2.5	3.5	3.0						
Copper	46.0	46.0	45.0	45.0						
Lead	69.0	62.0	97.0	70.0						
Zinc	105.0	108.0	98.0	102.0						
pH	5.5	4.9	6.4	4.9						
% LOI	12.6	8.3	14.3	10.7						
23.0 km										
Cadmium	3.5	4.0	2.5	2.5	1.5	x	2.0	x		
Copper	95.0	112.0	85.0	92.0	46.0	x	56.0	x		
Lead	173.0	175.0	144.0	171.0	70.0	x	88.0	x		
Zinc	286.0	174.0	163.0	176.0	105.0	x	134.0	x		
pH	6.7	7.2	5.3	7.0	6.4	x	6.6	x		
% LOI	8.9	8.7	8.8	9.0	17.1	x	14.6	x		
24.0 km										
Cadmium	1.5	1.5	2.5	2.0						
Copper	75.0	54.0	42.0	47.0						
Lead	99.0	65.0	75.0	72.0						
Zinc	94.0	98.0	101.0	117.0						
pH	5.3	5.3	6.0	6.0						
% LOI	12.2	6.2	16.4	12.1						
25.0 km										
Cadmium	2.5	2.5	2.0	3.5						
Copper	78.0	100.0	74.0	63.0						
Lead	124.0	115.0	113.0	92.0						
Zinc	131.0	159.0	99.0	117.0						
pH	5.9	6.0	5.8	5.3						
% LOI	11.8	9.3	23.7	13.3						
26.0 km										
Cadmium	2.0	2.0	1.5	1.5						
Copper	81.0	65.0	41.0	43.0						
Lead	103.0	85.0	53.0	55.0						
Zinc	112.0	121.0	89.0	95.0						
pH	6.2	5.7	6.2	4.9						
% LOI	11.8	8.1	10.6	9.8						

Table 2 - Total metal concentration, floodplain soil, south of the river

	distance from river							
km downstream	2 m 0-20cm	2 m 20-50cm	25 m 0-20cm	25 m 20-50cm	50 m 0-20cm	50 m 20-50cm	75 m 0-20cm	75 m 20-50cm
0.5 km								
Cadmium	2.5	2.5	3.0	2.5				
Copper	34.0	32.0	52.0	34.0				
Lead	55.0	50.0	89.0	43.0				
Zinc	135.0	104.0	136.0	113.0				
pH	6.0	5.2	7.0	6.6				
% LOI	7.0	5.5	7.1	5.8				
1.0 km								
Cadmium	4.0	3.0	3.0	3.5	2.5	2.5	2.5	2.5
Copper	106.0	75.0	62.0	44.0	102.0	56.0	118.0	42.0
Lead	106.0	66.0	95.0	51.0	71.0	39.0	76.0	52.0
Zinc	160.0	121.0	126.0	104.0	104.0	76.0	107.0	85.0
pH	6.9	6.6	7.0	6.7	6.4	6.2	6.9	6.2
% LOI	7.9	5.3	8.6	6.3	8.0	4.3	6.6	5.6
5.1 km								
Cadmium	3.5	5.0	4.5	4.5	4.0	3.0		
Copper	68.0	84.0	83.0	52.0	114.0	58.0		
Lead	14.0	168.0	144.0	83.0	150.0	76.0		
Zinc	241.0	262.0	181.0	132.0	185.0	124.0		
pH	6.8	6.8	6.6	6.7	6.8	6.5		
% LOI	10.0	9.5	10.0	7.3	11.4	7.9		
5.5 km								
Cadmium	4.0	3.8	3.7	3.8				
Copper	83.0	50.0	151.0	82.0				
Lead	96.0	58.0	125.0	55.0				
Zinc	129.0	115.0	120.0	93.0				
pH	5.7	6.8	5.9	6.0				
% LOI	8.8	5.2	9.4	6.3				
6.0 km								
Cadmium	3.8	3.5	4.8	4.7	6.3	5.8		
Copper	252.0	115.0	362.0	375.0	415.0	453.0		
Lead	119.0	93.0	137.0	125.0	136.0	97.0		
Zinc	172.0	135.0	191.0	158.0	208.0	181.0		
pH	6.4	6.3	7.1	6.9	6.6	6.6		
% LOI	7.5	5.2	7.7	7.4	6.7	5.6		
7.7 km								
Cadmium	2.7	2.2	1.4	1.7				
Copper	103.0	112.0	187.0	173.0				
Lead	150.0	151.0	144.0	148.0				
Zinc	238.0	240.0	205.0	188.0				
pH	6.5	6.4	6.5	6.5				
% LOI	6.3	6.3	8.6	7.5				
8.1 km								
Cadmium	5.3	5.1	4.1	3.8				
Copper	123.0	142.0	192.0	180.0				
Lead	130.0	200.0	198.0	197.0				
Zinc	237.0	260.0	242.0	234.0				
pH	6.3	7.2	6.5	5.7				
% LOI	5.9	7.8	8.1	6.1				
8.5 km								
Cadmium	6.3	4.3	3.1	3.4	5.1	2.2		
Copper	147.0	215.0	211.0	215.0	311.0	199.0		
Lead	176.0	240.0	231.0	221.0	276.0	219.0		
Zinc	242.0	317.0	298.0	291.0	382.0	283.0		
pH	6.9	6.4	6.7	6.6	6.8	6.7		
% LOI	8.8	10.0	8.5	10.0	10.6	10.9		
8.8 km								
Cadmium	4.7	3.7	4.8	5.0				
Copper	215.0	186.0	166.0	148.0				
Lead	200.0	140.0	164.0	129.0				
Zinc	214.0	136.0	231.0	198.0				
pH	6.6	6.2	6.3	6.5				
% LOI	9.3	6.3	7.5	6.0				
9.2 km								
Cadmium	5.3	6.9	5.7	7.5				
Copper	135.0	168.0	255.0	258.0				
Lead	171.0	200.0	270.0	268.0				
Zinc	228.0	216.0	321.0	330.0				
pH	6.9	6.5	6.8	6.7				
% LOI	8.2	7.7	7.6	11.1				

Table 3 - Pollution index, floodplain soil, north of the river

km downstream	distance from river									
	2 m 0-20cm	2 m 20-50cm	25 m 0-20cm	25 m 20-50cm	50 m 0-20cm	50 m 20-50cm	75 m 0-20cm	75 m 20-50cm	100 m 0-20cm	100 m 20-50cm
0.0 km PI value	0.403	0.335	0.289	0.304	0.850	na	0.476	0.383	0.384	0.292
1.0 km PI value	0.422	0.425	0.364	0.274	0.354	0.343	0.246	0.328	0.326	0.332
2.5 km PI value	0.204	0.155	0.775	0.666	0.704	0.628				
3.0 km PI value	0.630	na	0.588	na	0.964	na				
3.4 km PI value	0.577	0.597								
3.8 km PI value	0.487	0.584								
4.4 km PI value	0.647	0.650	0.422	0.391						
5.5 km PI value	0.827	0.856								
6.0 km PI value	0.736	0.716	1.948	1.949						
6.7 km PI value	0.384	0.301	0.932	0.658						
8.1 km PI value	0.650	0.860	0.889	0.810	1.010	1.272				
8.5 km PI value	0.518	0.567	0.525	0.646	0.529	0.387				
8.8 km PI value	1.159	1.148	0.868	na	0.958	0.747				
21.0 km PI value	0.402	na	0.333	na	0.407	na				
22.0 km PI value	0.297	0.313	0.372	0.333						
23.0 km PI value	0.654	0.647	0.498	0.543	0.278	na	0.351	na		
24.0 km PI value	0.360	0.288	0.310	0.309						
25.0 km PI value	0.447	0.505	0.391	0.419						
26.0 km PI value	0.406	0.361	0.244	0.254						

Table 4 - Pollution index, floodplain soil, south of the river

km downstream	distance from river 2 m 0-20cm	2 m 20-50cm	25 m 0-20cm	25 m 20-50cm	50 m 0-20cm	50 m 20-50cm	75 m 0-20cm	75 m 20-50cm
0.5 km PI value	0.296	0.270	0.384	0.274				
1.0 km PI value	0.570	0.407	0.405	0.336	0.442	0.297	0.483	0.282
5.1 km PI value	0.439	0.670	0.582	0.435	0.638	0.379		
5.5 km PI value	0.493	0.373	0.650	0.429				
6.0 km PI value	0.903	0.545	1.211	1.207	1.396	1.413		
7.7 km PI value	0.594	0.596	0.705	0.679				
8.1 km PI value	0.723	0.827	0.887	0.843				
8.5 km PI value	0.855	1.023	0.949	0.957	1.334	0.869		
8.8 km PI value	0.946	0.749	0.822	0.743				
9.2 km PI value	0.777	0.929	1.193	1.274				

Table 5 - Chemical speciation, floodplain soil, pH & loss on ignition

SITE	SURFACE FLOODPLAIN SOIL						SUBSURFACE FLOODPLAIN SOIL		
	Transect at 0.75 km downstream				2 m from river		2 m from river		
	5.0 m	31.0 m	70.0 m	110.0 m	8.5 km	8.6 km	0.025 km	0.05 km	0.4 km
CADMIUM % in each fraction	%	%	%	%	%	%	%	%	%
Exchangeable	neg	neg	30	41	23	39	46	40	3
Surface oxide & carbonate	29	32	20	43	24	neg	42	45	32
Fe/Mn oxide & hydroxide	7	7	12	11	14	26	neg	neg	10
Organic	14	13	9	neg	12	5	neg	9	10
Residual	50	48	29	5	27	30	12	6	45
Total (mg/kg)	11.1	11.6	6.8	7.4	14.7	10.8	6.9	6.7	11.6
COPPER % in each fraction	%	%	%	%	%	%	%	%	%
Exchangeable	6	neg	3	3	3	3	11	12	2
Surface oxide & carbonate	4	6	7	9	neg	3	17	19	8
Fe/Mn oxide & hydroxide	17	45	19	17	22	23	26	22	18
Organic	19	27	26	25	44	42	16	13	26
Residual	54	22	45	46	31	29	30	34	46
Total (mg/kg)	89.3	174.4	75.5	78.1	129.7	133.9	18.5	22.3	111.2
LEAD % in each fraction	%	%	%	%	%	%	%	%	%
Exchangeable	neg	38	15	15	16	15	53	51	17
Surface oxide & carbonate	12	8	11	8	7	neg	17	14	9
Fe/Mn oxide & hydroxide	44	37	55	52	57	62	26	25	61
Organic	9	7	7	14	11	12	3	1	8
Residual	35	11	12	11	9	11	1	9	5
Total (mg/kg)	65.6	95.9	79.6	156.2	217.1	183.1	45.1	41.3	105.3
ZINC % in each fraction	%	%	%	%	%	%	%	%	%
Exchangeable	8	10	4	10	5	2	17	22	1
Surface oxide & carbonate	3	4	3	5	4	12	10	8	3
Fe/Mn oxide & hydroxide	50	51	41	36	65	59	38	23	78
Organic	12	14	12	17	8	9	10	11	5
Residual	27	21	40	32	18	18	25	36	13
Total (mg/kg)	115.8	123.9	110.4	191.5	251.5	322.3	75.2	85.1	377.3
pH	5.4	5.0	5.1	5.3	6.1	5.8	5.8	6.3	6.0
LOSS ON IGNITION (%)	6.0	8.3	9.8	13.0	9.3	10.9	3.6	7.7	8.9

Table 6 - Sediment cores, total metal concentration, pH & loss on ignition

Apperley Bridge - 1.0 km downstream

Depth (cm)	Arsenic (mg/kg)	Cadmium (mg/kg)	Chromium (mg/kg)	Copper (mg/kg)	Lead (mg/kg)	Mercury (mg/kg)	Zinc (mg/kg)	pH	LOI %
5-10	12.05	1.15	22.80	74.19	61.36	0.00	117.46	7.1	11.7
16-21	7.99	1.15	17.91	68.94	49.92	0.00	110.32	6.5	7.2
34-39	2.22	1.17	19.94	20.80	16.93	0.72	54.69	6.7	4.5
48-53	5.12	1.56	18.26	16.55	16.21	0.12	55.75	6.8	3.1
65-71	4.26	2.22	31.75	24.41	13.74	0.16	75.65	6.5	4.7
84-89	3.25	1.26	14.9	20.53	17.60	0.08	64.80	7.0	3.6
104-109	6.64	2.06	15.43	15.92	10.96	0.28	70.05	7.0	1.4
135-140	3.19	1.21	11.05	14.40	8.03	0.00	47.71	8.1	3.6
150-155	4.37	1.41	17.31	16.74	9.03	0.00	98.48	8.3	2.7
160-165	4.31	1.33	12.72	13.18	9.96	0.00	45.99	8.3	2.8
174-179	3.98	1.24	18.01	20.89	15.63	0.46	62.70	8.1	3.6
190-195	3.91	1.70	22.69	16.54	9.14	0.00	70.66	8.3	3.1
202-207	2.60	1.23	15.79	12.22	6.60	0.00	62.12	8.2	1.3
223-228	3.06	1.82	25.83	15.95	12.29	0.25	98.07	8.0	2.3
247-252	3.91	1.60	16.20	12.66	9.20	0.00	67.81	8.2	1.5
261-266	4.62	2.46	24.41	21.59	10.63	0.00	78.60	7.6	1.7
295-300	3.30	2.54	13.31	24.18	12.84	0.00	98.95	8.2	2.4
313-318	3.56	1.40	40.9	27.11	13.22	0.00	82.11	8.0	1.4

Table 7 - Sediment cores, total metal concentration, pH & loss on ignition

Calverley - 3.0 km downstream

Depth (cm)	Arsenic (mg/kg)	Cadmium (mg/kg)	Copper (mg/kg)	Chromium (mg/kg)	Lead (mg/kg)	Mercury (mg/kg)	Zinc (mg/kg)	pH	LOI %
5-10	11.84	4.30	97.27	56.90	160.30	0.21	338.48	7.1	5.6
20-25	15.40	4.60	115.18	70.14	188.73	0.39	381.41	6.7	16.6
33-38	20.84	6.22	130.26	73.22	211.46	0.98	370.22	6.7	8.7
58-63	8.20	1.69	65.05	44.25	56.17	0.05	136.01	7.1	4.8
74-79	3.29	1.47	28.76	20.90	18.74	0.54	71.73	6.3	4.8
85-90	3.63	0.87	23.38	22.92	13.58	0.00	90.65	7.2	3.6
99-104	2.64	0.78	19.91	14.53	10.67	0.25	92.28	6.3	2.1
118-123	1.19	0.90	18.24	14.65	9.56	0.00	63.30	6.2	1.6
135-140	1.32	1.19	19.73	13.62	9.82	0.00	61.45	6.2	1.8
155-160	0.37	1.01	17.57	20.16	13.00	0.00	96.82	7.0	2.2
172-177	0.00	0.45	6.57	6.63	4.17	0.00	25.83	6.9	0.6
190-195	0.10	0.65	6.17	10.27	5.06	0.00	38.56	6.0	1.0
210-215	0.00	0.59	6.75	13.14	4.72	0.00	48.06	6.2	0.3
225-230	0.27	0.54	6.57	7.85	4.11	0.00	38.31	6.1	0.9
232-237	2.03	0.59	11.26	9.87	9.61	0.56	60.58	7.1	1.8
244-249	0.09	0.69	10.64	12.82	9.96	0.00	45.98	6.9	0.9
262-267	0.05	0.59	7.91	9.85	5.95	0.00	38.56	7.3	1.6
282-287	0.10	0.60	6.98	8.60	6.26	0.00	22.24	7.3	0.3

Table 8 - Sediment cores, total metal concentration, pH & loss on ignition

Rodley - 4.0 km downstream

Depth (cm)	Arsenic (mg/kg)	Cadmium (mg/kg)	Chromium (mg/kg)	Copper (mg/kg)	Lead (mg/kg)	Mercury (mg/kg)	Zinc (mg/kg)	pH	LOI %
6-11	12.18	2.62	51.37	82.22	135.84	0.00	232.18	6.9	13.2
20-25	11.94	1.71	41.76	64.79	100.46	0.00	159.34	7.0	5.9
32-37	10.28	1.52	43.91	56.20	83.06	0.00	137.69	7.1	5.4
49-54	2.20	1.06	21.15	18.26	18.24	0.00	64.09	7.4	2.3
69-74	1.26	1.06	19.33	13.84	12.99	0.00	57.73	7.3	2.5
80-85	1.09	1.10	19.61	15.41	15.20	0.00	58.62	7.4	2.4
95-100	0.86	1.01	19.84	12.49	10.23	0.00	53.22	7.3	2.3
111-116	1.54	0.96	13.24	10.87	9.58	0.00	44.80	7.4	2.3
120-125	1.53	1.11	17.35	14.00	14.97	0.00	56.82	7.3	2.8
135-140	0.61	1.46	19.81	12.24	12.92	0.00	71.81	7.3	2.8
156-161	1.72	1.44	28.60	15.49	15.94	0.00	108.69	7.2	3.4
177-182	1.54	1.37	30.36	14.81	16.47	0.00	123.83	7.1	3.4
195-200	0.54	0.98	24.95	14.70	11.46	0.00	86.30	7.3	2.7
211-216	1.57	1.07	23.33	14.92	12.29	0.00	77.49	7.1	3.1
235-240	2.68	1.54	21.26	17.15	17.46	0.13	85.03	7.1	2.4
257-262	0.06	0.98	29.35	21.38	16.39	0.00	90.64	7.2	3.7
274-279	0.00	0.67	25.30	22.87	11.31	0.00	66.62	7.2	3.3
286-291	3.17	0.38	11.32	12.62	7.31	0.07	33.15	7.3	2.0
304-309	4.56	0.58	12.77	7.79	6.28	0.00	23.46	7.2	1.5
313-318	1.44	0.78	16.63	11.16	9.65	0.00	47.84	7.3	2.2
332-337	1.33	0.51	7.44	5.62	3.71	0.00	18.82	7.2	1.2
365-370	0.00	0.91	14.64	11.14	6.76	0.00	48.58	7.3	1.5

Table 9 - Sediment cores, total metal concentration, pH & loss on ignition

Kirkstall Allotments - 8.5 km downstream

Depth (cm)	Arsenic (mg/kg)	Cadmium (mg/kg)	Chromium (mg/kg)	Copper (mg/kg)	Lead (mg/kg)	Mercury (mg/kg)	Zinc (mg/kg)	pH	LOI %
4-9	6.70	1.08	54.43	70.40	69.47	0.00	101.10	6.4	4.9
24-29	5.23	1.06	51.95	69.31	66.47	0.00	98.81	6.3	5.0
46-51	4.83	0.72	32.83	45.26	60.14	0.00	50.73	6.5	4.0
60-65	3.15	1.18	27.37	30.11	54.56	0.00	67.34	6.3	2.9
77-82	1.90	0.95	17.53	15.33	24.86	0.00	55.28	6.4	2.3
92-97	0.71	0.90	18.73	13.96	20.69	0.00	48.79	6.4	2.6
108-113	1.29	0.82	15.37	10.57	11.26	0.00	42.40	6.4	2.0
126-131	1.10	0.81	15.59	11.17	11.06	0.00	40.32	6.5	2.0
134-139	0.32	0.85	14.08	10.90	9.87	0.00	47.83	6.4	1.6
152-157	0.56	0.96	17.01	9.78	8.48	0.00	63.63	6.4	2.4
170-175	0.34	1.08	18.99	11.16	9.42	0.00	78.90	6.2	2.5
186-191	0.00	1.44	24.49	12.38	12.11	0.00	110.80	6.4	3.0
207-212	0.12	1.02	13.75	7.96	7.33	0.00	63.22	5.9	1.9
226-231	0.00	0.92	14.29	11.03	10.75	0.00	77.65	5.9	2.2
235-240	0.52	1.42	17.54	12.46	10.72	0.00	83.21	5.9	2.1
256-261	0.00	0.47	4.70	3.61	3.13	0.00	18.07	6.0	0.7
272-277	0.30	0.56	8.04	7.99	5.10	0.00	37.52	5.9	1.1
290-295	0.50	0.53	5.51	5.73	3.51	0.00	28.79	6.4	0.4
307-312	0.00	0.73	8.80	5.86	3.78	0.00	33.42	6.3	0.7
322-327	1.64	0.98	10.42	7.65	4.87	0.00	36.46	7.3	1.5
336-341	0.15	0.57	6.73	4.67	3.83	0.00	25.78	6.6	0.8
353-358	0.96	0.69	10.47	8.60	3.90	0.00	31.41	7.5	1.1
370-375	1.16	0.98	10.83	11.59	5.72	0.00	39.16	7.6	1.8
385-390	1.03	0.97	13.17	14.28	6.82	0.00	50.17	7.4	2.1
400-405	0.66	1.12	15.30	14.09	7.50	0.00	51.34	7.4	2.2
419-424	1.21	1.13	18.53	18.29	9.82	0.00	56.85	7.1	2.1

Table 10 - Sediment cores, total metal concentration, pH & loss on ignition

Kirkstall Nature Reserve - 10.0 km downstream

Depth (cm)	Arsenic (mg/kg)	Cadmium (mg/kg)	Chromium (mg/kg)	Copper (mg/kg)	Lead (mg/kg)	Mercury (mg/kg)	Zinc (mg/kg)	pH	LOI %
5-10	37.96	0.99	30.57	90.68	77.86	0.00	97.70	7.5	8.4
22-27	78.64	0.69	7.54	50.99	41.39	3.51	31.45	7.1	61.3
35-40	97.94	1.04	14.09	124.69	40.49	0.00	49.88	6.5	29.3
50-55	81.08	0.87	12.75	96.05	39.53	0.00	53.86	6.3	31.4
68-73	79.02	0.88	11.15	90.82	55.04	0.00	39.22	6.2	13.7
86-91	93.26	1.05	13.59	108.99	65.80	0.00	46.65	6.4	27.2
100-105	71.93	0.83	12.47	90.36	37.32	0.00	42.56	6.6	30.0
120-125	68.63	0.69	8.47	80.57	33.08	0.47	31.61	6.4	30.4
135-140	64.56	0.72	10.69	80.46	28.22	0.00	34.03	6.3	30.4
152-157	76.89	0.95	12.29	97.85	34.34	0.00	44.42	6.3	22.3
171-176	29.05	2.52	85.38	77.47	123.84	0.39	230.15	6.5	7.4
187-192	52.66	8.81	17.62	71.05	50.42	0.00	72.18	7.7	30.3
203-208	10.09	1.47	77.48	80.22	92.35	0.00	134.07	6.8	4.8
220-225	6.13	1.47	71.56	69.52	109.81	0.00	105.75	7.3	4.3
230-235	6.65	1.57	74.64	59.98	93.59	0.00	115.39	7.3	3.8
248-253	5.07	1.58	64.16	60.04	136.23	0.00	100.00	7.4	4.8
267-272	3.02	1.07	28.54	45.83	51.49	0.00	56.81	7.3	3.2
282-287	8.22	1.81	74.96	132.15	159.99	0.00	126.30	7.1	7.5
299-304	2.61	1.09	20.20	38.63	46.34	0.00	71.92	7.1	4.0
320-325	0.05	0.84	13.99	10.92	9.96	0.00	47.62	7.0	2.2
334-339	0.21	0.86	14.18	10.19	8.47	0.00	48.30	7.0	1.9
350-355	0.20	0.88	13.40	11.29	8.63	0.00	50.23	6.9	2.1
367-372	1.23	0.63	7.78	5.44	4.15	0.00	27.50	6.9	1.4
375-380	1.53	0.73	31.64	12.10	8.19	0.00	36.65	6.7	2.7

Table 10 - Sediment cores, total metal concentration, pH & loss on ignition

Kirkstall Nature Reserve - 10.0 km downstream

Depth (cm)	Arsenic (mg/kg)	Cadmium (mg/kg)	Chromium (mg/kg)	Copper (mg/kg)	Lead (mg/kg)	Mercury (mg/kg)	Zinc (mg/kg)	pH	LOI %
396-401	3.83	1.78	15.39	10.37	13.18	0.76	72.27	6.4	3.2
412-417	2.68	1.08	17.08	12.75	9.91	0.00	56.76	6.0	3.1
426-431	0.09	1.08	32.91	21.66	17.57	0.00	96.51	7.1	2.4
441-446	1.53	0.06	29.16	19.79	15.61	0.00	85.27	6.4	7.0
460-465	1.42	1.20	18.97	9.60	11.03	0.35	80.41	6.3	7.2
475-480	2.09	0.74	11.23	11.95	9.73	0.00	32.60	6.7	1.3
493-498	0.59	0.74	14.69	10.31	8.43	0.00	46.76	6.1	2.7
512-517	1.58	0.43	6.91	3.80	3.88	1.59	29.04	6.4	1.1
537-542	4.08	2.07	20.2	12.14	11.81	0.32	144.56	6.5	9.0
556-561	0.98	1.62	15.56	10.25	9.55	0.17	95.75	6.5	7.5

Table 11 - Sediment cores, total metal concentration, pH & loss on ignition

Globe Road - 14.0 km downstream

Depth (cm)	Arsenic (mg/kg)	Cadmium (mg/kg)	Chromium (mg/kg)	Copper (mg/kg)	Lead (mg/kg)	Mercury (mg/kg)	Zinc (mg/kg)	pH	LOI %
5-10	13.41	1.74	47.39	49.01	76.34	1.19	148.06	7.5	5.6
18-23	7.10	1.61	34.86	26.35	37.46	0.39	105.41	7.5	6.5
33-38	11.70	1.59	27.04	35.66	48.03	0.99	116.12	7.7	3.8
45-50	76.23	2.37	169.32	300.8	424.41	0.75	308.95	7.0	13.9
64-69	16.08	1.48	20.95	31.82	50.13	0.72	76.53	7.1	5.6
81-86	7.23	1.08	20.36	17.59	20.95	0.00	66.04	7.3	5.1
98-103	3.21	1.55	19.60	12.40	16.45	0.30	100.86	7.4	2.5
111-116	5.14	1.94	22.76	13.08	17.35	0.56	122.06	7.5	3.5
122-127	6.86	2.10	40.39	16.83	23.04	0.64	176.93	7.5	6.4
142-147	3.87	1.00	25.41	10.32	11.16	0.00	86.37	7.5	1.9
159-164	4.67	1.15	16.14	9.33	9.32	0.71	80.79	7.5	3.1
173-178	3.43	1.31	25.04	16.32	20.69	0.47	109.05	7.4	4.1
194-199	3.47	1.20	15.79	10.16	11.23	0.22	76.70	7.4	2.5
212-217	0.00	0.89	18.98	11.18	12.67	0.00	77.00	7.4	2.7
225-230	2.43	1.01	16.93	9.39	11.73	0.00	70.53	7.5	2.4
242-247	2.20	0.82	15.24	8.44	7.62	0.00	70.12	7.5	2.1
261-266	0.56	0.38	4.78	4.07	4.27	0.00	0.82	7.3	1.0
280-285	1.61	0.79	16.81	10.34	10.83	0.00	62.51	7.5	1.3
296-301	1.75	0.77	7.85	6.12	5.89	0.00	33.83	7.4	1.2
307-312	2.57	0.78	14.29	9.74	12.61	0.00	61.32	7.5	2.4
335-340	2.22	0.54	6.65	3.31	3.64	0.00	27.77	7.4	0.5
360-365	0.12	0.28	5.48	3.41	3.71	0.00	21.04	7.4	0.7
389-394	1.23	0.54	8.52	5.06	5.44	0.00	33.60	7.4	1.0

Table 12 - Sediment cores, total metal concentration, pH & loss on ignition

Knostrop - 19.0 km downstream

Depth (cm)	Arsenic (mg/kg)	Cadmium (mg/kg)	Chromium (mg/kg)	Copper (mg/kg)	Lead (mg/kg)	Mercury (mg/kg)	Zinc (mg/kg)	pH	LOI %
114-119	20.97	1.40	28.53	22.02	33.53	0.79	135.89	7.5	3.5
145-150	83.22	3.14	96.36	64.49	85.44	1.37	560.23	7.6	5.2
175-180	18.91	2.22	46.69	48.12	82.48	0.17	191.02	7.6	4.4
190-195	16.05	2.06	39.11	42.38	59.63	0.56	180.32	7.5	4.3
226-231	15.85	2.12	68.24	69.16	131.84	0.00	253.90	7.4	5.8
249-254	21.06	2.11	61.26	82.54	128.77	1.06	248.14	7.9	7.2

Table 13 - Sediment cores, total metal concentration, pH & loss on ignition

Copper Works - 23.0 km downstream

Depth (cm)	Arsenic (mg/kg)	Cadmium (mg/kg)	Chromium (mg/kg)	Copper (mg/kg)	Lead (mg/kg)	Mercury (mg/kg)	Zinc (mg/kg)	pH	LOI %
10-15	25.58	0.89	152.15	159.44	304.77	1.74	125.10	4.7	22.2
35-40	20.07	5.55	360.65	166.60	383.76	0.49	432.41	6.2	12.0
49-54	10.79	1.33	105.70	76.20	168.06	1.46	182.06	6.8	8.1
68-73	7.25	0.86	51.39	53.75	120.67	1.24	122.70	7.0	6.5
84-89	8.33	0.92	63.52	65.29	130.00	1.29	134.56	7.2	5.7
98-103	4.13	0.83	16.90	23.05	31.60	2.36	89.00	7.2	4.0
114-119	4.81	1.14	21.20	17.48	27.27	0.00	64.95	7.0	4.9
131-136	3.48	1.35	15.64	16.52	19.64	1.60	113.95	7.0	4.0
148-153	2.85	0.56	10.79	11.05	11.27	1.39	64.75	6.6	3.2
164-169	10.06	1.21	84.41	68.49	125.12	1.47	157.83	6.5	8.0
178-183	4.87	1.08	19.35	20.92	24.10	1.13	117.60	6.8	4.9
194-199	3.09	1.22	17.57	20.05	24.05	1.46	125.79	6.9	4.2
211-216	4.43	1.20	22.45	13.01	16.69	0.00	76.38	6.6	3.3
227-232	3.12	0.78	15.88	19.05	31.10	1.56	92.30	6.4	4.7
255-260	3.58	0.79	13.90	17.72	26.70	1.68	92.18	6.4	3.8
270-275	3.58	0.80	14.95	16.48	19.97	1.49	73.93	6.8	3.3
287-292	3.97	1.47	27.78	29.22	43.29	1.33	165.84	6.7	6.9
299-304	1.92	1.68	26.15	25.88	45.16	0.00	94.76	6.9	6.2
313-318	5.92	1.54	25.23	28.84	46.34	2.00	164.21	6.9	6.3
332-337	3.78	1.37	22.69	26.10	38.30	1.41	164.14	6.6	6.1
350-355	5.09	1.57	23.75	27.53	39.14	1.58	156.53	7.0	5.0
375-380	2.96	1.38	27.20	25.59	33.72	1.22	146.32	6.9	6.4
394-399	2.53	1.16	16.89	16.91	25.25	0.00	65.94	7.0	4.4
414-419	2.80	0.90	10.36	14.98	20.81	1.26	88.00	7.1	4.2

Table 13 - Sediment cores, total metal concentration, pH & loss on ignition

Copper Works - 23.0 km downstream

Depth (cm)	Arsenic (mg/kg)	Cadmium (mg/kg)	Chromium (mg/kg)	Copper (mg/kg)	Lead (mg/kg)	Mercury (mg/kg)	Zinc (mg/kg)	pH	LOI %
430-435	2.60	0.72	12.72	12.94	15.44	1.23	76.60	6.8	3.6
440-445	5.08	1.01	38.13	35.55	58.37	1.29	134.11	6.9	6.6
465-470	3.67	0.81	19.12	19.2	29.16	1.18	80.35	6.6	3.6
483-488	8.34	0.44	3.03	3.31	4.40	0.00	16.33	6.1	1.5
500-505	7.35	0.52	4.44	8.12	7.10	0.96	36.43	6.7	2.5
517-522	3.26	0.57	7.21	9.70	12.98	1.52	59.48	6.8	2.4

Table 14 - Sediment cores, total metal concentration, pH & loss on ignition

Swillington Bridge - 26.0 km downstream

Depth (cm)	Arsenic (mg/kg)	Cadmium (mg/kg)	Chromium (mg/kg)	Copper (mg/kg)	Lead (mg/kg)	Mercury (mg/kg)	Zinc (mg/kg)	pH	LOI %
5-10	7.10	1.10	39.29	27.63	48.52	0.00	98.89	6.9	9.1
20-25	4.42	0.85	31.45	25.70	43.14	0.00	71.20	7.5	6.4
35-40	2.13	0.87	45.96	21.90	18.77	0.00	89.17	7.7	5.9
48-53	5.37	0.68	35.53	19.72	22.91	0.00	55.19	7.8	5.3
65-70	7.48	0.64	17.78	28.10	96.22	0.00	102.97	8.2	6.0
84-89	2.19	1.10	30.85	13.96	18.46	0.00	80.65	8.1	5.3
100-105	1.40	0.74	16.00	8.85	11.79	0.00	56.97	7.9	3.0
116-121	1.33	0.64	15.17	7.49	8.86	0.00	47.66	7.7	2.7
133-138	2.50	0.63	12.38	5.97	7.47	0.00	38.38	7.8	1.8
155-160	1.53	0.82	17.83	8.66	11.53	0.00	59.48	7.8	2.6
165-170	1.77	0.78	21.21	8.82	13.33	0.00	64.86	7.8	3.3
181-186	0.61	0.97	18.74	9.22	12.39	0.00	62.63	7.6	2.6
197-202	1.37	0.90	20.71	8.43	12.11	0.00	58.63	7.0	3.0
217-222	3.54	0.89	16.98	7.37	9.59	0.00	52.05	7.1	3.0
235-240	0.46	0.88	18.57	8.25	11.14	0.00	57.48	6.6	2.8
253-258	2.00	0.54	9.33	5.25	7.61	0.00	38.22	6.9	1.9
266-271	1.41	0.60	12.25	6.40	9.33	0.00	45.73	6.8	3.1
280-285	2.08	0.94	6.73	4.38	4.26	0.00	33.68	7.2	2.0
308-313	2.40	0.96	11.33	5.47	5.50	0.00	43.84	7.1	2.2
325-330	1.78	0.63	7.85	4.04	4.81	0.00	33.85	7.0	2.0
344-349	2.97	0.92	9.51	4.07	3.95	0.00	33.44	7.1	1.2
360-365	1.88	0.79	10.17	4.15	3.93	0.00	37.81	7.0	1.7
377-382	3.62	1.51	9.76	5.34	6.28	0.00	55.02	7.2	3.3
399-404	2.43	1.06	11.50	5.43	7.23	0.00	41.09	7.1	3.1

Table 15 - Sediment cores, chemical speciation (% in each fraction)

Apperley Bridge - 1.0 km downstream

Depth 34 - 39 cm	Arsenic %	Cadmium %	Chromium %	Copper %	Lead %	Mercury %	Zinc %
Exchangeable	13.4	22.9	0.2	6.8	0.0	3.5	1.7
Oxide & carbonate	17.0	0.0	6.6	17.2	11.2	47.0	2.7
Fe / Mn oxides	0.0	29.2	12.8	11.9	68.2	0.0	20.9
Organic	61.4	22.9	26.3	28.0	14.6	49.5	30.2
Residual	8.2	25.0	54.1	36.1	6.0	0.0	44.5

Depth 135 - 140 cm	Arsenic %	Cadmium %	Chromium %	Copper %	Lead %	Mercury %	Zinc %
Exchangeable	0.0	11.9	0.3	6.5	0.0	0.0	0.0
Oxide & carbonate	24.1	9.5	7.6	15.1	12.2	49.0	3.0
Fe / Mn oxides	0.0	48.9	11.7	12.8	60.2	0.0	22.5
Organic	57.7	8.3	27.4	21.0	5.5	51.0	21.8
Residual	18.2	21.4	53.0	44.6	22.1	0.0	52.7

Depth 190 - 195 cm	Arsenic %	Cadmium %	Chromium %	Copper %	Lead %	Mercury %	Zinc %
Exchangeable	8.2	7.1	0.1	5.8	0.0	0.0	0.0
Oxide & carbonate	21.8	15.0	6.4	13.8	12.6	14.0	3.8
Fe / Mn oxides	0.0	53.5	13.1	17.1	78.9	0.0	27.7
Organic	70.0	10.2	28.7	23.7	8.5	86.0	23.4
Residual	0.0	14.2	51.7	39.6	0.0	0.0	45.1

Depth 295 - 300 cm	Arsenic %	Cadmium %	Chromium %	Copper %	Lead %	Mercury %	Zinc %
Exchangeable	1.2	1.1	0.0	2.9	0.0	0.0	0.0
Oxide & carbonate	15.6	5.1	7.6	6.7	4.2	46.0	2.8
Fe / Mn oxides	0.0	62.9	0.2	45.6	64.6	0.0	37.3
Organic	51.2	6.2	26.5	16.4	11.0	54.0	18.3
Residual	32.0	24.7	65.7	28.4	20.2	0.0	41.6

Table 16 - Sediment cores, chemical speciation (% in each fraction)

Calverley Bridge - 3.0 km downstream

Depth 33 - 38 cm	Arsenic %	Cadmium %	Chromium %	Copper %	Lead %	Mercury %	Zinc %
Exchangeable	8.6	34.8	0.0	3.3	0.0	0.0	0.7
Oxide & carbonate	12.3	27.2	6.2	12.7	14.0	31.9	15.5
Fe / Mn oxides	22.2	31.1	36.7	21.1	57.3	63.1	50.0
Organic	40.9	3.9	40.3	46.2	25.2	5.0	22.0
Residual	16.0	3.0	16.8	16.7	3.5	0.0	11.8

Depth 99 - 104 cm	Arsenic %	Cadmium %	Chromium %	Copper %	Lead %	Mercury %	Zinc %
Exchangeable	4.7	6.8	0.0	5.1	0.0	0.0	0.0
Oxide & carbonate	18.8	1.4	5.6	11.7	0.8	0.0	1.8
Fe / Mn oxides	28.0	76.7	36.8	16.0	98.8	58.9	46.4
Organic	48.5	12.3	19.1	28.2	0.4	41.1	25.0
Residual	0.0	2.8	38.5	39.0	0.0	0.0	26.8

Depth 190 - 195 cm	Arsenic %	Cadmium %	Chromium %	Copper %	Lead %	Mercury %	Zinc %
Exchangeable	3.3	23.8	0.0	7.1	0.0	0.0	0.0
Oxide & carbonate	19.8	33.3	14.0	16.3	58.4	46.4	6.5
Fe / Mn oxides	1.9	23.8	9.0	7.2	41.6	0.0	28.3
Organic	61.1	19.1	27.3	20.0	0.0	53.6	31.8
Residual	13.9	0.0	49.7	49.4	0.0	0.0	33.4

Depth 262 - 267 cm	Arsenic %	Cadmium %	Chromium %	Copper %	Lead %	Mercury %	Zinc %
Exchangeable	10.4	8.3	0.0	7.1	0.0	0.0	0.0
Oxide & carbonate	36.5	33.3	10.5	16.3	25.7	34.6	8.0
Fe / Mn oxides	0.0	16.7	6.5	7.2	74.3	0.0	31.3
Organic	53.1	41.7	21.2	20.0	0.0	65.4	32.8
Residual	0.0	0.0	61.8	49.4	0.0	0.0	27.9

Table 17 - Sediment cores, chemical speciation (% in each fraction)

Rodley - 4.0 km downstream

Depth 32 - 37 cm	Arsenic %	Cadmium %	Chromium %	Copper %	Lead %	Mercury %	Zinc %
Exchangeable	3.7	39.6	0.1	4.2	1.4	0.0	4.2
Oxide & carbonate	14.3	8.3	5.8	10.4	14.2	23.6	5.7
Fe / Mn oxides	13.2	30.2	37.2	23.2	61.3	0.0	40.6
Organic	43.7	6.3	34.2	34.3	19.6	76.4	28.4
Residual	25.1	15.6	22.7	27.9	3.5	0.0	21.1

Depth 95 - 100 cm	Arsenic %	Cadmium %	Chromium %	Copper %	Lead %	Mercury %	Zinc %
Exchangeable	2.3	19.3	0.0	5.4	0.0	0.0	1.0
Oxide & carbonate	22.1	10.6	8.3	19.4	38.1	80.9	4.2
Fe / Mn oxides	0.7	42.1	12.0	8.4	54.2	0.0	30.5
Organic	74.9	14.0	32.0	19.9	5.9	19.1	30.9
Residual	0.0	14.0	47.7	46.9	1.8	0.0	33.4

Depth 177 - 182 cm	Arsenic %	Cadmium %	Chromium %	Copper %	Lead %	Mercury %	Zinc %
Exchangeable	25.3	15.6	0.0	5.9	0.0	0.0	0.2
Oxide & carbonate	27.9	7.8	6.0	13.1	12.1	32.0	1.6
Fe / Mn oxides	0.0	42.2	10.0	17.1	72.9	0.0	15.7
Organic	46.8	15.6	27.6	24.3	12.8	68.0	39.5
Residual	0.0	18.8	56.4	39.6	2.2	0.0	43.0

Depth 274 - 279 cm	Arsenic %	Cadmium %	Chromium %	Copper %	Lead %	Mercury %	Zinc %
Exchangeable	19.2	36.7	0.0	6.7	2.7	0.0	0.1
Oxide & carbonate	17.2	13.3	7.7	14.7	41.2	38.3	3.7
Fe / Mn oxides	0.0	33.3	18.0	11.5	30.6	0.0	21.0
Organic	63.6	16.7	39.6	32.6	12.2	61.7	45.8
Residual	0.0	0.0	34.7	34.5	13.3	0.0	29.4

Depth 332 - 337 cm	Arsenic %	Cadmium %	Chromium %	Copper %	Lead %	Mercury %	Zinc %
Exchangeable	4.8	83.3	0.0	8.9	0.0	0.0	0.0
Oxide & carbonate	33.0	4.2	12.6	21.1	34.7	55.7	8.7
Fe / Mn oxides	0.0	6.9	14.6	8.2	65.3	0.0	27.2
Organic	62.2	5.6	26.5	27.1	0.0	44.3	41.6
Residual	0.0	0.0	46.3	34.7	0.0	0.0	22.5

Table 18 - Sediment cores, chemical speciation (% in each fraction)

Kirkstall Allotments - 8.5 km downstream

Depth 46 - 51 cm	Arsenic %	Cadmium %	Chromium %	Copper %	Lead %	Mercury %	Zinc %
Exchangeable	7.8	7.9	0.2	4.5	0.3	0.0	0.0
Oxide & carbonate	15.4	7.9	6.7	10.9	12.6	14.8	5.2
Fe / Mn oxides	7.5	34.2	34.9	18.4	63.6	0.0	29.0
Organic	59.2	23.7	31.2	28.7	20.0	85.2	34.1
Residual	10.1	26.3	27.0	37.5	3.5	0.0	31.7

Depth 108 - 113 cm	Arsenic %	Cadmium %	Chromium %	Copper %	Lead %	Mercury %	Zinc %
Exchangeable	9.1	21.2	0.0	6.2	0.0	0.0	0.0
Oxide & carbonate	32.8	21.2	9.5	13.5	14.2	21.0	5.7
Fe / Mn oxides	0.0	51.5	12.3	7.6	73.0	0.0	31.6
Organic	58.1	6.1	30.9	20.5	12.8	79.0	31.1
Residual	0.0	0.0	47.3	52.2	0.0	0.0	31.6

Depth 186 - 191 cm	Arsenic %	Cadmium %	Chromium %	Copper %	Lead %	Mercury %	Zinc %
Exchangeable	16.8	36.5	0.0	7.9	0.0	0.0	0.8
Oxide & carbonate	17.1	15.7	6.1	14.1	26.1	13.9	3.2
Fe / Mn oxides	0.0	38.3	13.7	12.5	49.5	0.0	28.4
Organic	66.1	7.8	33.6	34.7	20.0	86.1	38.0
Residual	0.0	1.7	46.6	30.8	4.4	0.0	29.6

Depth 290 - 295 cm	Arsenic %	Cadmium %	Chromium %	Copper %	Lead %	Mercury %	Zinc %
Exchangeable	18.7	0.0	0.0	7.6	0.0	0.0	2.4
Oxide & carbonate	0.0	0.0	9.6	10.6	0.0	0.0	7.7
Fe / Mn oxides	0.0	70.0	8.5	12.2	100.0	0.0	45.5
Organic	81.3	30.0	21.7	23.6	0.0	100.0	29.2
Residual	0.0	0.0	60.2	46.0	0.0	0.0	15.2

Depth 385 - 390 cm	Arsenic %	Cadmium %	Chromium %	Copper %	Lead %	Mercury %	Zinc %
Exchangeable	9.2	14.8	0.0	8.2	0.0	0.0	0.0
Oxide & carbonate	0.0	3.2	5.4	13.7	0.0	0.0	10.7
Fe / Mn oxides	0.0	59.0	25.6	13.0	100.0	0.0	35.6
Organic	81.9	6.6	26.8	33.9	0.0	100.0	27.7
Residual	8.9	16.4	42.2	31.2	0.0	0.0	26.0

Table 19 - Sediment cores, chemical speciation (% in each fraction)

Kirkstall Nature Reserve - 10.0 km downstream

Depth 50 - 55 cm	Arsenic %	Cadmium %	Chromium %	Copper %	Lead %	Mercury %	Zinc %
Exchangeable	1.1	10.0	0.1	2.4	0.0	7.8	0.4
Oxide & carbonate	1.2	0.0	4.1	4.1	0.0	0.0	1.5
Fe / Mn oxides	31.6	66.6	8.8	16.1	55.5	0.0	51.1
Organic	38.9	16.7	20.5	45.6	39.6	92.2	28.2
Residual	27.2	6.7	66.5	31.8	4.9	0.0	18.8
Depth 135 - 140 cm	**Arsenic %**	**Cadmium %**	**Chromium %**	**Copper %**	**Lead %**	**Mercury %**	**Zinc %**
Exchangeable	2.8	11.2	0.0	3.5	0.0	0.0	0.0
Oxide & carbonate	0.0	0.0	5.8	6.0	0.0	0.0	4.2
Fe / Mn oxides	48.1	44.4	8.3	15.5	62.1	0.0	37.6
Organic	38.6	22.2	19.0	37.4	37.9	0.0	33.1
Residual	10.5	22.2	66.9	37.6	0.0	0.0	25.1
Depth 230 - 235 cm	**Arsenic %**	**Cadmium %**	**Chromium %**	**Copper %**	**Lead %**	**Mercury %**	**Zinc %**
Exchangeable	8.4	28.6	0.1	4.4	0.0	0.0	0.7
Oxide & carbonate	0.0	17.9	5.0	10.7	10.8	0.0	9.8
Fe / Mn oxides	11.4	39.2	59.6	29.7	72.7	0.0	51.7
Organic	33.1	10.0	23.3	34.3	14.9	0.0	23.9
Residual	47.1	4.3	12.0	20.9	1.6	0.0	13.9
Depth 334 - 339 cm	**Arsenic %**	**Cadmium %**	**Chromium %**	**Copper %**	**Lead %**	**Mercury %**	**Zinc %**
Exchangeable	25.3	42.8	0.0	8.2	0.0	0.0	1.2
Oxide & carbonate	0.0	2.4	4.4	18.5	0.0	0.0	1.9
Fe / Mn oxides	0.0	35.7	9.8	18.4	76.0	0.0	34.4
Organic	69.6	14.3	20.4	24.8	24.0	0.0	37.6
Residual	5.1	4.8	65.4	30.1	0.0	0.0	24.9
Depth 426 - 431 cm	**Arsenic %**	**Cadmium %**	**Chromium %**	**Copper %**	**Lead %**	**Mercury %**	**Zinc %**
Exchangeable	23.0	26.8	0.0	7.3	0.0	0.0	1.9
Oxide & carbonate	0.0	3.6	4.0	11.2	0.0	0.0	3.1
Fe / Mn oxides	0.0	46.4	14.7	10.0	59.1	0.0	28.1
Organic	77.0	12.5	28.4	38.1	26.1	0.0	38.4
Residual	0.0	10.7	52.9	33.4	14.8	0.0	28.5
Depth 512 - 517 cm	**Arsenic %**	**Cadmium %**	**Chromium %**	**Copper %**	**Lead %**	**Mercury %**	**Zinc %**
Exchangeable	0.0	46.7	0.0	9.4	0.0	0.0	3.1
Oxide & carbonate	0.0	6.7	9.8	10.3	0.0	0.0	7.1
Fe / Mn oxides	0.0	33.3	8.9	6.3	57.8	0.0	41.0
Organic	100.0	13.3	24.0	24.6	0.0	0.0	34.4
Residual	0.0	0.0	57.3	49.4	42.2	0.0	14.4

Table 20 - Sediment cores, chemical speciation (% in each fraction)

Globe Road - 14.0 km downstream

Depth 45 - 50 cm	Arsenic %	Cadmium %	Chromium %	Copper %	Lead %	Mercury %	Zinc %
Exchangeable	1.9	25.0	0.0	2.5	1.3	0.0	2.6
Oxide & carbonate	0.3	15.3	7.5	12.7	16.3	0.0	6.6
Fe / Mn oxides	32.9	37.5	36.2	29.4	54.4	0.0	41.2
Organic	27.2	9.7	25.5	40.6	23.2	0.0	26.0
Residual	37.7	12.5	30.8	14.8	4.8	0.0	23.6

Depth 122 - 127 cm	Arsenic %	Cadmium %	Chromium %	Copper %	Lead %	Mercury %	Zinc %
Exchangeable	12.3	13.2	0.1	5.2	0.0	100.0	0.5
Oxide & carbonate	0.0	32.9	2.1	7.2	0.0	0.0	4.4
Fe / Mn oxides	0.0	28.7	15.0	36.2	52.9	0.0	21.3
Organic	48.1	7.2	17.7	29.6	33.5	0.0	32.4
Residual	39.6	18.0	65.1	21.8	13.6	0.0	41.4

Depth 212 - 217 cm	Arsenic %	Cadmium %	Chromium %	Copper %	Lead %	Mercury %	Zinc %
Exchangeable	16.6	25.5	0.0	3.7	0.0	0.0	0.8
Oxide & carbonate	0.0	3.9	0.7	4.2	0.0	0.0	1.7
Fe / Mn oxides	27.5	47.0	2.7	23.1	64.0	0.0	25.0
Organic	55.9	11.8	4.7	18.8	20.4	0.0	33.6
Residual	0.0	11.8	91.9	50.2	15.6	0.0	38.9

Depth 280 - 285 cm	Arsenic %	Cadmium %	Chromium %	Copper %	Lead %	Mercury %	Zinc %
Exchangeable	25.6	11.8	0.0	6.9	0.0	0.0	0.2
Oxide & carbonate	0.0	1.3	3.5	13.1	0.0	0.0	1.8
Fe / Mn oxides	0.0	25.0	9.2	17.8	67.7	0.0	26.7
Organic	74.4	6.6	19.8	34.5	18.6	0.0	37.0
Residual	0.0	55.3	67.5	27.7	13.7	0.0	34.3

Depth 360 - 365 cm	Arsenic %	Cadmium %	Chromium %	Copper %	Lead %	Mercury %	Zinc %
Exchangeable	25.2	16.0	0.0	9.5	0.0	0.0	1.1
Oxide & carbonate	0.0	0.0	3.1	11.0	0.0	0.0	2.5
Fe / Mn oxides	0.0	16.0	7.5	15.2	61.5	0.0	39.6
Organic	74.8	12.0	15.7	26.7	17.6	0.0	29.5
Residual	0.0	56.0	73.7	37.6	20.9	0.0	27.3

Table 21 - Sediment cores, chemical speciation (% in each fraction)

Knostrop - 19.0 km downstream

Depth 145 - 150 cm	Arsenic %	Cadmium %	Chromium %	Copper %	Lead %	Mercury %	Zinc %
Exchangeable	2.7	8.9	0.1	3.2	0.0	100.0	0.6
Oxide & carbonate	18.1	47.2	9.3	7.4	40.1	0.0	38.9
Fe / Mn oxides	34.0	32.8	40.3	18.3	42.3	0.0	43.9
Organic	16.7	9.4	27.1	49.3	16.3	0.0	8.6
Residual	28.5	1.7	23.2	21.8	1.3	0.0	8.0

Depth 226 - 231 cm	Arsenic %	Cadmium %	Chromium %	Copper %	Lead %	Mercury %	Zinc %
Exchangeable	7.3	14.9	0.0	3.9	0.0	0.0	0.5
Oxide & carbonate	4.3	24.4	8.4	12.9	37.3	0.0	26.1
Fe / Mn oxides	20.4	15.3	47.9	18.3	42.6	0.0	47.7
Organic	40.9	4.1	25.4	50.7	17.5	0.0	16.6
Residual	27.1	41.3	18.3	14.2	2.6	0.0	9.1

Table 22 - Sediment cores, chemical speciation (% in each fraction)

Copper Works - 23.0 km downstream

Depth 35 - 40 cm	Arsenic %	Cadmium %	Chromium %	Copper %	Lead %	Mercury %	Zinc %
Exchangeable	2.6	49.4	0.3	2.6	4.1	0.0	19.3
Oxide & carbonate	0.2	12.8	3.2	9.6	11.0	3.3	7.7
Fe / Mn oxides	21.9	29.1	60.3	28.1	62.0	64.7	29.6
Organic	17.2	2.9	24.7	37.1	13.9	32.0	20.1
Residual	58.1	5.8	11.5	22.6	9.0	0.0	23.3

Depth 114 - 119 cm	Arsenic %	Cadmium %	Chromium %	Copper %	Lead %	Mercury %	Zinc %
Exchangeable	0.8	22.2	1.9	7.3	12.7	16.9	4.1
Oxide & carbonate	0.0	7.2	1.9	21.2	7.9	7.5	2.3
Fe / Mn oxides	27.7	34.6	11.8	23.0	47.0	51.7	17.3
Organic	0.0	7.2	15.7	23.4	13.0	23.9	33.1
Residual	71.5	28.8	68.7	25.1	19.4	0.0	43.2

Depth 211 - 216 cm	Arsenic %	Cadmium %	Chromium %	Copper %	Lead %	Mercury %	Zinc %
Exchangeable	3.8	13.7	1.1	10.0	13.7	5.0	2.6
Oxide & carbonate	16.1	8.1	1.4	22.2	13.4	15.7	1.3
Fe / Mn oxides	66.8	38.3	6.3	14.3	30.5	78.5	15.9
Organic	0.0	6.0	9.7	26.1	12.1	0.8	33.7
Residual	13.3	33.9	81.5	27.4	30.3	0.0	46.5

Depth 299 - 304 cm	Arsenic %	Cadmium %	Chromium %	Copper %	Lead %	Mercury %	Zinc %
Exchangeable	0.0	29.1	0.3	3.8	10.1	2.4	5.2
Oxide & carbonate	2.3	10.6	0.5	12.9	13.9	1.1	3.1
Fe / Mn oxides	44.3	37.0	2.7	19.7	42.0	22.1	17.8
Organic	0.0	5.3	4.1	30.3	14.6	0.0	41.6
Residual	53.4	18.0	92.4	33.3	19.4	74.4	32.3

Depth 394 - 399 cm	Arsenic %	Cadmium %	Chromium %	Copper %	Lead %	Mercury %	Zinc %
Exchangeable	0.0	4.6	0.0	9.9	7.9	20.8	5.6
Oxide & carbonate	8.7	22.9	0.5	16.9	18.8	0.9	6.2
Fe / Mn oxides	22.7	59.9	2.3	27.5	43.6	28.0	20.3
Organic	6.1	12.6	5.1	27.1	8.7	7.0	36.6
Residual	62.5	0.0	92.1	18.6	21.0	43.3	31.3

Depth 483 - 488 cm	Arsenic %	Cadmium %	Chromium %	Copper %	Lead %	Mercury %	Zinc %
Exchangeable	0.0	20.0	0.9	11.0	41.6	9.1	16.2
Oxide & carbonate	0.0	13.3	0.4	24.4	20.1	3.1	7.7
Fe / Mn oxides	46.7	40.0	1.6	24.0	16.1	39.4	22.2
Organic	9.5	26.7	1.2	20.6	5.6	12.2	15.3
Residual	43.8	0.0	95.9	20.0	16.6	36.2	38.6

Table 23 - Sediment cores, chemical speciation (% in each fraction)

Swillington Bridge - 26.0 km downstream

Depth 48 - 53 cm	Arsenic %	Cadmium %	Chromium %	Copper %	Lead %	Mercury %	Zinc %
Exchangeable	12.6	6.7	0.0	6.1	0.0	0.0	0.0
Oxide & carbonate	0.0	0.0	2.5	7.1	0.0	0.0	6.3
Fe / Mn oxides	0.0	33.3	9.4	18.6	72.7	0.0	25.1
Organic	30.4	20.0	17.7	28.1	21.5	0.0	30.7
Residual	57.0	40.0	70.4	40.1	5.8	0.0	37.9

Depth 133 - 138 cm	Arsenic %	Cadmium %	Chromium %	Copper %	Lead %	Mercury %	Zinc %
Exchangeable	22.0	27.3	0.0	3.3	0.0	0.0	0.8
Oxide & carbonate	0.0	3.0	2.4	4.5	0.0	0.0	3.0
Fe / Mn oxides	0.0	66.7	24.8	66.8	91.2	0.0	56.3
Organic	58.7	3.0	16.8	14.3	8.8	0.0	21.8
Residual	19.3	0.0	56.0	11.1	0.0	0.0	18.1

Depth 197 - 202 cm	Arsenic %	Cadmium %	Chromium %	Copper %	Lead %	Mercury %	Zinc %
Exchangeable	1.9	20.8	0.0	8.0	0.0	0.0	1.8
Oxide & carbonate	0.0	18.8	4.9	14.5	0.0	0.0	3.4
Fe / Mn oxides	0.0	54.1	10.9	24.2	52.1	0.0	35.2
Organic	55.6	6.3	25.5	25.4	12.2	0.0	32.4
Residual	42.5	0.0	58.7	27.9	35.7	0.0	27.2

Depth 266 - 271 cm	Arsenic %	Cadmium %	Chromium %	Copper %	Lead %	Mercury %	Zinc %
Exchangeable	22.9	28.8	0.0	8.4	0.0	0.0	4.6
Oxide & carbonate	0.0	15.3	2.6	10.2	0.0	0.0	7.7
Fe / Mn oxides	0.0	30.5	9.8	18.3	80.4	0.0	43.3
Organic	57.4	8.5	16.8	36.5	19.6	0.0	29.5
Residual	19.7	16.9	70.8	26.6	0.0	0.0	14.9

Depth 377 - 382 cm	Arsenic %	Cadmium %	Chromium %	Copper %	Lead %	Mercury %	Zinc %
Exchangeable	6.0	8.3	0.0	6.2	0.0	0.0	1.7
Oxide & carbonate	0.0	4.6	3.2	8.2	0.0	0.0	5.0
Fe / Mn oxides	0.0	30.6	6.5	26.3	54.5	0.0	31.7
Organic	31.5	2.8	13.6	21.1	22.0	0.0	17.8
Residual	62.5	53.7	76.7	38.2	23.5	0.0	43.8

APPENDIX V

RESULTS DATA, SEDIMENT & HEAVY METAL BUDGETS

Calculations:

Total suspended sediment concentrations, associated metal concentrations and dissolved metal concentrations transported, were calculated in the following way:

$$SS = Q \times ss$$

where SS = total suspended sediment transported (g/s → tonnes/annum)
Q = discharge (m^3/s)
ss = suspended sediment concentration (mg/l → g/m^3)

$$MC = mc \; / \; 1{,}000{,}000 \times ss \times Q$$

where MC = total metal tranported (g/s → kg/annum)
mc = metal concentration in sediment (mg/kg → mg/l → g/m^3)

$$DM = Q \times dm$$

where DM = total dissolved metal transported (μg/s → kg/annum)
dm = dissolved metal concentration (μg/l → $\mu g/m^3$)

The total amount of leached heavy metals from the alluvial aquifer were calculated in the following way:

$$L = mc \times ps \times aa$$

where L = total metals leached (($\mu g.mm.m^2$) / (l.yr) → kg/annum))
mc = metal concentration in the alluvial aquifer (μg/l)
ps = precipitation surplus (mm/yr)
aa = alluvial area (m^2)

Note: → indicates unit of measurement transformation from calculated result to figure utilised.

Table 1 - Average discharge and suspended sediment concentration for 1996

	Discharge m^3/s	Suspended sediment mg/l
Apperley Bridge	7.35	22.50
Swillington Bridge	13.25	20.17
Knostrop STW	2.71	25.52

Table 2 - Average solid-bound metal concentration, River Aire, 1996

	Solid-bound metal concentration (mg/kg)
cadmium	10.22
copper	1054.85
lead	131.04
zinc	5167.46

Table 3 - Average dissolved metal concentration, 1996

	Dissolved metal concentration (µg/l)			
	Apperley Bridge	Swillington Bridge	River Aire	Knostrop STW
cadmium	0.11	0.21	0.11	0.15
copper	6.31	6.70	4.80	6.23
lead	1.27	2.15	1.41	2.12
zinc	23.94	26.83	21.41	21.41

Table 4 - Storage of sediment & heavy metals in the River Aire in Leeds

	Short-term storage stream domain	Long-term storage floodplain domain
volume of soil / sediment (m^3)	33696	1374000
bulk density (Mg)	1.2	1.6
sediment (tonnes)	33696	21984000
cadmium (kg)	209	81341
copper (kg)	2426	2506176
lead (kg)	5358	2857920
zinc (kg)	9064	4352832

Table 5 - Average heavy metal concentrations in flood sediments & contemporary within channel sediment

	Flood sediments (mg/kg)	Within channel sediment (mg/kg)
cadmium	8.5	3.8
copper	106.5	71.9
lead	147.1	107.2
zinc	742.3	236.9

Table 6 - Heavy metal concentrations in the Leeds atmosphere, 1993

	Annual average, 1993 (ng/m^3)
cadmium	0.45
copper	7.00
lead	60.00
zinc	54.00