An evaluation of river catchment quality in relation to restoration issues.

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An Evaluation of River Catchment Quality in Relation to Restoration Issues.

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Tables and Figures:

Abstract

Soil samples from the surface and subsurface of the floodplain of the River Rother were analysed for selected heavy metal concentrations at 12 locations along the river in order to discover whether the high concentrations, reported in previous studies from 1982 to 2002, had changed. The aim was to review the levels of heavy metal contamination along the floodplain of the Rother.

Thirty-seven soil samples were taken along the River floodplain, at different sites and from different depths, collected in two phases. Samples collected, were dried, ground, digested and analysed by Atomic Absorption (AA) and Inductively Coupled Plasma (ICP) techniques.

While the results from up-stream sites were mainly satisfactory, according to the New Dutch List Standard and Kelly Indices, the results obtained from downstream sites were variable probably due to a flood event (November 2002) and/or earlier tipping of wastes.

Previous research identified a major heavy metal contamination plume within the sediments along the Rother. By 1995 the plume appears to have divided with one part migrating faster and therefore separating from the second (Duty, 1995). This is further supported by the evidence presented for lead and zinc (Figure 6.1). The present study confirms the two plumes at Renishaw and at Catcliffe indicating a further migration even over the short timescale.

Natural hydrological cleansing processes will continue to operate but may accelerate with increases in periods of heavy rainfall causing more flood episodes to occur. Even though there is metal contamination it is not having a deleterious effect on the biodiversity present along the river corridor.

Recommendations for reclamation are presented for the purpose of cleaning up the contamination and reusing the derelict land in some meaningful way. The areas of heavy contamination have been subject to major clean-up processes involving not only the removal or burial of the metals but re-landscaping the sites to make them suitable for active recreation. Examples of such reclamation have been completed at Poolsbrook and Rother Valley Country Park and are still being carried out at the present time at the Avenue site and at Orgreave.

The implications for the future use of the river corridor as part of the leisure and tourism scene look very good as the worst sites are reclaimed and the others are given over to passive recreation and conservation.

If such actions are taken then all areas of the floodplain have the potential for re-use at some future date when the river corridor, at surface level, would be clean and restored to a tranquil fluvial environment with floristically rich riverside meadows interspersed with sites of active water-based recreation..

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CHAPTER 1 : INTRODUCTION

1. Introduction

1.1 Introduction

The industrial revolution and associated developments in the United Kingdom during the eighteenth and the nineteenth centuries are recognized as having a huge impact on the environment (Goudie, 1977). Associated with these impacts significant contamination occurred on land and water around the affected sites (Goudie, 1977), especially in areas where heavy industrial plants were established.

Since heavy metals do exist naturally in the environment, emitted from natural sources, they are generally of low concentrations. However, greatly increased concentrations may occasionally cause a problem. This may lead to their incorporation into the food chain by methylation, which occurs in side reactions in plants and in contaminated sediments. One of the most disturbing aspects of this phenomenon is not the incorporation of the heavy metals into the food chain at ambient water pollution levels, but of their incorporation into concentration gradients that occur in both plants and bio-concentration (DoE, 1976).

The River Rother and its catchment was one such area affected (EA, 1990s reports). As a sequence of industrial developments in the late eighteenth century and early nineteenth century led to a period of gross pollution of this environment it was converted to a grossly polluted river with associated river landscape features substantially degraded.

A number of studies have been carried out over the last twenty years to measure and evaluate the heavy metals and other contamination of the sediments of the Rother and the other associated local rivers. These include the rivers Hipper, Whitting, Drone, and Doe Lea.

The catchment area of the local rivers Don and Rother is bordered by the Calder and lower Aire catchment to the north, the Pennines to the west and the

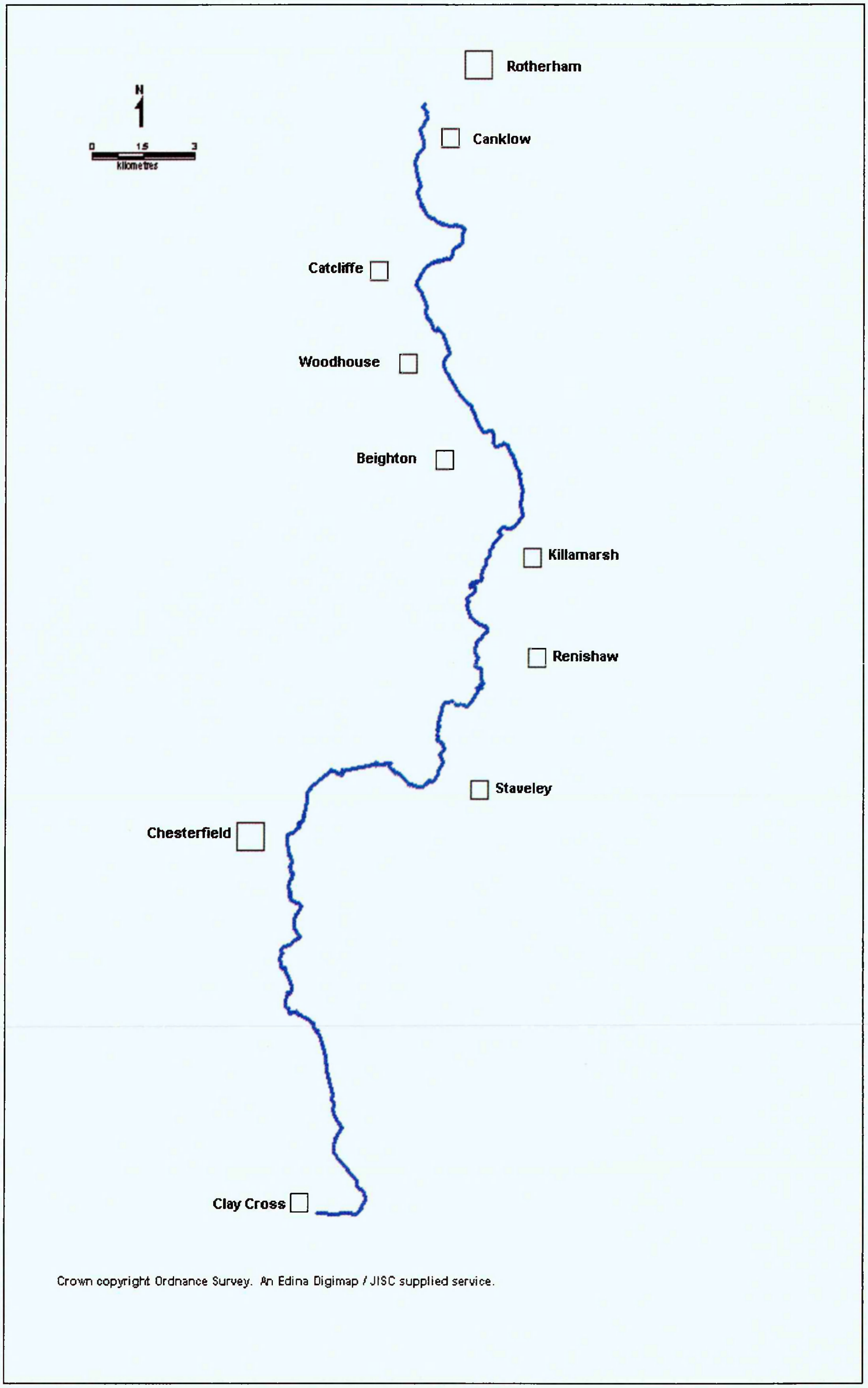
Trent catchment to the south-east (Figure 1-1 shows the River Rother Clay Cross to Rotherham).

1.2 Study Area

The River Rother, which lies within the southern operating division of the Environment Agency (EA) and Yorkshire Water plc – formerly Yorkshire Water Authority (YWA), flows from the south of Chesterfield to Rotherham (Murfin, 1988).

The Rother catchment falls within the North East region of the Environment Agency (EA) - formerly National Rivers Authority (NRA) - which has responsibilities concerned with pollution control, fisheries, water resources and flood defence. The headwaters of the Rother are located in the Peak District National Park including one of its main tributaries, the river Hipper. The Rother flows through the urban and industrial areas of Chesterfield, North East Derbyshire and South Yorkshire before its confluence with the River Don near Rotherham town centre. The average rainfall of the catchment is 733mm, varying between 850mm at Linacre Reservoirs in the Peak District National Park (SK 424 921) and 640mm at Woodhouse Mill Sewage Treatment Works in Sheffield (SK 432 857). The average river flow measured at Woodhouse Mill is 410 Megalitres (Ml) per day but this ranges between less than 100 Ml /day in dry weather and over 6000Ml/day in severe flood conditions.

Figure 1-1 Map showing the River Rother from Clay Cross to Rotherham



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1.3 Water Quality Control in UK

Responsibility for controlling water pollution has been exercised by different organizations in different parts of the United Kingdom. In mainland Scotland, it rests with the seven river purification authorities, and the Scottish Islands Councils. In Northern Ireland, protection of river quality is a function of the Department of the Environment for Northern Ireland.

In England and Wales, control of water pollution was until recently the responsibility of ten water authorities, which were established in 1974 but on 1st September 1989 this responsibility passed to the National Rivers Authority (NRA) as a new independent body established under the provisions of the Water Act 1989.

As well as its pollution control activities, the NRA's responsibilities included the management of water resources, the protection of land and property from flooding, the promotion of nature conservation and recreational activities, and the maintenance and development of inland fisheries.

Since 1958 a series of surveys has been carried out to assess the quality of rivers water, canals and estuaries in England and Wales. A survey was completed in 1990 that used a classification scheme in which four quality categories were identified (table 1-1).

1n April 1996 the NRA became the Environment Agency (EA) but retained the same activities and responsibility of controlling the water resources in England.

The 1990 River Quality Survey showed that river and estuary quality in the UK was generally very high (Anon, 1996). The National Rivers Authority (NRA) reported that of nearly 40,000 kilometres of rivers surveyed in England and Wales, almost 90% was classified as being of good or fair quality.

Since 1958 there has been an overall improvement in the quality of river water.

Old system		New system	
Class	Comment	Class	Comment
		1A	High quality
1	Unpolluted	1B	Good quality
2	Doubtful	2	Fair quality
3	Poor	3	Poor quality
4	Grossly polluted	4	Bad quality

Table 1-1 **Old and new river classification (Environment in Trust, 1990).**

This research considers the pollution in light of Netherlands Standards for Soil Contaminations, the Department for Environment, Food and Rural Affairs (DEFRA) standards, and inorganic contaminants of soils in England and Wales (1998) (see Appendix 5).

1.4 The History of the Rother and its valley:

Industrial pollution of the River Rother dates back to the middle of the eighteenth century after the industrial revolution started in England. This had a huge impact in both Derbyshire and Yorkshire. The area abounds with water resources such as rivers, and energy resources such as coal. In the early eighteenth century, the Rother and Upper Don Valleys were still providing some of the finest countryside in the area.

These rivers supported around thirty-six species of fish along with otters and a host of other local flora and fauna. In 1840 it was reported in the *Doncaster Journal* that fishermen had recorded thirty-eight species of fish in the river and that salmon, trout and otters were a “common sight” (Murfin, 1988). After the 1850s, the diversity of fish in the river depleted rapidly and the last recorded otter was a specimen shot near the old Hartington Colliery at Staveley in 1895 (Murfin, 1988). The quality of the Rother fell quickly as a result of the industrial development in the middle of the eighteenth century. By the late 1900s, approximately, 64% of the Rother’s 49 km length fell into the lowest classification “poor” (Duty, 1995). It was reported that the river had become a victim of the industrial revolution.

Much of the industrial pollution of the past has come from steel, mining, chemical works and sewage treatment works. The following pages contain maps showing the historical background to Rother industrial purposes. (Fig 1-2, 1-3, 1-4 and 1-5).

In 1850 (Fig 1-2), the River Valley was dominated by water-powered mills, some of which were corn mills while others were used for iron and steel trades. Some collieries, such as Grassmoor, Halfway, Ballifield and Millmoor, were in operation by 1850 and were discharging mine waters to the Rother.

The valley formed the routeway of the Great Central Railway Company to build its line linking Nottingham with Chesterfield and Sheffield prior to 1850.

During the later part of the nineteenth century massive industrialization took place, led by the Victorians, who sank collieries and created iron and steel works along the Rother Valley. Coal processing was commonplace for the production of coke.
All these industries used water from the river and also discharged their waste back into the river.

During the Victorian period the Midland Railway Company expanded its system by adding new lines between Derby, Clay Cross, Chesterfield and Rotherham. This line serviced most of the collieries along the Rother valley and facilitated the export of the coal to other parts of Britain.

Increases in the working population was catered for by an expansion in house building and the development of improved sewage systems leading to increased discharges from the various sewage works sited along the valley floor.

Towards the end of the twentieth century much of the famed industrial strength of the valley was lost through the closure of the collieries and attendant coke works. Several of these sites have been cleansed and reclaimed either for smaller industrial and business parks or for recreational space, such as at Poolbrook and Rother Valley Country Park.

Other sources of pollution that now affect the water quality in the area are abandoned mine waters, contaminated land and agriculture. In addition to the industrial contamination sources was the combined effect of organic pollution (Table 3) resulting from inadequately treated sewage (Firth, 1997).

In the 1980s and early 1990, mercury was identified as one of the main pollutants affecting the River Rother. The source of mercury in the Rother was derived from the chlor-alkali plant at Rhône-Poulenc Chemicals Ltd., formerly Staveley Chemicals situated in Staveley, near Chesterfield (Duty, 1995).

Figure 1-2 The distribution of industrial sites along the River Rother in 1850.

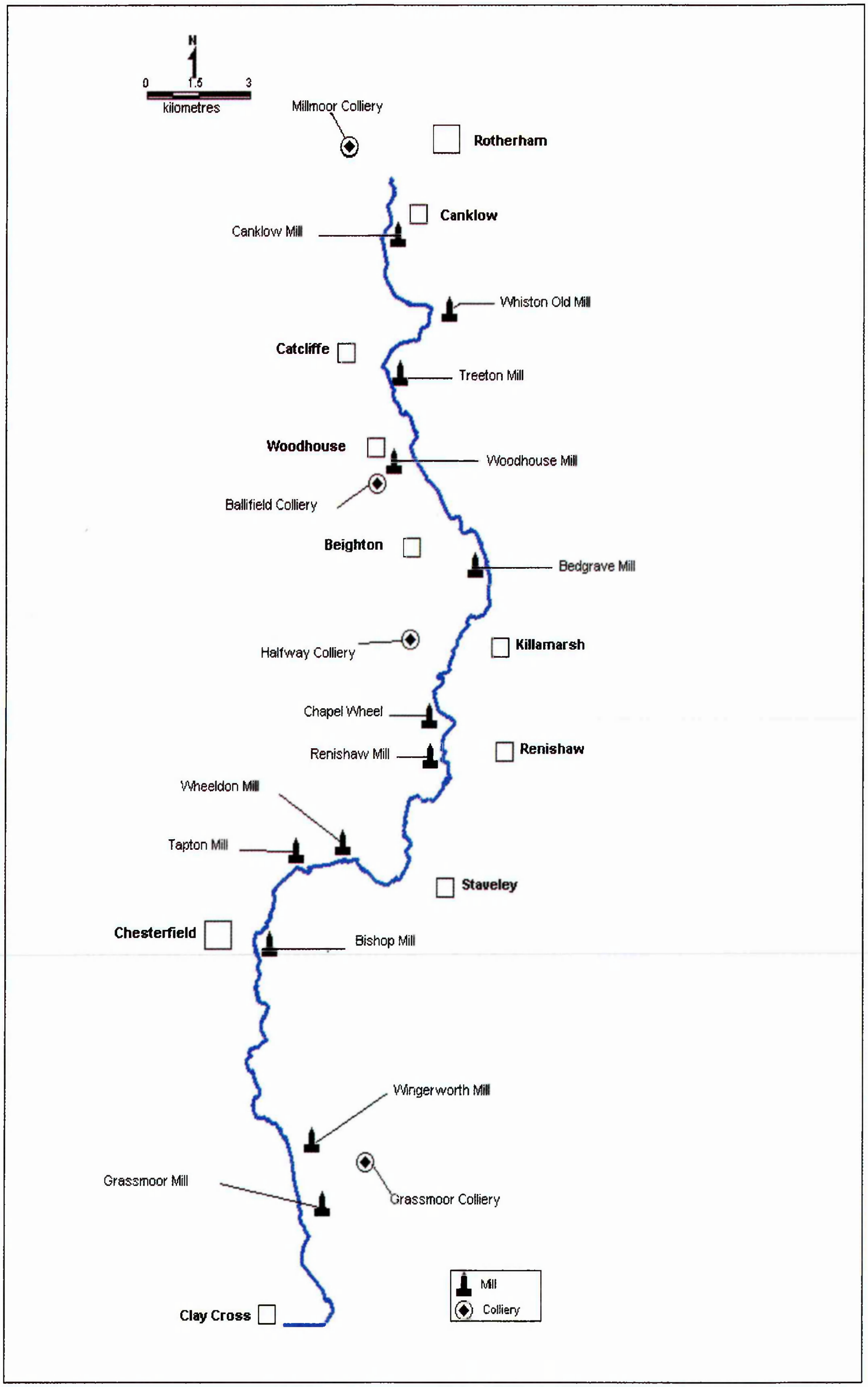

Figure 1-3 The distribution of industrial sites along the River Rother in 1900.

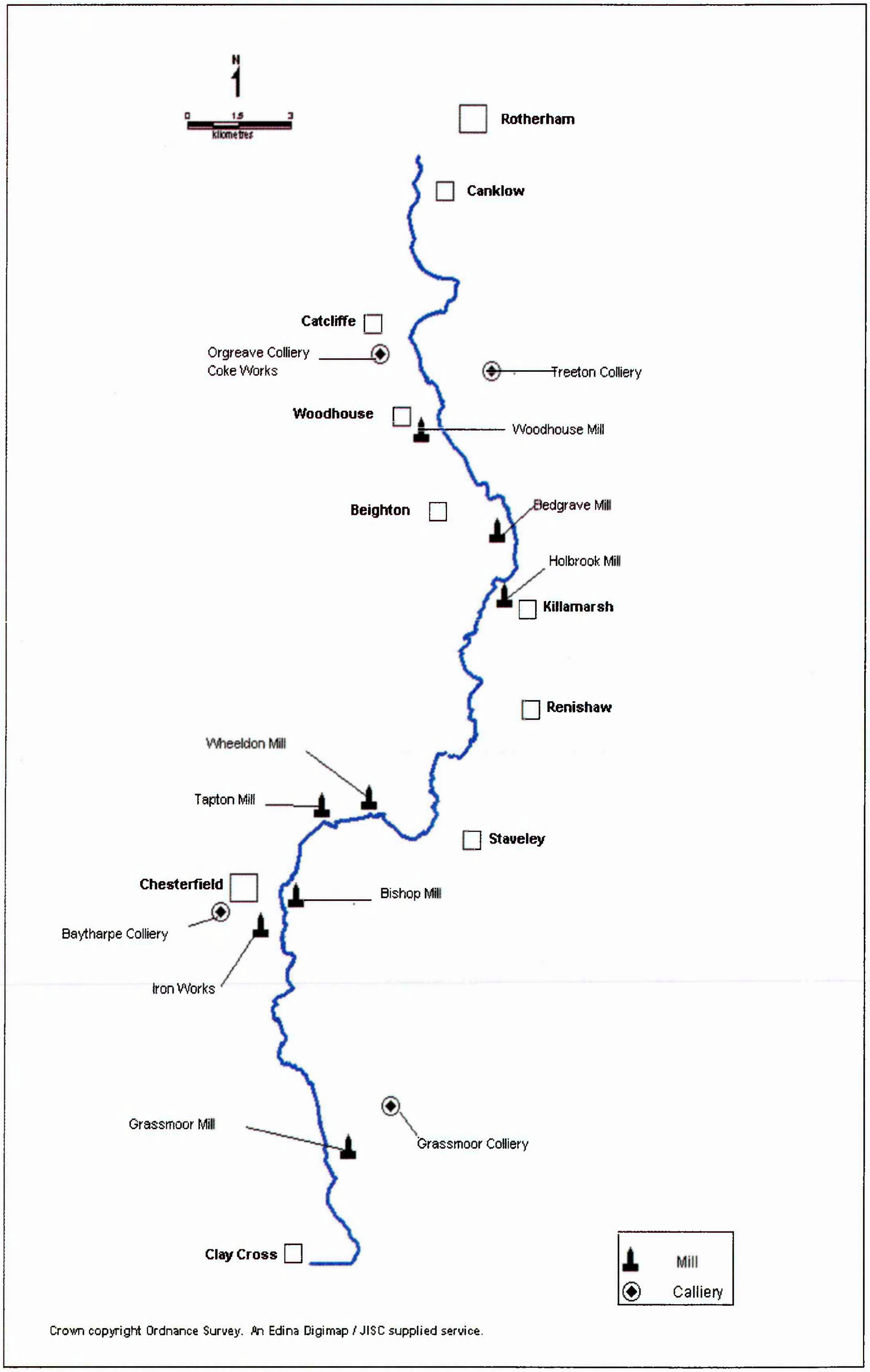

Figure 1-4 The distribution of industrial sites along the River Rother in 1960.

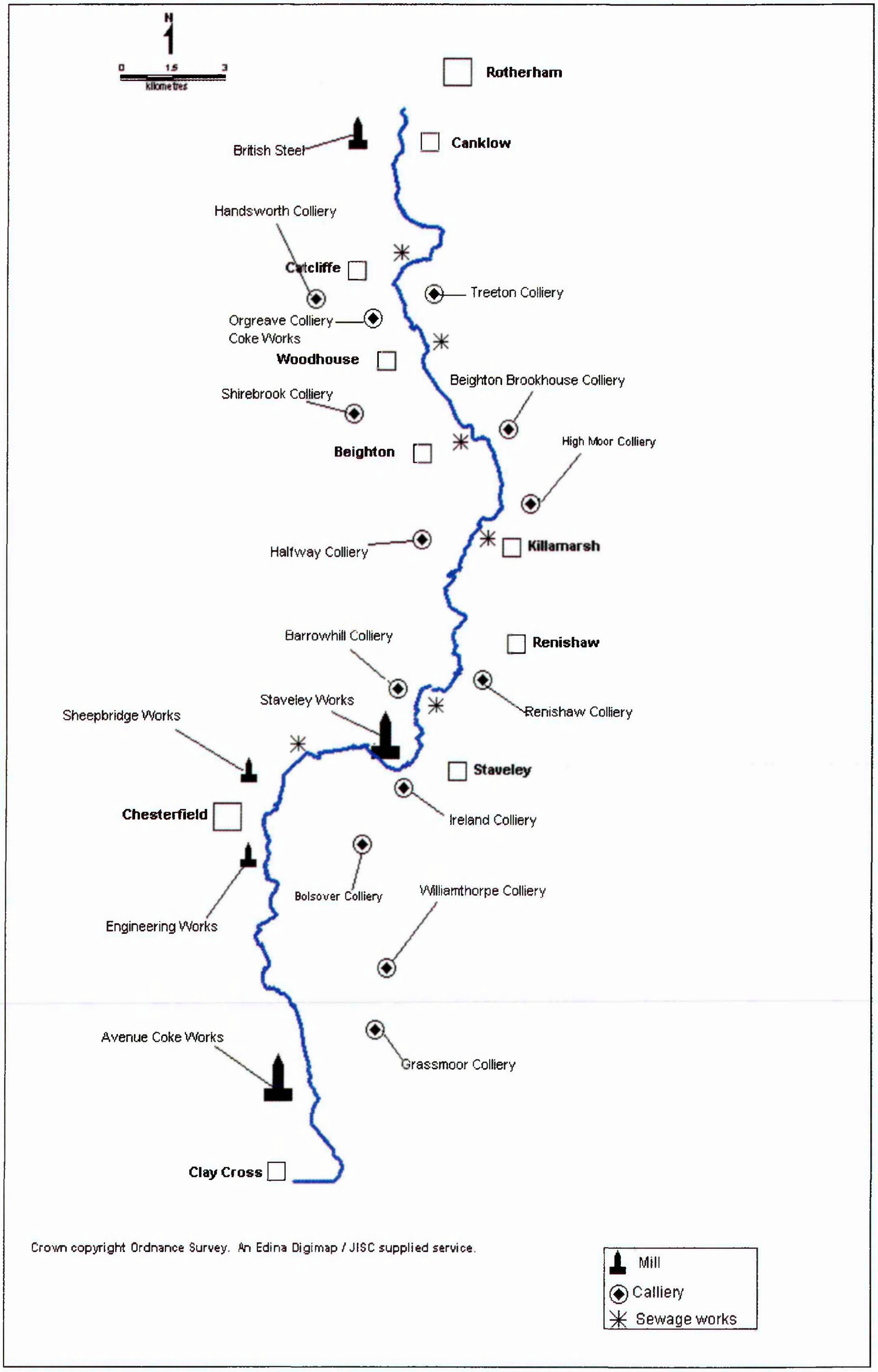

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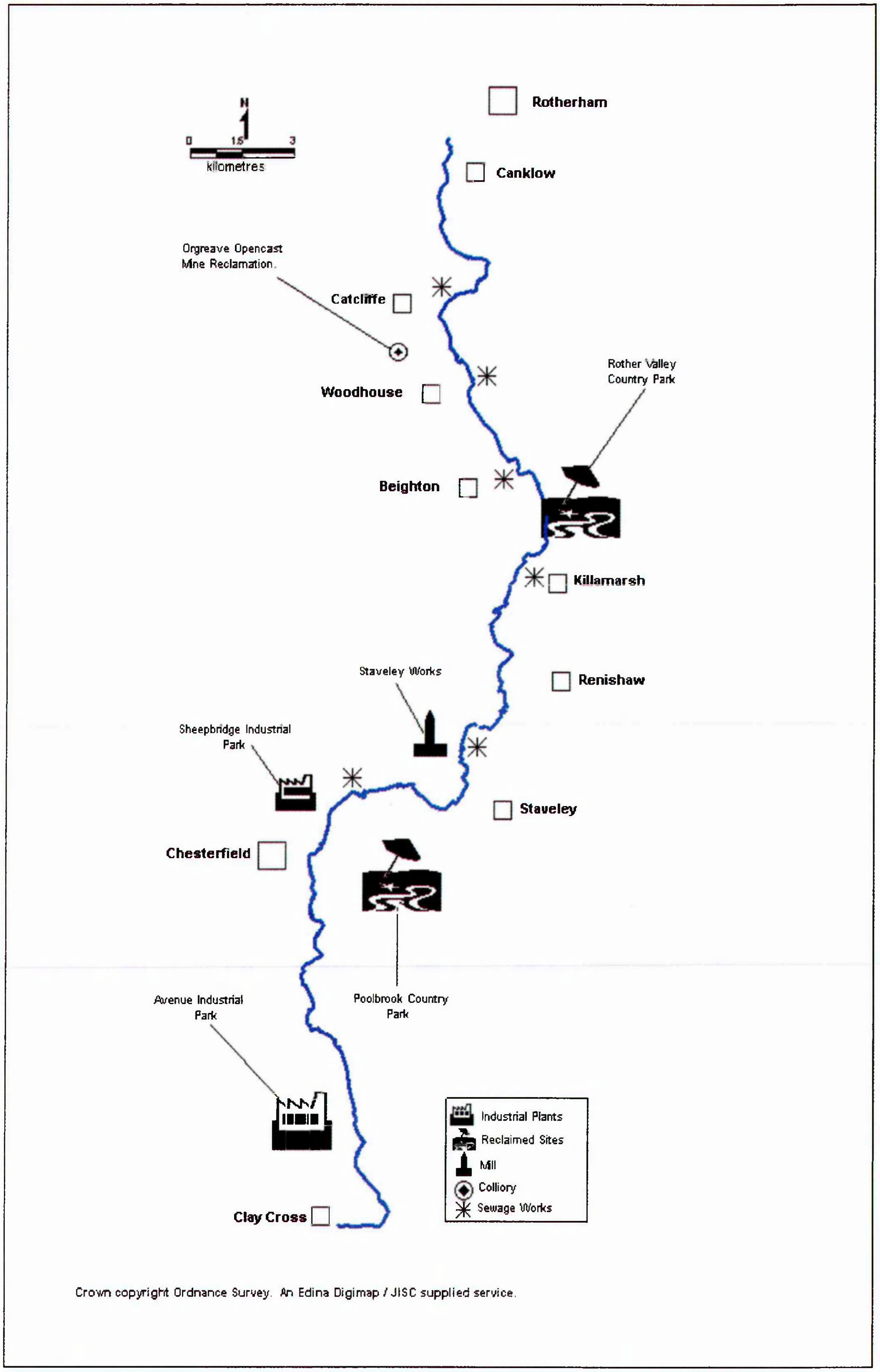
Figure 1-5 The distribution of industrial and reclaimed sites along the river Rother in 2000.



1.4.1 Rhône-Poulenc Chemicals Ltd. (Staveley Chemicals Ltd.)

Rhône-Poulenc Chemicals Ltd., formerly Staveley Chemicals, occupies a single site covering an area of 75 hectares and houses administrative offices and four principle manufacturing units: sulphuric acid and chlor-alkali plant, benzole-benzene refinery and dichloroaniline plant (Anon., 1993).

The most significant on the site was the chloro-alkali plant, established in 1921, which produced several kinds of chemicals for trade purposes including chlorine, caustic soda, hydrogen and sodium hypochlorite. These are reagents utilized in chemical manufacture, water treatment, disinfection and bleaching. The pollution occurred because the plant was discharging its effluent into the river following insufficient treatment (Duty, 1995).

The annual levels of the mercury amount lost from the chloro-alkali system have been estimated to be:

The system	**The estimated amount**
From chlorine system.	<1g/tonne of product.
From brine system.	Up to 50g/tonne.
From hydrogen system.	<1g/tonne.
From caustic soda system.	15-20g/tonne.
From caustic wastewater.	<10g/tonne.
From ventilation system.	15-25g/tonne

Table 1-2 The estimation of loss levels of mercury from the chloro- alkali system (Duty 1995).

Pathways of mercury loss from the plant may be as follows (Biokon, 1978):

1. Dissolved mercury escapes with the gaseous chlorine and hydrogen, and the aqueous sodium hydroxide products.
2. Mercury vapour is lost from the intermediate and end boxes of the electrolysis equipment.
3. The mercury spilt during maintenance or other handling is washed into sumps for recovery.

4. Mercury dissolved in wash water requires separate treatment.

The total losses from a typical system have been estimated to be 200g per tonne of chlorine the equivalent to a 5% loss of the annual inventory (Harrison, 1992). It was estimated that the total mercury burden on the Rother might have been over 4 tonnes of mercury since the plant was established in 1921.

In recognition of the problems associated with pollutants in general, The European Community introduced Directive 76/464/EEC, known as the (Dangerous Substances Directive). The European Community issued two Directives relating to mercury emission into water in the early 1980s (Barfield, 2001). The Directive, which is of greatest interest, is (Dangerous Substances Directive 76/464). This Directive seeks to establish a framework for the elimination or reduction of specified pollutants in inland, coastal and territorial waters.

The Directive spawned several pollutant specific papers. The proposal that affected the Rother was the Council Directive on the control of list one substances (Table 3) particularly the directive 82/176, (proposed 14/6/79), "Limit values and quality objectives for mercury discharges by the Chlor-alkali Electrolysis industry".

This Directive is concerned with only mercury from List One.

Yorkshire Water then used the aims of these Directives to set up limits, eventually, resulting in Rhône-Poulenc Chemicals Ltd. (Staveley Chemicals) installing a plant to remove the mercury from the wastewater by absorbing it onto a resin bed and binding it chemically in solid form. This plant is called the Total Mercury Recovery (TMR). TMR was successful in reducing mercury levels in discharged water from entering the river (Firth, 1997) (Figure 1-6).

1- Organohalogen compounds and substances which may form such compounds in the aquatic environment. *Organo-fluorine: aerosols, refrigeration, water treatment, metals preparation (degreasing).* *Organo-chlorine: insecticides, paper manufacture.* *Organo-bromine: automotive anti-knock compounds, flame-proofing, fumigants.* *Organo-iodine: photography, medicine.*
2- Organophosphorus compounds. *Phosphate esters flame proofing cotton & synthetic materials, petroleum additive, solvents.*
3- Organotin compounds. *Fungicides, wood preservatives, plastic stabilisers.*
4- Substances in respect of which it has been proved that they possess carcinogenic properties or via the aquatic environment
5- Mercury & its compounds. *Electroplating equipment (switches), batteries, pesticides, catalysers*
6- Cadmium & its compounds. *Electroplating, batteries, metal alloys, pigment (e.g. plastics, phosphors in televisions)*
7- Persistent mineral oils & hydrocarbons of petroleum origin. *Cyanides, dyes, organic, synthesis, plastics*
8- Persistent synthetic substances which may float, remain in suspension or sink & which may interfere with the use of the waters. *Solids e.g. plastic (bags/fibres/pieces of debris etc.), rubber, paints, solvents, oils, emulsions (anti-foam agents etc.)*

Table 1- 3 List One substances as detailed in Directive 76/464/EEC, including examples of origin **(Blanksby & Doncaster, 2000).**

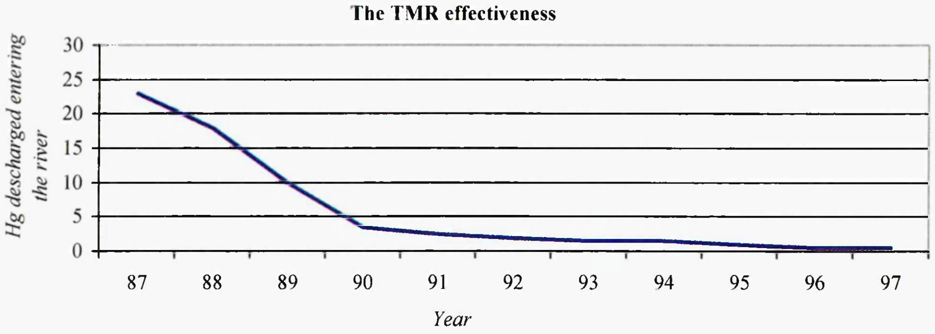


Figure 1-6 Levels of mercury in discharged water entering the River Rother

In other words, implementation of controls following the EC Directive has succeeded in bringing mercury levels in the river water down to acceptable levels. However, the mercury levels in the river Rother sediments were still high in the late 1980s (Murfin, 1988).

Murfin in his study in 1988, following detailed analysis of the characteristics and case history of the sediments and environmental conditions, concluded that the full recovery of the Rother to an acceptable amenity standard could not occur in the near future.

The Environment Agency (EA), which was formerly called the National Rivers Authority (NRA), had a big role to play in improving the Rother by setting tough standards for effluent discharges in relation to quality objective and standards set for the receiving waters.

1.5 Geographical Information System (GIS)

It is useful to introduce the Geographical Information System (GIS), in terms of background to the system and its potential to publish the maps used to represent the history of the Rother and its valley. Also the program is used to show the sites along the River.

The Geographical Information System (GIS) is a computer-based system to input, store, manipulate, analyse and output spatially referenced data. The program can be used aid to the study of ecological phenomena (Wadsworth and Treweek, 1998).

Maps have always per-formed an important role in environmental study and will no doubt continue to do so. It is therefore worth considering what it is that makes GIS potentially more useful than straightforward paper maps in the study of ecological phenomena.

1.5.1 The Origins and History of GIS

Historically maps have been used to obtain spatial information about the world. In fact, until relatively recently, the paper maps, sometimes with a memoir, were the only form of spatial database that existed. Maps have been around since the dawn of civilization and GIS with its roots in mapping technology has a surprisingly long history (Maguire *et al.,* 1991) (Wadsworth and Treweek, 1998).

Developments in computer technology in the 1960s and 1970s made it possible to automate the mapping process (digital cartography), thereby removing some of these limitations. As well as making it quicker, easier and cheaper to produce and update maps, additional benefits of automation soon became apparent. These included the ability to create maps for specific users, experiment with different graphic representations, facilitate interactions between statistical analyses and mapping and more easily control the effects of classification and generalisation on the quality of input data.

While GIS evolved out of the application of computers to cartography, GIS and digital cartography should not be considered identical. A GIS does not actually contain maps: rather it contains the information from which maps can be generated. A GIS can also be distinguished from database management systems or from visualization packages through its specialized capability for spatial analysis. As well as new ways to produce maps, new ways to collect and process data have appeared over the last few decades. These include satellites, which provide synoptic information over large areas at frequent intervals, and global positioning system (GPS), which allow for the collection of point data without the need for an extensive and expensive ground control network. For environmental scientists, the availability of new sources of data combined with the GIS technology needed to store, interpret and display it has opened up whole new areas of research and application.

1.6 Research Programme

The major aim of this research is the evaluation of the quality of floodplain sediments along the valley of the River Rother in relation to the contamination and recovery of a major industrial river catchment.

The industrial revolution in the UK during the eighteenth and the nineteenth centuries and associated developments, are recognized as having huge impacts on the environment. Associated with these impacts significant contamination occurred on land and water particularly in areas adjacent to industrial plants.

1.7 Aims and Objectives

The research has a number of primary aims:

The first is to enhance the understanding of the role of industrial contamination in the functioning of the river catchment, and its implications for conservation and economic regeneration.

This aim has three main secondary components:

1. To evaluate the contaminated floodplain soils in a major river catchment;
2. To assess the pollution impact of aquatic habitats and adjacent floodplain;
3. To understand the implications of the historical aspects of (1) and (2) for any resolution of the environmental conditions of the catchment, and in particular for conservation, leisure and tourism use.

To achieve these several aims key objectives were set:

1. To carry out a desk study and literature search of previous work on the Rother;
2. To evaluate the location of industrial contamination sources along the catchment;
3. To examine the links between the historical contamination and the present day environment;
4. To review information on the contamination up to the present time;
5. To carry out site sampling of the River Rother watercourse (selected floodplain soil samples);
6. the development of a "model" to determine the downstream migration of pollutant and any influence of trapped contamination.

This research forms part of an ongoing study looking at heavy metals contamination in the River Rother undertaken approximately every five years.

At the outset of this project, the River Rother had recently suffered a 1 in 100 years flood episode.

1.7.1 Plan of Work

In order to organise the necessary work and achieve the project objectives, a plan was made with two broad areas of work: theoretical and practical. The theoretical work included the critical literature review, information analysis and a detailed site assessment.

For the determination of appropriate methodology, the focus was to find an appropriate sampling strategy, and assess appropriate methods of analysis for critical pollution and carry out necessary evaluation.

The practical work included visiting the sites and both collecting and analysing the samples.

Core samples were taken from the sediments at the selected sites along the river floodplain. These were as near as possible to those sites used in earlier studies.

Plan of work:
Literature Review: (see Chapter 2, p. 21, and Chapter 3, p. 43)
Developing Methodology: (see Chapter 4, p. 64)
Sampling Techniques: (see Chapter 4, p. 65)
Analysis Techniques: (see Chapter 4, p. 70)

A scene-setting chapter ranging over the attributes of the River Rother and the history of industrialization along the valley which has caused the heavy metal pollution of the flood-plain sediments.
The chapter ends with a statement of the aim and objectives of the present investigation to monitor levels of heavy metals to ascertain if natural processes are moving the contamination downstream and what impact that may have on conservation and/or commercial development in the future.

CHAPTER 2: LITERATURE REVIEW

2. Literature Review

2.1. Introduction

The River Rother and its tributaries have a reputation for being one of the most contaminated rivers in England. In the late 1980s 33km of its length were classified as "poor" (Edwards, 1990). As a result, many studies have been carried out to survey the river sediments and its floodplain for heavy metal contamination.

Heavy metal contamination on a global scale is widely distributed in both surface and underground sediments such as rivers, lakes and wells. This reflects industrial developments around the world especially in the industrialised countries. Many studies have been carried out on this issue.

This literature review is organised historically in order to help the reader follow the sequence of published work and that done, in the area, over five year intervals. Work to address contaminants in local water sources has been similarly arranged in chronological order.

2.2 The Environment and the Attempts to Determine the Degree of Pollution

The decision to evaluate the quality of the soil and water resources started in the middle of this century. The assessment of previous industrial sites and their contamination problems was the main goal for many researchers who were concerned with environmental issues. However, the environmental issues were taken from different aspects in order to assess their importance to the human need and safety. The researchers deal with this issue according to their interests and concerns.

"Like ecology, the environmental science is multi- and interdisciplinary" (Ehrlich *et al.*,1977). The author builds his book on three main sub-disciplines of environmental science and they are: population, resources and environment.

The growth of population could possibly be considered the essential cause of the environmental crisis. The rising, anthropogenic impact on the biosphere is a function of two factors: the human growth population and the environmental impact per person. These factors vary greatly among and within countries, mainly depending on the nature and level of industrialisation (Freedman, 1995).

The natural resources that are available to sustain human activities include; nonrenewable resources that exist in a limited supply, which are consumed by mining and use, and renewable natural resources that can provide a flow of materials or energy that are sustainable over the longer time. This can happen if the resources are managed correctly. However, unsuitable management or over-exploitation of any potentially renewable resource may corrupt it irrevocably.

The third sub-discipline is the environment. This sub-discipline of the environmental science deals with the ways in which the integrity of the biosphere, and of purely human environments, is affected by various anthropogenic and natural influences (Freedman, 1995).

The author (op.cit) states "the effects of pollution, disturbance and other stresses on natural and managed ecosystem are the primary subject material of this book. Although the purview of "environment" also includes the direct effects of pollution and other stresses on the health of humans, and their constructed environments in some respects these are not ecological issues because they do not deal with natural ecosystems and wild species" (Freedman, 1995, p.1-2). Nevertheless, a number of key aspects of these anthropocentric topics were addressed, especially with respect to air contamination, toxic elements, pesticides and warfare.

This book is concerned with the ecological effects of stresses, with particular reference to those associated with human activities upon the environment.
From the author's point of view, the massive growth of the human population should be kept in mind when starting to consider any environmental problems, he states: "the environmental effects of people and their societies can be modified by technological strategies such as pollution control and the conservation of natural resources. However, the size of the human population remains a root cause of the ecological degradations caused by our species" (Freedman, 1995, p.4).

Balogh *et al.* (1999) was a study that took place on Lake Pepin. This is a natural lake on the Upper Mississippi river in the USA. In order to determine historical trends in mercury (Hg) accumulation in the lake, sediment core samples were taken for analysis. It was found that the whole-basin Hg accumulation rates increased from 3 kg/yr before European settlement (*ca.*1830) to maximum of 357 kg/yr in 1960s.

The authors state "the recent Hg accumulation rate (110 kg/ yr, 1990-1996) was experimentally indistinguishable from measured Hg loadings in the River entering the Lake, indicating that accumulation rates in Lake Pepin correspond quantitatively to river loadings" (Balogh *et al.*, 1999, p.3298).

The current growth rate represents that there is a decline of approximately 70% from the peak value, reflecting large decreases in Hg inputs to the Mississippi River from industrial and public point sources in the metropolitan Minneapolis/ St. Paul area upstream. A sum of 18.1 t of Hg has been deposited in the Lake since 1800; half of that (9.0 t) was deposited between 1940 and 1970, when regional growth accelerated quickly but pollution control mechanisms were insufficient. Point sources accounted for approximately 60% of the Hg accumulating in Lake Pepin in the 1960s. However, these inputs have been practically eliminated since that time.

This study showed the cumulative relation between the rapid regional growth and the increase of the mercury pollution in the river sediments.

In his study, Eastwood (1987), described lead and its sources in the environment. Soil sampling and surveying (sampling technique) were based on taking transects and point samples from within a 1 km reference grid proved to be popular and were used efficiently.

Soil depth was an important factor in this research where different depths were taken in order to determine the lead concentration at different depths.
A selection of extraction methods such as acetic acid extract, acetate extracts, liquid- liquid extracts and EDTA extracts were used in this study.

Polythene bags were used to collect soil samples. Air-drying was recommended, because the oven drying tended to increase moisture absorption. The results of tests recommended that soil should be kept moist and aerobic during storage, in order to facilitate restoration to a metastable state on addition of water, which is of particular importance in the analysis of plant existing lead. Flame atomic spectroscopy was considered to be the most popular technique, with flameless technique increasing in popularity.

In the north of France, large amounts of heavy metals such as zinc, lead and cadmium in suburban areas have become an increasing problem for several years (Frangi and Richard, 1997). The main aim of the author's paper was to present the cartography of pollution by heavy metals to analyse the scale of contamination. The pollution was fairly high as a result of the discharge from metallurgical industries of heavy metal in numerous chemical forms during the smelting of non-ferrous metals.

The study area is situated in the north of France between Lens and Douai (Nord Pas de Calais, France), which covers about 100km^2 and involves approximate 60, 000 people. Natural content of heavy metals in soil in this area is estimated to be at < 40 ppm for lead and <0.6 ppm for cadmium (Luttringer and de Cormis, 1979). All along the same axis, 150 samples were taken and located at 1, 1.5, 2,3, 4, 5, 6, and 7 km from the main source.

The authors reported that: the results were treated statistically to demonstrate both concentration and spatial distribution. The soil samples were analysed by standard techniques of The France Normalisation Association (norm AFNOR NF X 31147). The concentrations of lead and cadmium were measured by flame atomic absorption spectrometry (Hitachi model AAS 180-70) and the accuracy is of 10% for the lead and 5% for the cadmium. The spatial representation of lead and cadmium concentrations shows the degree of the pollution and its distribution.

"Isoconcentration profiles were very useful to identify and to delimit the levels of soil contamination whereas; pedological studies of this region enabled the researchers to determine the concentration of these elements in soil. This study was carried out on the basis of experimental measurements acquired during a field experiment. The spatial representation resulting from these studies enables the researchers to associate a concentration to each spatial point at a given time" (Frangi and Richard, 1997, p.77).

A spatial and temporal study would enable the researchers to evaluate the evolution of the contamination level. It would be possible to use biomonitoring, X-ray fluorescence, or to associate both methods. A monitoring network providing regular data would enable the researchers to combine *in-situ* measurements with GIS to create thematic maps. The implementation of different kinds of measurements with GIS would improve our understanding of the dynamics of pollution. Finally, information on data required at regular intervals would allow the researchers to quantify the transported amounts and to follow the extent of the polluted zone, by use of an appropriate model, also to anticipate and to take appropriate decisions concerning public health.

As norms were expressed in total contents without distinction between chemical species, the metal concentration in the environment is not the only parameter that must be accounted for in the evaluation of risks and the improvement of the regulations. For this reason, the AFNOR norm U44-041, which is applied to the spreading in agricultural soils of sludge resulting from wastewater treatment stations, cannot express a real level of pollution, as it does not take into account bio-availability. Therefore it is essential to define other parameters, such as speciation, physical and chemical properties of soil and water to obtain a real idea of the extent of the contamination.

The researchers showed that it is possible to evaluate and estimate the lead and cadmium concentrations in soils by using spatial interpolation of point measures. This was a preliminary study, which formed a basis in order to implement action for the reinstatement of soils in this contaminated region.

Research took place in Germany in 1998 by Manz *et al.* involving the examination of heavy metals levels within the agricultural soils in the research area revealed that the actual contamination levels are fairly similar to those of other agricultural locations in Germany except for two sites that were subject to emissions from smelting works. Heavy metals content of agricultural topsoil was experimentally determined at fourteen areas in the German Leipzig-Halle-

Bitterfeld region covering *ca.* 3700km². Detailed analyses of the soil-borne contamination pattern using a sequential extraction scheme showed a generally low mobility and potential bioavailability, which can be traced back to the relatively high average pH of the soils. In this paper, the researchers had used different techniques to analyse and measure the heavy metals in soil such as:

- The acid-soluble fraction of metals in the soils was measured using the aqua regia dissolution method.
- The solutions obtained were measured with inductively coupled atomic emission spectrometry (ICP-AES).
- Quantitative analysis of the entire metal content was pre-formed using angular depressive X-ray fluorescence analysis (WDXRF).
- Sequential extraction was used to better estimate the contaminant potential caused by pollution.
- The very low concentrations of heavy metals (like Cd, Pb) in the solutions were measured using graphite furnace atomic adsorption spectrometry (GF-AAS).
- The other elements were determined with (ICP-AES)".

This paper represented valuable techniques to determine the concentration of heavy metals in soils, providing an opportunity to review some of them in order to use them in this research.

To determine the impact of abandoned mines on surface water and groundwater in the historical mining region of the Cerbat Mountains in Arizona, Roesener (1998) reports that "the heavy metal concentrations of unaffected surface water and groundwater are far below the Drinking Water Standards (DWS) except for naturally elevated iron content". In comparison, directly downstream of old tailings and of flowing edits the surface water is overloaded to a significant level by heavy metals. However, their concentrations decrease relatively quickly after about 1000 - 1500 m downstream. Elevated arsenic, cadmium, and iron concentrations were detected in most surface water samples. This can possibly be attributed to the widespread use of arsenic and cadmium containing chemical substances for ore processing. On the contrary, the lead, zinc, and copper content in fact differ from area to area, depending on the ore mined. The iron concentration was found to be naturally high, but it is also clearly increased in the mined areas due to an increase in adsorption sites. The groundwater in the immediate surroundings of old mines that processed ore on-site is heavily contaminated while the aquifer serving the town of Chloride actually remained unaffected by any contamination from the upstream historical mining areas. Roesener (op. cit) reports, "Three explanations can be considered for the very low concentration of heavy metals in the Chloride groundwater. The first explanation would be the influence of specific solubility and mobility of heavy metals in soil and groundwater on their transfer (Brümmer *et al.*, 1986; Schachtschable *et al.,* 1992; Hütter, 1994). Therefore the heavy metals could be immobilized in the soil by chemical reaction and adsorption. A second possible explanation is a dilution effect after the rainy season in the spring. A third explanation would be that there is no groundwater flow from the nearby mining district east of Chloride to the town's aquifer. This seemed the most likely reason, as the groundwater in the proximal mountain foothill zone is found in the fractured and weathered zone of the Precambrian igneous and metamorphic rocks" (ADWR, 1990).

Mining sites are one of the very dangerous locations for chemical contamination. This is because the abandoned tailings can extend contaminants in surrounding regions and can affect soil, water and wildlife adversely (Barafieri and Dadea, 1998). Samples were collected next to and away from the mine tailings. The whole concentrations in contaminated sites represent the starting point with the aim of evaluating the pollution levels.

In this paper, a simplified procedure of sequential extraction was used for the analysis of heavy metal mobility. The results were compared with a model of three levels of risk for hazard evaluation based on the mobile species obtained with the sequential extraction mentioned before.

The authors conclude that the area examined was not highly contaminated so risks for humans could be limited, however, the spread of these toxic metals in the longer term in nearby areas can increase the levels of contamination thereby compromising soil quality.

A study about the spread of mercury in a polluted river took place in Fars Province, Iran by Moussavi and Saber (1999) who found that the source of pollution was a nearby chlor-alkali plant. The results of experiments indicated that some of the reactive mercury is changed into organo-mercurials by micro-organisms. The major transformation process of mercury occurs in the bed-load sediments. Organo-mercurials are released from bed-load sediments into the river water because of low adsorption characteristics of solid matter. The release of some surfactants from sugar mill waste into the river causes a local increase of mercury in the water. Also there was an obvious decrease in organic mercury in the bed-load sediment at the end of the research, which may indicate a process of reduction via surfactants.

This study represented the mercury pollution problem in the rivers and its catchments and provided information about the mercury changing into organo-mercurials by microorganisms that helped to understand the phenomena.

In 1999 Marice *et al.* report that mercury contamination due to the amalgamation of gold in small-scale mining is an environmental problem of increasing concern, mainly in tropical regions like the Amazon, where a new boom of such gold mining started in the 1970s. In Brazil, research into these problems has been carried out for many years, but there is no existing data for Bolivia. This article surveys mercury contamination of a Bolivian river system in the Amazon drainage basin, measured through samples of water, fish, and human hair. High concentrations in fish and human hair from consumers of carnivorous fish species are reported. The possible health risk from eating was obvious in people living downstream of gold-mining activities, but not in the mining population itself.

This study confirmed that the contamination could be affecting the human population as well as other life forms in the area by the movement of the contaminated sediments downstream over a short time. It is not necessary for people to be affected by the contaminants even though they work in the mines.

Roeva and Ispravnikova in 1999 in their paper examined the major migration forms of mercury in a river and their real contributions to the migration of this highly toxic pollutant were evaluated. The dynamics of variations of the content of suspended forms of mercury and also organic and inorganic complexes of mercury was studied, depending on the hydrological regime and the distance from the pollution source. A method for the determination of the major migration forms of mercury in river water was proposed. A procedure for the determination of organic and inorganic forms of mercury at a level of 0.2 mg/l was developed.

The study showed obviously the relation between mercury pollution and, the hydrological regime and the distance travelled from the pollution source.

2.3 The Restoration of Contaminated Land

Papassiopi *et al.* in 1997 started research aimed to assess the use of EDTA for the elimination of heavy metals from contaminated soils in Greece. Soil samples were taken from contaminated sites. These sites were past mining and smelting activities in Lavrion, Greece. The samples were calcareous and contained variable levels of contaminants, ranging from 35,000 down to 500 mg/kg in Pb. The extraction of lead was found to vary for different soil samples (from 50% to 98%). Zinc and cadmium extraction was under 50% for the majority of samples examined. The residual concentrations of metals that followed the two stage treatments were above the limits that were set by the international organisations for soils. However, the metals that were able to leach out were efficiently removed and treated soils were all acceptable in terms of toxicity.

The authors (op.cit) report, "This experimental work has demonstrated that the soil matrix is of great importance for the overall evaluation of the EDTA leaching as a cost effective remedial option. The simultaneous dissolution of calcite was found to consume approximately 90% of the available EDTA". Therefore, it was concluded that for the treatment of calcareous soils, the criteria design and the estimated cost should be based on the calcite content of the soil.

Past attempts of restoring urban rivers in the USA, funded by the Superfund Program, have met with limited success. This led to establishing a new cooperative program to restore rivers that were affected by contaminated sediments. This new approach, titled the Urban River Restoration Initiative, envisages a new urban industrial river restoration initiative for the U.S. Army

Corps of Engineers, working in conjunction with the EPA and other appropriate federal, state and local agencies (Deason, 2001).

The lower Passaic River in New Jersey, which is located in the heart of the U.S.A. industrial revolution that began in the late 19th century, was identified as a guide project area for the Urban River Restoration Initiative.
In 2000, the first step to activate the initiative on the lower Passaic River was undertaken.

The author (op.cit) reports:" since publication of the landmark National Research Council report Contaminated Marine Sediments: Assessment and Remediation in 1989, much has been learned about how to address contaminated urban waterways. One of these learning points is that remedial technologies alone will not solve the problem. Solution must consider aspects of source reduction, natural attention, *insitu* containment and treatment, dredging, ex-situ treatment and other technological and institutional tools. All these solution components must be considered in the context of appropriate human health and ecological risk considerations, cost-benefit considerations, and a host of other relevant waterway restoration factors".

Because of the extent of the contamination problem and its important reflux on the environment generally, many attempts of treating and redeveloping derelict and contaminated sites has been published. Published works primarily address the technical issues and give limited attention to the financial issues involved, such as Cairney (1987) and Fleming (1991).

Contaminated sites have formerly been used for a large range of purposes, often over a period of several centuries. Throughout this time, the use may well have changed and quite often buildings may have been constructed over the remains of earlier developments (Syms, 1997).

Fleming (1991) has remarked that the state of such land is often very poor as to be inappropriate for continued use or re-use without major land engineering works. In its definition of derelict land; "land, which has been so damaged by industrial and other development that it is incapable of beneficial use without treatment" (DoE, 1986), the Department of the Environment presents a view similar to that of Fleming.

In 1987, Kivell noted that, the total area of dereliction in England had increased from 43,300 hectares in 1974, to 45,700 hectares in 1982, according to review prepared by the Department of the Environment. This increase happened in spite of the major programmes of reclamation that dealt with 17,000 hectares during the same time period (Syms, 1997). However, the equivalent review showed a reduction to 41,456 hectares by 1988 (DoE, 1991), at the same time as the 1993 survey indicated an additional reduction to 39,600 hectares of land being recorded as derelict in England (DoE, 1995).

The derelict land survey gives only a small part of the overall view. There are numerous locations that are still in use, or may be semi-derelict, which experience the same instability or contamination problems such as those locations that are officially classed as derelict. Kivell gave Stoke-on-Trent as an example.

In 1984, Stoke-on-Trent identified 332 hectares of derelict land, but added 291 hectares likely to become derelict, where existing industrial activities are expected to close down shortly. A further 538 hectares was classed as neglected land (Kivell, 1987).

Estimates suggest that 50,000 – 100,000 sites may be considered to be contaminated covering about 50,000 hectares. However, only a small percentage of these is likely to pose an immediate threat to community health or the environment (Hobson, 1991). The 1988 survey of the Department of the Environment gave information of the post reclamation use of almost 12,000 hectares of derelict land that was reclaimed between 1982 and 1988 A similar analysis was given in the report on the 1993 survey (Syms, 1997).

Tables (2-1 and 2-2) showing how local authorities play a main role in the reclamation of derelict land.

Land use	**By local authority with grant**	**By local authority without grant**	**By other agencies ***	**Total**
Industry	901	44	622	1 567
Commerce	118	11	460	589
Residential	294	79	675	1 048
Sub total (hard end use)	1313	134	1757	3 204
Sport and recreation	793	96	251	1 140
Public open space	3 078	251	475	3 804
Agriculture/ forestry	1 282	199	1 212	2 693
Sub total (soft end use)	5 153	546	1 938	7 637
Others	289	103	736	11 969
Total	6 755	783	4 431	11 969

* Including private sector developers and commercial organizations.

<u>Table 2-1 The use of land after reclamation, 1982 – 1988,</u> *(hectares). Department of the Environment (1991) ((Syms, 1997).*

Land use	By local authority with grant	By local authority without grant	By other agencies	Total
Industry	579	54	687	1 319
Commerce	120	18	518	656
Residential	89	16	816	922
Sport and recreation building	82	17	82	181
Other development	281	60	301	643
Sub total (hard end use)	1 152	165	2 404	3 721
Agriculture	226	4	607	837
Forestry / Woodland	561	5	51	617
Public open space	1 269	103	192	1 564
Outdoor recreation	906	133	336	1 375
Nature conservation	180	54	94	328
Sub total (soft end use)	3 142	299	1 280	4 721
Total	4 293	465	3 684	8442

Table 2-2 <u>The use of land after reclamation, 1988 – 1993,</u> *(hectares). Department of the Environment (1995) ((Syms, 1997).*

Although the Department of the Environment report gives a useful insight into the extent of the derelict land problem in England, Syms reported, "they do not cover the whole of the United Kingdom, nor do they provide information in respect of the industrial land still controlled by manufacturing companies and not officially classified as 'derelict'" (Syms, 1997).

Government intervention, since the late 1980's, in the clean up of contaminated land through English Partnerships and Regional Development Agencies has brought brown-field sites into use for business, housing and recreational use.

2.4 The River Rother

The principal aim of Doyle's study in1984 was to assess the degree of heavy metal pollution found in an aquatic ecosystem namely the River Rother. The reason for this analysis was to ascertain the level and extent of the heavy metals contamination of the local rivers considered (Rother, Sheaf, Porter and Little Don).

The Rother was singled out as being most in need of investigation of the regional network of rivers on suspicion of greater levels of contamination. The three other rivers, the Sheaf, Porter and Little Don, were chosen primarily because of their comparable geology, ecology, climatology and historical use.

The actual choice of sites was governed by a number of factors. All the sites had to be physically and legally accessible and were within 0.5 km of a road. It was decided to have eight sample sites on the chosen stretch of the River Rother adjacent to the chemical works at Staveley. This was in order to provide a sound database for assessing the levels and impacts of the chemical plant's discharges.

Doyle (op.cit) states, "All water and sediment samples were collected in accordance with standard procedure to prevent degradation of samples prior to analysis. Cold vapour atomic absorption spectrophotometry (C.V.A.A.S.), and atomic absorption spectrophotometry (A.A.S.) were used to analyse mercury, nickel, cadmium and chromium with modification for each metal type.

All of the local rivers surveyed were pollution free with respect to mercury except one area of contamination stretching downstream of the chloralkali plant at Staveley. Some possible solutions for the alleviation of problems caused by various waste products are recommended".

The research gives a good representation for the Rother, especially around Staveley, where the concentrations were higher than at the other sites. This establishes a background for the following studies and researches.

In order to judge the true effectiveness of European Community EEC environmental legislation on persistent wastes, Murfin in 1988 started his study by using the River Rother as a case study. The Directive "Dangerous Substances 76/464" seeks to establish a framework for the elimination or reduction of specified pollutants in inland, coastal and territorial waters. The Directive spawned several pollutant-specific papers and the proposal, which affected the Rother, was the council directive on the control of List 1 substances particularly the Directive 82/176".

The study suggested that further sampling operations after implementation of the EEC Directive may indicate the duration of river clean-up operations. Forty-seven samples were taken from the bed load of the Rother at approx. 1.5 km intervals, and the same analytical method as used in Doyle's survey was used, which was the cold vapour absorption (CVAAS). Reductions of contamination levels since the previous survey in 1984 appear to be dramatic, but the reliability of the data was unknown.

In his report Humphries (1988), included the results of the analysis of soil samples taken from land at Pithouse West Beighton for heavy metals. Twenty-one hand augured samples were taken within four different depth categories between 11th October and 10th November 1988 and four bulked borehole samples with the same depths were taken between 18th and 21st November by Norwest Holst Soil Engineering Ltd.

The results indicated that high amounts of lead, zinc, and cadmium existed on land around Beighton Flashes (SK 445 836).

The National Rivers Authority did a report, before it became part of the Environment Agency, by Edwards in 1990. Its aims included working with companies, industry, farmers, local authorities and others to stop or minimize pollution and to regulate any occurrences.

The report demonstrated that there were many sources of pollution within the area such as:

- The effluent from Danesmoor Sewage Treatment Works (STW), which serves Clay Cross, on Upper Rother (SK392 630).
- The effluent from Coal Products Ltd's, Avenue Coking Works discharges (SK 396 679), which were still responsible for downgrading 2.5km of the main river to "poor".
- The effluent of the ochreous discharges from the abandoned mine waters in the Rivers Hipper, Whittling and Drone, and
- The discharge from Old Whittington STW (SK 393 743), which serves Chesterfield, and Staveley Chemical Works (SK 416 752) and its discharges from the chlor-alkali plant in particular.

Until the mid 1980s, mercury was discharged from the chlor-alkali plant at Staveley Works in amounts above the environmental quality standard of the EC Dangerous Substances Directive.

Edwards (op. cit) reports: work by the NRA's laboratory in Leeds has shown complex mixtures of organic substances in effluents from some industrial discharges. The identification of many of these chemicals, even with advanced gas chromatography-mass spectrometers, is difficult. The NRA is requiring the provision of treatment facilities in order to remove these substances. Toxicity screening of effluents is also being introduced.

Schemes to improve sewage treatment works and industrial effluent discharges at the catchments should lead to marked improvements. Actions to achieve water quality standards are taken in the Rother and its tributaries and the NRA sets tough but fair standards for effluent discharges in relation to quality objective and standards set for the receiving waters. In the Rother catchment, much of the pollution stems from discharge consent standards being too lax. These consents will be reviewed and appropriate standards set.

The magnitude and the cost of cleaning up the Rother must not be underestimated. It must be emphasised that the NRA is committed to achieving the clean up as speedily as possible for the benefit of the community as a whole.

In 1991, Gunn started his study aiming to seek out any significant pollution of the Rother Valley by selected heavy metals (lead, zinc, and cadmium). Samples of soils and vegetation from the channel banks together with water and river sediments at different depths taken from the river channel were analysed

Gunn (op.cit) reports, on 19th June 1990, the survey was carried out at the following sample sites:

1. The New Beighton Flashes (SK 445 835).
2. Opposite Bank to the New Beighton Flashes (SK 447 840)
3. The Rother Valley Country Park (R.V.C.P) (SK 457 825).
4. Killamarsh Meadows (SK 448 813).

A hand soil auger was used to take all soil samples, and collecting jars were used for the sediment and water samples. In the laboratory, samples were dried overnight at 40°C in an oven and then sub-sampled. The sediment samples were limited to where wading into the channel was possible. The water samples once collected needed to be kept refrigerated. The analysis was done by using Atomic Absorption Spectrophotometry (A.A.S).

Furthermore Gunn (op.cit) concludes, "The floodplain of the River is in areas contaminated with significant levels of lead, zinc and cadmium, all likely to have a detrimental effect on the ecosystem. It is also very likely that other toxic substances are present. It has been shown that the River Rother and its floodplain does contain variable amounts of heavy metal pollution some of which could pose health risk and suggestions as to the sources and methods of deposition are made.

This study raises some questions which further research could investigate. It was suggested that research could follow up this study by looking in greater detail at surface floodplain concentrations or perhaps sample to greater sediment depths to try and establish whether or not the concentrations are mobile. Other work might look at the toxic effects of other metals and toxic substances such as organic halogens, which may form such compounds in the aquatic environment.

Setting up a continuing experiment to establish whether metals are still accreting today through water and sediment analysis, might be a useful area for research".

As a follow-up study, Duty in 1995 began collecting samples from the same sites as for the earlier studies (1984 and 1988) so that direct comparisons could be made. The sampling techniques and preparation were modified to overcome errors identified in the earlier investigations. At some sites, coring was done while at others a screw auger was used to facilitate collection. Samples were dried, ground to fine powder and placed in small, labelled airtight bags.

Duty (op. cit) found that "the movement of sediment and their pollution loads downstream has been exhibited quite conclusively, and some project limitations and recommendations for further studies are presented".

This study established wide background information about the Rother and its catchment, and explained the phenomenon obviously in relation to the previous information. Also it presented the explanation to the obscurity points, which appeared in the previous studies such as the mobility of contaminated sediments.

2.5 Initiatives Relating to the Restoration of the River Rother

A report, as a visitor survey for Rother Valley Country Park (RVCP) in 1988, was done by a team of first year students from the Sheffield City Polytechnic Recreation Management degree that undertook the interviews under the supervision of Dr Ralph Hebden, Head of the School. The Park was created as part of the restoration of the valley following opencast coaling and to enhance the water-based recreation facilities of the area. The River was confined to its own new channel and the lakes were supported with clean water from other local streams. This survey obviously represented the success of the project and encouraged further development for leisure use.

The company report of Staveley Works in 1993 outlined a pilot project undertaken to treat the effluent of the manufacturing area before discharge to the Rother. As a result of the very low operating and maintenance costs of a reed bed, it was predicted that the provision of a reed bed in this area could provide the necessary treatment action. This technology was environmentally acceptable and could be used to develop good public relations with the local community. However, from the investigation, it was obvious that the area of land required for polishing the liquid effluent was the same as that required for when the conventional effluent treatment plant was not used, i.e. untreated effluent fed directly to the reed bed.

There were basically two types of reed bed used for the treatment of wastewaters. One uses gravel as the substrate and the other uses soil. Reed beds can be designed for two operating modes horizontal feed and vertical feed. The latter was found more effective and therefore the land area requirement is reduced.

The Rivers Dearne and Rother are the two main tributaries of the River Don, the three rivers together making up a separate catchment or drainage area (Anon., 1996). The Don itself rises on Dunford Moor in the Pennines, 485m above sea level, near to the point where the counties of West Yorkshire, Derbyshire and Greater Manchester meet. It flows from its source to Penistone before turning south to Sheffield. From Sheffield it flows in a north-easterly direction to join the tidal River Ouse at Goole, which feeds the Humber Estuary, some 111.3 km from its source. The Rother rises 90 m above sea level flowing 40.7 km from its source near Clay Cross in Derbyshire to join the Don in Rotherham. The Dearne rises west of Denby Dale, 6 km to the east of Holmfirth, near the border between South and West Yorkshire. It flows east to Barnsley then south-east to Mexborough where it joins the River Don, 46.7 km from its source.

The report describes the chequered history of the use of the rivers, the water quality today and its future, the pollution and its effect on fisheries and geology.

The main aim of the *River Rother Wildlife Strategy* is preserving existing key sites and creating new habitats (Anon., 1994). This strategy is a joint initiative by Bolsover District Council, Chesterfield Borough Council, Derbyshire County Council, North East Derbyshire District Council, Rotherham Borough Council and Sheffield City Council.

The report described the valley of the River Rother, over much of its length, as grossly polluted on the bases of the 1989 River Quality Classification that showed 64% of length of the Rother as being Class 4, which means bad quality or grossly polluted and likely to cause a nuisance. This could give the impression that the river and its associated habitat types are valueless and dispensable. However, the remaining patchwork of wetland, marshy grasslands, open water and wild flower meadows are also becoming rare throughout the rest of the country (Anon., 1994). This issue made many locations along the Rother very important. However, many chances will be missed if each site is undertaken separately rather than strategically.

From the reporter's point of view, there were two major reasons for the need for a comprehensive protection and development plan for the wildlife throughout the valley of the River Rother. Firstly, individual proposals for development in parts of the catchment cannot be judged separately. Secondly, in order to manage the use and enjoyment of the area, there was the need to increase joint initiatives between the local authorities.

2.6 Standards for Soil Contamination

Many authors, including Lord (1987), McEntee (1991), Smith (1991) and Beckett (1993), considered the subject of site investigation (Syms, 1997). The Department of the Environment commissioned reports containing guidance on the investigation and sampling of contaminated land (DoE, 1994), the Welsh Department Agency produced an inclusive manual on the remediation of contaminated land (Welsh Department Agency, 1993), and Scottish Enterprise has published its *Requirements for contaminated land site investigations* (Scottish Enterprise, 1993).

Kelly Indices Guidelines for Contaminated Soils, which was formerly (GLC), specifically developed for gasworks sites in London: that suggested range of values (mg/kg) on air-dried soils, except for pH (Society of the Chemical Industry, London 1980). (Appendix No. 1)

The ICRCL guidance note 59/83 (ICRCL, 1987) stressed that 'the aim therefore should always be to check whether a site is contaminated before deciding on the form of development'. This was the most succinct advice given to those contemplating a new development (Syms, 1997) and provided specific threshold values for selected metal contaminants at which action had to be taken. (Appendix No. 2)

As part of a comprehensive review of remedial treatment for contaminated land, The Construction Industry Research and Information Association published guidance on the best practice for site investigation and assessment (CIRIA, 1995), A number of conference papers have also considered the issues involved, including Fletcher (1992), Ferguson, 1993), Waters (1993) and Crowcroft (1994).

The New Dutch list which is based on the public Intervention values and target values - soil quality standards and issued by *The Ministry of Housing, Spatial Planning and Environment,* perhaps the newest standards that present values for contaminant metals in contaminated land. (Appendix No. 3)

The Netherlands standards for Soil Contamination that presented the values for soil and ground water contamination and classified them to three levels (A, B and C). Level (A) acts as a reference value, level B is an assessment value and Level C is to be regarded as the assessment value above which the pollutant(s) should generally be treated. (Appendix No. 4)

In 1998, the Ministry of Agriculture, Fisheries and Food (MAFF),
subsumed into the Department for the Environment and Rural Affairs (DEFRA) introduced the *Soil Code* (the Code of Good Agricultural Practice for the Protection of Soil), which is the practical guide to help all farmers and growers avoid causing long-term damage to soils that they farm. This Code provided the basis of the "*Contaminated Land (England) Regulations 2000 & Statutory Guidance: Regulatory Impact Assessment (Final)* as the main point of reference for land contamination and the protection and improvement of the condition of the soil. (Appendix No. 5)

The Contaminated Land Branch of DEFRA declared, in December 2002, that the values as set out by the ICRCL would no longer be used for reference for contaminated land but that the new DEFRA Soil Code would become the point of reference.

In the present study the use of the updated standards has been adopted therefore, it was decided to use the DEFRA Standards and the Netherlands Standards as a guide to investigate and assess the present contamination.

A review of literature dealing with aspects of the impact of pollution and its causes on people, resources and environment. The literature demonstrates the multi-faceted impact of anthropogenic activity superceding natural causes of pollution. Comparative studies on the international scale are reviewed with relevance to the present investigation.

Recent interest in re-claiming derelict, contaminated land has increased rapidly in view of current national policies in re-cycling “brownfield" sites. Levels of increased use of reclaimed land are tabulated.

Past studies on the River Rother are reviewed in order to set into context the significance of the current investigation and to seek out evidence of change against past records. The results obtained need to be compared to international standards for soil contamination in order to provide guidelines for any potential re-use of the floodplain land.

CHAPTER 3 : THE HEAVY METALS

3. Heavy Metals

3.1 An Overview of Heavy Metals in the Natural Environment.

Heavy metal elements are to be found disseminated throughout the lithosphere. However, due largely to tectonic processes, including volcanic activity they are found in local centres of concentration. These centres include mineral veins and larger ore bodies within the crustal rocks of the Earth. As the geological cycle turns the metals in the concentration centres are weathered and eroded to release them again into the environment. At this point new secondary minerals may be formed through chemical reactions with air or other chemical solutions. Alternatively, the fragments of the primary minerals may be dispersed within the new sediments. Being part of a cyclic set of processes the metals can be entombed in one collection of rocks only to be released through the weathering and erosion processes acting upon those rocks at a much later date in geologic time. Some of the principal heavy metal minerals are presented in Table 3.1. (Based on guidance from F. Spode pers. com)

Metal	Principal mineral & Formula	Secondary Mineral
Cadmium	Greenockite CdS	
Copper	Native copper Cu Cuprite Cu_2O Chalcopyrite $CuFeS_2$ Chalcocite Cu_2S	Malachite $CuCO_3.Cu(OH)_2$ Chalcanthite $CuSO_4.5H_2O$.
Lead	Galena PbS Minium Pb_3O_4	Cerussite $PbCO_3$ Phosgenite $PbCO_3.PbCl_2$
Mercury	Cinnabar HgS	Calomel Hg_2CL_2
Nickel	Millerite NiS Pentlandite $(Fe,Ni)S$ Niccolite $NiAs$	
Zinc	Zincite ZnO. Zinc Blende ZnS Sphalerite ZnS	Smithsonite $ZnCO_3$ Goslarite $ZnSO_4.7H_2O$

Table 3-1 Heavy metal minerals

Thus any area of sedimentary rocks is likely to have background concentrations of heavy metals in them. These will vary widely depending upon the age of the sediments, their lithology and environment of accumulation. Thus river systems will tend to have higher levels of metals because they are actively eroding fresh rock outcrop and carrying such materials downstream with each spate episode. River systems which cut across former mineral veins or ore bodies will have higher concentrates in the sediment deposits of the floodplain downstream of the outcrop compared to rivers which do not expose enriched deposits.

In the context of the River Rother, it is a drainage system which has its source on the eastern flanks of the Pennines and then flows northwards to the confluence with the River Don. It is known that the southern Pennines were mineralised during Permo-Triassic times leaving deposits of the sulphides of Copper, Lead and Zinc with possibly traces of other sulphides including Cadmium and Silver within them. There are no records of the minerals for Mercury or Nickel present in the southern Pennines.

While the main orefield is further to the west of the main tributaries of the Rother, it is still possible for some residual fragments of ore minerals to be contained in the Carboniferous sediments through which the river has eroded its channel. In this way a background level of contamination from geologic sources is present in the alluvial sediments of the Rother floodplain. (F. Spode pers. com.)

3.2 Comments on the Chamalenitis of the Environmentally Significant Heavy Metals:

3.2.1 Cadmium

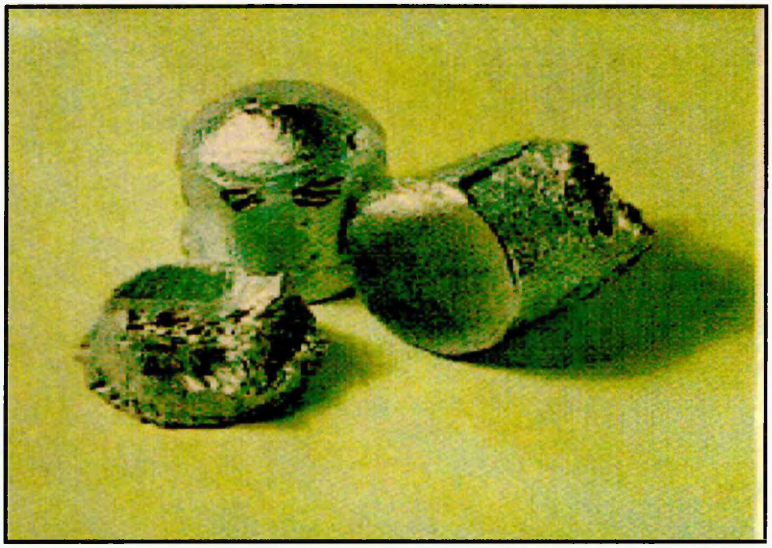


Figure 3-1 **Cadmium Cd.**

In 1817, Stromeyer of Germany made the cadmium discovery as a distinct element. Cadmium and zinc are often together in nature because they are similar in atomic structure and chemical behavior.

Cadmium and its salts are used in numerous and varied industrial processes. Electroplating is the major use of the metal itself. Cadmium is a constituent of fusible alloys and aluminum solder. It is utilized in such different applications as process engraving, amalgam in dentistry, and nickel-cadmium storage batteries as well.

Some cadmium salts, the oxide and iodide, were used to a limited extent as anthelminthics in swine and poultry. During the early 1900s cadmium salts were used sporadically in treating human syphilis and tuberculosis (Goodman and Gelman, 1955).

3.2.2 Toxicity of Cadmium

Many cadmium compounds are believed to be carcinogenic. In 1858, Sovet described what are probably the first reported cases of cadmium poisoning.

This when three servants polishing silverware with cadmium carbonate apparently inhaled great quantities of the dust and developed respiratory and gastrointestinal problems. However, Marme's paper regarding the toxic effect of cadmium seems to be the first important work on this subject (Marme, 1867).

Cadmium metal is believed to represent a cancer risk. In fact, it is highly toxic if inhaled.

3.2.3 Copper

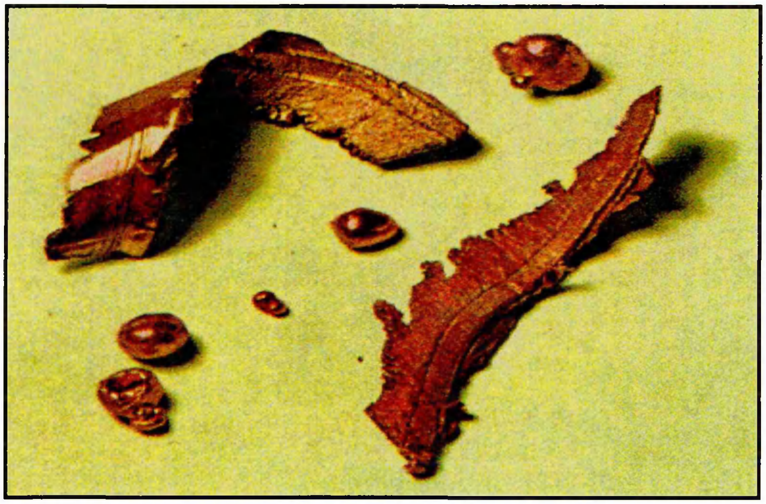


Figure 3-2 **Copper Cu**

Copper, one of the earliest known metals, is lustrous, ductile, malleable, and a good conductor of heat it may have been the first metal worked by ancient people 8000 years ago. Artifacts hammered from copper that date back to 6000 BC have been found in the Near and Middle East. Tubal-Cain, who forged implements of copper and iron, was described as but seven generations removed from Adam and is the first metallurgist of record in western civilization (Genesis, Chapter 4, Verse 22). Smelting and casting of copper became common in the Near and Middle East after 4000 BC. Bronze, an alloy of copper and tin, was invented about 2500 BC. Brass, an alloy containing copper and zinc primarily, was not developed until the Roman era.

Copper is an essential element. It is present in all organisms, land and marine. The early literature is rich with accounts of investigations concerning the presence of copper in different life forms. Some of the earliest observations were made upon marine organisms (Margaf, 1768) and (Bizio, 1833).

The essential role of copper became established when McHargue (1928) observed its value in diets for rats (McHargue, 1925 and 1926), and Hart *et al.* demonstrated that copper, in addition to iron, was necessary for blood formation Soon reports began to appear from various regions that certain disorder of grazing sheep and cattle were due to deficiencies of copper and had responded to copper supplements (Bennetts and Chapman, 1937), (Neal *et al.,* 1931), and (Sjollema, 1933 and 1938).

Enzymes containing copper include tyrosinase, ascorbic acid oxidase, cytochrome oxidase, monamine oxidase, uricase, and δ-aminolevulinic acid dehydratase. Several of the manifestations of copper deficiency in animals appear to be related to decreased tissue concentrations of certain of these enzymes.

Various aspects of copper metabolism and transport in man and animals have been studied in depth in both health and in disease states. Copper occurs in all bodily tissues. The distribution varies with age, species and diet. Liver, heart, brain, kidney and hair contain high concentration compared to other tissues. Glandular tissues, such as, pituitary, thyroid and prostrate, contain low levels. Tissues containing intermediate concentrations include bones, skin, muscles, pancreas and spleen (Cunningham, 1931) and (Smith, 1967). Levels of copper in the human brain increase with age, while levels in the liver, spleen and lung decrease (Schroeder *et al.*, 1966).

Blood copper levels of healthy animals vary rather widely, but for the higher mammals are of a similar magnitude. According to Beck (1956), most values lie between 80 and 120*μg*%. Levels ranging between 23 and 35*μg*% have been reported for domestic fowl. Other investigators report similar blood copper levels (Cartwrigh, 1950), (Nielsen, 1944) and (Schenker *et al.,* 1969).

3.2.4 Toxicity of Copper

Toxic signs of copper intake have been known for centuries. As early as 1785, for example, Thomas Percival (1959) described the symptomatology of copper ingestion in a young girl who had eaten pickles containing a large quantity of copper salts. Other instances of poisoning through food and beverage contaminated with the metal have been reported in the past (Deveragi, 1959) and (Hattingberg, 1940).

A rather unusual incident was reported in 1968 when thirty workmen suffered acute copper poisoning after drinking morning tea made with water from an unserviced gas water heater. The copper concentration of the water in brew pan was 3 mg per 100 ml (Nicholas, 1968).

Salts of copper have found limited application as germicides, fungicides, insecticides and astringents. At one time, those were also used as emetics. Salts are used as pigments in ceramics and in the textile industry.

A number of cases, some lethal, of copper poisoning following dialysis have been described. Copper was leached from the tubing in the dialysis bath (Matter *et al.,* 1969), (Ivanovich, 1969) and (Manzler and Schreiner, 1970). Serum copper levels rose above 2 mg per 100 ml in some instances.

Exposure to copper dusts and fumes generated during various industrial process is manifested by respiratory and dermatology complaints (Cohen, 1974). Salts have been known to induce a conjunctivitis and edema of the eyelids.

3.2.5 Lead

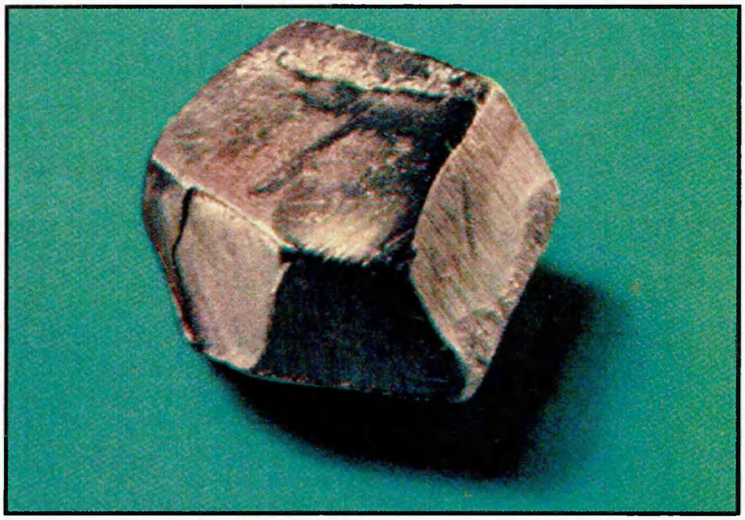


Figure 3-3 **Lead Pb**

Lead, one of the seven metals of antiquity, has accompanied all civilizations since their beginnings. It was in use before the time of the Hebrew exodus from Egypt. Lead does not occur in the elemental state in nature but as its sulfide ore or Galena. Discovery of metallic lead may have resulted from the accidental dropping of galena into a campfire.

Lead is mentioned in the tribute lists of the Pharoah Thotmes III (c. 1500 BC). Ancient peoples used lead for many purposes, including amulets, rings and other ornaments; dishes and trays; as a core for bronze statuettes and figures; sinkers for fishing nets *etc*. Probably the first use of galena was as an eyepaint.

The Greeks and Romans are said to have used lead extensively in cooking. Bronze pots gave food a bitter taste, but lead sweetened it. Olive oil was often stored in lead-lined vessels. The system of Roman aqueducts was lead lined. Horace, about 25 BC, questioned the purity of water in relation to lead pipes and rather wisely prefers that from a murmuring book.

The use of pewter and earthenware with high lead contents for food preparation and storage added to the body burden of lead among inhabitants of early America. Galena, along with iron ore, began being mined near Jamestown in

1621, fourteen years after the founding of the colony (McCord, 1953). Soils near lead smelters acquire an increased lead content.

3.2.6 Toxicology of Lead.

Lead is a general protoplasmic poison that is cumulative, slow acting and subtle, and produces a variety of symptoms. Like other heavy metals, it has an affinity for sulphur. Though it exerts much of its activity through sulphhydryl inhibition, lead interacts with carboxyl and phosphoryl groups also. The element interferes with hormone synthesis.

Lead may be absorbed into the body by ingestion, inhalation and through the skin. Absorption is governed by chemical structure. Inorganic lead salts do not penetrate the intact skin but can be absorbed through cuts and abrasions. Significant quantities can also be absorbed from a bullet or shot wound. Lead shot (buckshot) is considered particularly dangerous, because of its larger surface area permitting greater absorption. There have been cases reported of lead poisoning occurring within a month after a bullet wound.

3.2.7 Mercury

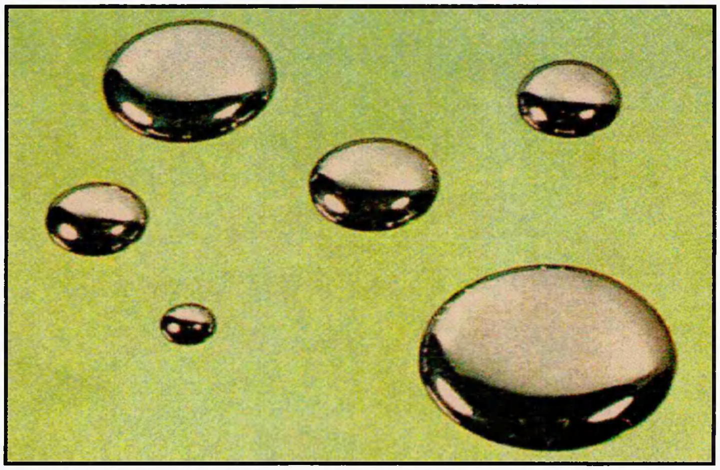


Figure3-4 **<u>Mercury Hg</u>**

Mercury, both as the metallic from (quicksilver) and the sulfide (cinnabar), was known to different people around the world for thousands of years and has played a prominent role in therapeutic, alchemy and folklore. Aristotle mentions the metal is in his *Meteorologica*, referring to it as fluid silver.

Procedures for the reduction of mercury from its ores were understood long before 400 BC apparently. Theophratus, a disciple of Aristotle, discusses a method whereby. Quicksilver is obtained by rubbing cinnabar with vinegar in a 'brass mortar with a brass pestle' (Agricola, 1950). Both Dioscorides and Pliny describe the distillation apparatus used to recover quicksilver.

Dangers inherent in mining quicksilver and in the reduction of mercury ores were appreciated by the ancients. Romans initially only used slave labour in their mines. Later these were worked by convicts.

Mercury and its salts enjoyed medical uses in ancient India, China etc., but until the sixteenth century when Paracelsus noted its effectiveness in treating syphillis; they were not used therapeutically in the western world.

The Greek and Romans considered them too toxic for therapeutic use. Following Paracelsus, however, though its hazard potential was appreciated, mercury came to be considered a panacea, a universal antidote for all ills. Woodall describes mercury as 'the hottest, the coldest, a true healer, a wicked murderer, a precious medicine, and a deadly poison-a friend that can flatter and lie' (Woodall, 1639).

Mercuric oxide, salicylate and chloride salts were used as topical antiseptics. Red mercuric sulphide preparations were used in treating syphillis, as were mercuric benzoate, mercurous acetate and mercurous iodide.

The importance of the mercury and its compounds as therapeutic agents has declined in recent years. Organic mercurials, such as, metaphen and merbromin (mercurochrome) exert a weak bacteriostatic action and are employed as local antiseptic agents. Some compounds like mercurin are still used as diuretics to a limited extent.

3.2.8 Toxicology of Mercury.

Mercuric ions act as potent enzyme inhibitors, protein precipitants, and corrosives. Mercury, like arsenic, has a great affinity for sulphhydryl groups. It also combines with phosphoryl, carboxyl, and amide and amine groups.

The biochemical toxicology of the different compounds varies greatly with the chemical form and entrance route into the body. Divalent inorganic mercurials, being more soluble than monvalent compounds are more rapidly absorbed and hence are much more toxic following oral administration.

Elemental mercury, being lipid soluble, can be absorbed through the intact skin. However, negligible amounts of elemental mercury are absorbed through the gastric mucosa. Experiments on rats have show that the gastrointestinal absorption of elemental mercury is less than 0.01% (Bornmann *et al.,* 1970). Hence mercury, swallowed during the course of breaking a thermometer in one's mouth accidentally, is of lesser concern than are the glass particles that may be swallowed concurrently.

On the other hand mercury vapour, even in minimal concentrations, is hazardous. It has been estimated from animal experiments that 75-100% of the mercury vapour inhaled are taken up by the animal body (Hayes and Rothstein, 1962). Approximately 75% of mercury vapor concentrations between 50 and 350 μg m^{-3} are reported to be retained by exposed man (Teisinger and Fiserova-Bergerova, 1965) (Nielsen-Kudsk, 1965). Inhaled mercury rapidly leaves lungs for the circulatory system (Magos, 1968), (Berlin *et al.,* 1969). Toxic effects are produced after the elemental metal diffusing into the erythrocytes and other tissues is oxidized to the mercuric ion (Magos, 1967). Clarkson, *et al.* in their studies on the equilibration of mercury vapor with blood has demonstrated the rapid bio- transformation in vitro of mercury from the elemental form to the mercuric ion. Catalase is considered to be the enzyme responsible (Clarkson, 1972).

Alkyl mercurials are of great importance as contamination in the environment, the greatest concern being contamination of the blood chain. Chloroethyl mercury is employed as a fungicide for treating seeds.

In addition to agricultural uses, phenyl mercury, the least toxic of the organo-mercurials, is also employed as a preservative in the manufacture of paints and adhesives, and in the paper industry as a slime-mold retardant.

Methyl mercury compounds are the most toxic of the alkyl mercurials used, as well as the most important of the environmental mercury contaminants. The fact that elemental mercury and mercury compounds can be converted to methyl mercury by microorganisms is a matter of great interest and some concern (Jensen and Jernelow, 1969) (Jernelow, 1969).

This biotransformation of mercurials to methyl mercury may be a possibility in humans as well.

Edwards reported the first recorded cases of methyl mercury poisoning in 1865. Two laboratory technicians at St. Bartholomew's Hospital, using dimethyl mercury whilst researching into the valency of metals and metallic compounds, began complaining of numbness of the hands, deafness, poor vision, sore gums, and ataxia. They both died subsequently although a third technician recovered.

More recent concern with alkyl mercurials stems from repeated outbreaks of methyl mercury poisoning in Japan (Okajima *et al.,* 1976) and elsewhere (Gerstner and Huff, 1977). Possibly the most famous incidents were those occurring in Minimata, Japan from 1953 to 1960. Minimata disease, so called, was caused by the ingestion of fish and shellfish contaminated by industrial effluents containing methyl mercury. Poisonings in Iraq arising from the consumption of bread made from treated grains (despite warning) occurred later (Baker *et al.,* 1973)

3.2.9 Minamata Disease.

Douglas Allchin wrote: It started out quite simply, with the strangeness of cats "dancing" in the street--and sometimes collapsing and dying. Who would have known, in a modest Japanese fishing village in the 1950s, that when friends or family members occasionally shouted uncontrollably, slurred their speech, or dropped their chopsticks at dinner, that one was witnessing the subtle early symptoms of a debilitating nervous condition caused by ingesting mercury? Yet when such scattered, apparently unconnected, and mildly mysterious events began to haunt the town of Minamata, Japan, they were the first signs of one of the most dramatic and emotionally moving cases of industrial pollution in history.

The outcome was tragic: a whole town was both literally and figuratively poisoned. Yet for those of us, now, who can view it more distantly, this episode also offers a conceptually clear and affectively powerful example of the concentration of elements in food chains, the sometimes unexpected interconnectedness of humans and their environment, and the complex interactions of biology and culture. In short, it is a paradigm for teaching ecology and science-society issues.

in 1956, new vinyl chloride factory, which was Chisso Corporation chemical plant, was built on the shores of Minamata Bay in Japan. The Year after the plant started production an epidemic spread among the people around the bay. In 1959, mercury poisoning was suspected as the cause that was confirmed in 1960. This was one of the first major human disasters to highlight the danger of chemical pollution, and the toxicity of mercurial compounds in particular.

The story started in 1953, when inhabitants of Minamata fishing village were affected by an unusual neurological epidemic. The vinyl chloride was produced using mercuric chloride as a catalyst, yielding inorganic mercury as a by-product (Barfield, 2001). This waste was discarded into the bay with the factory's effluent. The anaerobic organisms metabolised the organic mercury that was in the bottom sediments by methylation, forming methyl mercury. Methyl mercury then became incorporated into the food chain, bioaccumulating in the fish of the bay. Eating of the contaminated fish resulted in mercury poisoning of the people and their cats.

By 1983, Minamata disease had killed more than 300 people and about 1,500 more had suffered symptoms including blindness, convulsions and brain damage (Pope *et al.*, 1991).

3.2.10 Nickel

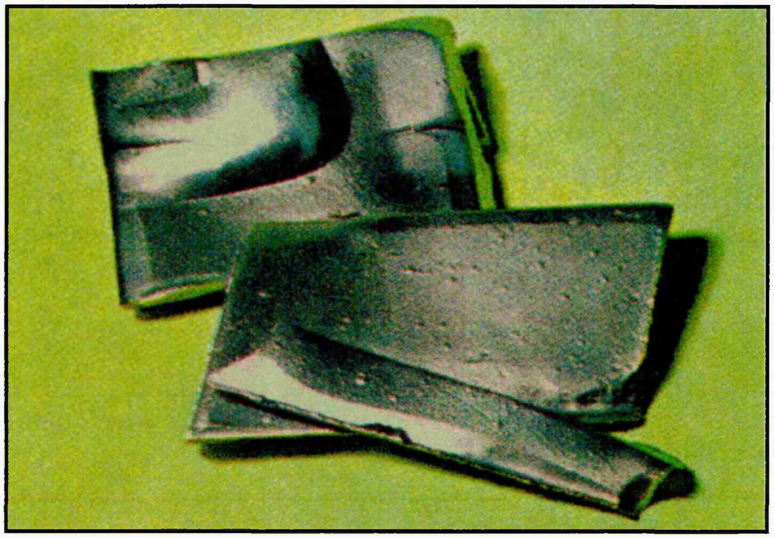


Figure 3-5 Nickel Ni

Metallic nickel has been known for about 200 years, but interest in its biochemical and toxicological activities is fairly recent. It is found in many ores in combination with sulphur, arsenic or antimony. Nickel occurs free in meteorites. Soils contain 40-ppm nickel on average compared, for example to 2-ppm molybdenum, 10-ppm lead or 6-ppm arsenic (Bowen, 1966).

Except for certain industrial exposures, nickel is considered as a relatively non-toxic element. Dietary nickel is poorly absorbed. Contamination of foods during their preparation is not considered a serious hazard (Underwood, 1977).

Fairly studies have indicated that nickel is an essential element in animal nutrition. Its physiological role has not been resolved as yet. Significant concentrations of nickel have been shown to be present in RNT and DNA (Wacker & Vallee, 1959 ; Sunderman, 1965). Nickel is now considered being among the essential metals.

3.2.11 Toxicology of Nickel

Acidic foods take up nickel from cooking and storage vessels. However, since it is poorly absorbed, nickel ingested from foods is relatively non-toxic. Exposure to nickel and its compounds in industry or elsewhere is another matter. It is said that there are at least 3000 known nickel alloys (Hamilton & Hardy, 1974). Applications are versatile and widespread: storage batteries, automobile and aircraft parts, spark plugs, electrodes, coins, cooking utensils, *etc.* Raney nickel, made by fusing equal parts of aluminium and nickel, is employed as a catalyst for the hydrogenation of oils and other organic compounds with gaseous hydrogen.

Certain nickel salts, such as the cyanide, chloride, carbonate, hydroxide, nitrate and sulfate are used in nickel-plating processes. Various nickel salts are utilized as pigments. For example, nickel dimethylglyoxime, a redcolored complex, is found in sun-fast paints, lacquers and cosmetics. Nickel phosphate is used as a yellow pigment for water colors and oils. Nickel sulphate serves as a mordant in dyeing and printing fabrics.

Exposure to nickel carbonyl is the most hazardous of all industrial exposures to nickel (Sunderman *et al.*, 1975) This highly volatile compound, formed during a process employed for the production of pure nickel, is toxic even in low concentration. Initial symptoms of exposure, including nausea, dizziness, headaches and chest pain, disappear within a few hours. After 12-36 hours, or as long as five days after exposure, sever pulmonary symptoms, tachycardia and profound weakness develop. Death has occurred within 4-13 days.

Hypersensitive to nickel in industry, i.e. (nickel itch) is not uncommon (Sunderman *et al.,* 1975). Approximately 9% in the above study were sensitized. Nickel dermatitis caused by wearing nickel-plated watches, other jewelry, spectacle frames, etc. is well known as a dermatological syndrome that is readily cured by removing the source of exposure.

3.2.12 Zinc

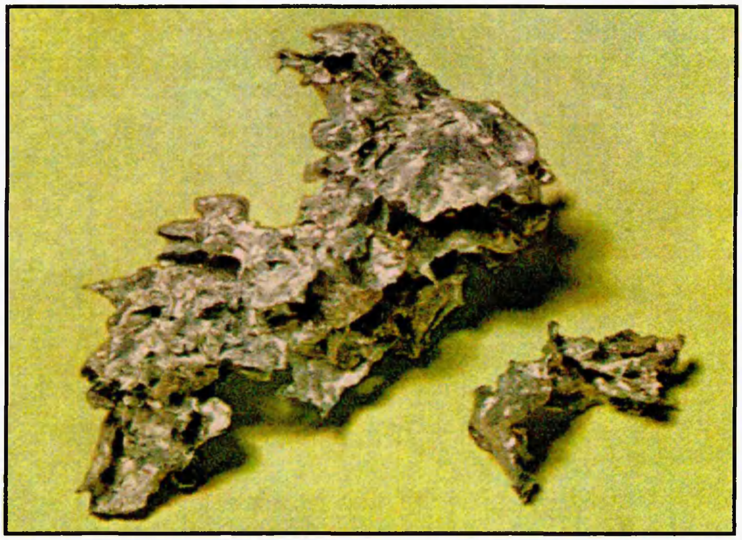


Figure 3-6 **<u>Zinc Zn</u>**

Zinc ores mixed with copper were employed by the ancients in making brass. Oxides of zinc obtained from furnace fumes by constructing dust chambers to collect the sublimate, were used for medicinal purposes about 2000 years before zinc metal itself became generally known (Prassad, 1966).

Erasmus Ebener of Nurnberg is said to have been the first European to recognise metallic zinc and make brass directly with zinc with zinc globules recovered from the reduction of ores (Prassad, 1966). The metal may have been known in the Far East (China and India) much earlier.

Zinc ores are widely distributed. Calamine and zincite consist primarily of zinc oxide. Franklinite is composed of oxides of zinc and iron, while Gahnite consists of zinc and aluminium oxides. Willemite is a zinc silicate ore; Sphalerite is essentially zinc sulphide.

The metal has various industrial uses, the most ancient being the manufacture of bronze and brass. It is employed as a coating on iron and steel. Zinc sheets are utilised for building purposes.

Zinc salts, being astringent, mildly antiseptic and corrosive in action, have limited application in medicine. Zinc chloride, a soluble salt, is more irritating than the oxide. The oxide, stearate, oleate, and sulfate are incorporated into lotions for the relief of pruritic conditions. Zinc acetate is employed as a styptic; zinc sulfate has been utilized as an emetic (Goodman and Gelman, 1955).

Zinc has been considered an essential element since Raulin in 1869 demonstrated (Raulin, 1869 in Underwood, 1971) that it was necessary in the nutrition of the mould *Aspergillus niger.*

Zinc was subsequently shown to be an essential constituent in animal nutrition (Todd, Elvehjem and Hart, 1934) and (Dynna and Haver, 1963). Its role as essential nutrient for man was established following investigations by Prasad *et al.* in Iran and Egypt (Prasad *et al.,* 1961,1963).

A number of enzymes including alkaline phosphatase, aldolase, alcohol dehydrogenase, carboxy peptidase, carbonic anhydrase, and latic acid dehydrogenase are zinc dependent (Valllee, 1959).

3.2.13 Toxicity of Zinc

True zinc intoxication is an infrequent occurrence. Many of the toxic effects attributed to zinc may have been due to other metals present, namely, cadmium, lead, antimony and arsenic.

Metal fume fever, also called brass founders' ague, brass chills, zinc shakes, galvo, spelter shakes, has been attributed to zinc oxide fumes and dusts ((Valllee, 1959), (Stokinger, 1963) and (Papp, 1968).

Inhalation of zinc fumes causes fever, malaise, depression, coughing, which might induce vomiting, salivation and headache (Berman, 1980).

Zinc, unlike lead, cadmium, arsenic, antimony, is not cumulative (Batchelor *et al.,* 1926). Batchelor *et al.* in their observations of workmen exposed for 2-35 years to zinc oxide dusts poor in lead and cadmium did not uncover any acute or chronic illness attributable to zinc.

According to Hamilton and Hardy chronic industrial poisoning due to zinc is probably nonexistent (Hamilton and Hardy, 1974). Acute zinc intoxication manifest by nausea, vomiting, and severe anemia is reported to have occurred in a patient in renal failure who had been dialyzed with water stored in a galvanized tank (Gallery *et al.,* 1972). Undoubtedly other toxic metals were also involved.

Toxic quantities of zinc can be brought into solution when acidic foods (vegetables, meats, fruit juices, salads, cocoa, *etc.*) are prepared or stored in galvanized utensils.

Gastrointestinal symptoms and fever have been reported to occur within 20 min or to be delayed as long as twelve hours following ingestion. Symptoms may be due to other metals present (lead, cadmium, iron, arsenic). The emetic action of zinc is a protective mechanism (Furchener and Richmond, 1962) and (Hath *et al.,* 1966).

However, dehydration, electrolyte imbalance, dizziness, lethargy, and muscular uncoordination may follow. Occurrence of acute renal failure following ingestion of zinc chloride has been reported (Csata *et al.,* 1968). The purity of the zinc is not known.

3.3 Heavy Metals in the Environment and Their Sources:

Heavy metals have a density of greater than 6 g /cm^3 (some authors use a value of > 5 g /cm^3) and an atomic number greater than 20 (Alloway, 1996), and occur naturally in rocks and soils but concentrations are frequently elevated as a result of pollution. The term "heavy metal" is imprecise but widely used although others such as "toxic metals", "potentially toxic elements" and " trace metals" are possible alternatives.

Heavy metals belong to the group of elements described geo-chemically as "trace elements" because they collectively comprise <1% of the rocks in the earth's crust. All trace elements are toxic to living organisms at excessive concentrations, but some are essential for normal healthy growth and reproduction by both plants and animals at low but critical concentrations. These elements are referred to as "essential trace elements" or "micronutrients" and deficiencies can lead to disease and even death of the plant or animal. The essential trace elements include Co, Cr, Cu, Mn, Mo, Ni, Se, Zn, B, Fe, I, Si, Cl. The last five elements are not dense enough to be classed as heavy metals but they are also essential trace elements. Other elements, including Ag, As, Ba, Cd, Hg, Tl, Pb, Sb, Have not known essential function and cause toxicity above a certain tolerance level. The most important heavy metals with regard to potential hazards and occurrence in contaminated soils are As, Cd, Cu, Cr, Hg, Pb and Zn (Alloway, 1993).

3.4 Sources of Heavy Metals

Heavy metals sources can include both the natural and industrial and can be classified as follows (Alloway 1997):

a) Metalliferous Mining: this is an important source of contamination by a wide range of metals, especially As, Cd, Cu, Ni, Pb and Zn, because ore bodies generally include a range of minerals containing both economically usable metals (in ore minerals) and uneconomic elements (in gangue minerals). Most mine sites are contaminated with several metals and accompanying elements (sulphur). Wind-blown tailings (finely ground particles of ore and country rock) and ions in solution from the weathering of ore minerals in heaps of tailing tend to be the major sources of pollution from abandoned metalliferous mine sites.

b) Metal Smelting: this is the process of producing metals from mined ores and so can be a source of many different metals. These pollutants are mainly transported in air and can be in the form of fine particles of ore, aerosol-sized particles of oxides (especially important in the case of the more volatile elements, such as As, Cd, Pb and Tl) and gases (SO2). In some cases, pollution is directly traceable in soil < 40 km downwind of smelters.

c) Metallurgical Industries: pollution can include aerosol particles from the thermal processing of metals and solutions of metals and solids wastes, effluents from the treatment of metals with acids and solutions of metals salts used in electroplating.

d) Other Metals-using Industries. These can be a sources of metals in gaseous/ particulate emissions to the atmosphere, effluents to drains and solid semiconductors, contacts, circuits, solders and batteries. Plating (Cd, Ni, Pb, Hg, Se, and Sb); pigment and paints (Pb, Cr, As, Sb, Se, Mo, Cd, Co, Ba, and Zn); the plastics industry (polymer stabilizers such as Cd, Zn, Sn, and Pb); and the chemical industry which uses metals as catalysts and electrodes including Hg, Pt, Ru, Mo, Ni, Sm, Sb, Pb, and Os.

e) Waste Disposal: Municipal solids wastes and hazardous wastes from many sources can contain many different metals.

f) Corrosion of Metals in Use. Corrosion and chemical transformation of metals used in structures, *e. g.* Cu and Pb on roofs and in pipes, Cr, Ni, and Co in stainless steel, Cd and Zn in rust preventative coatings on steel, Cu and Zn in brass fitting, and Cr and Pb from the deterioration of painted surfaces.

g) Agriculture: this mainly includes As, Cu, and Zn, which are (or have been) added to pig and poultry feeds, Cd and U contaminants in some phosphatic fertilizers, and metal-based pesticides (historic and current) such as As, Cu, Mn, Pb and Zn.

h) Forestry and Timber Industries: Wood preservatives containing As, Cr and Cu have been widely used for many years and have caused contamination of soil and waters in the vicinity of timber yards. Several organic chemicals, including tar derivatives (creosote) and pentachlorophenol, are also used as wood preservatives.

i) Fossil Fuel Combustion: Trace elements present in coals and oils include Cd, Zn, As, Sb, Bo, Se, Ba, Cu, Mn and V and these can be present in the ash or gaseous/ particulate emissions from combustion. In addition, various metals are added to fuels and lubricants to improve their properties (Se, Te, Pb, Mo, and Li).

j) Sports and Leisure Activities: Games, fire works and clay pigeon shooting involves the use of pellets containing Pb, Sb and As but alternatives to these metals such as steel, Mo and Bi are also being introduced (Alloway 1996).

Numerous case studies have described the contamination of terrestrial environments by heavy metals. These include naturally occurring sources or more frequently, situations where anthropogenic emissions of pollutants have contamination local environments. The naturally occurring sources, particularly surface Metalliferous mineralization, frequently contain metal concentration in thousands of ppm or higher in soils and vegetation, and thus they are comparable in the degree of contamination to the worst of the human affected situation.

Of special significance among the various human sources of contamination are emissions of various heavy metals from industrial sources.

Even the heavy metals can be naturally occurring in the environment, it can cause a problem to the organism and the vegetation in cases above the permitted values recommended in the standards.

A review of the natural origin of the heavy metals and their significance in terms of their toxicity towards animals and humans. In addition, a review of other sources of heavy metal pollution from anthropogenic activities including metal mining and smelting.

CHAPTER 4 : METHODOLOGY

4. Methodology

4.1 Introduction

Many of the protocols detailed have been developed for such government agencies as the United States Environmental Protection Agency (U.S EPA). These agencies often expect a *quality assurance project plan* (QAPP), previously known as the quality assurance/ quality control plan (QA/QC). The Environment Agency in UK accepts this plan which covers the following key points:

- *Sampling Strategies:* Number and type of samples, locations, and depth, times, and intervals.
- *Sampling Methods*: Specific techniques and equipment to be used.
- *Sampling Storage*: Types of containers, preservation methods, and maximum holding times.
- *Analyses*: A list of all parameters to be measured and detection limits.
- *Analytical Methods:* A list of acceptable filed and/or laboratory analytical procedures.

The overall goal of a well-designed sample plan is to produce data with the following characteristics:

- *High Quality*: The data have a known degree of accuracy and precision.
- *Defensible*: Documentation is available to validate the sampling plan.
- *Reproducible*: following the sampling plan can reproduce the data.
- *Representative*: The data truly represent the environment sampled.
- *Useful*: The data can be used to meet the objective of the monitoring plan (Pepper *et al.,* 1996).

Practicing the plan described above in this project:

- High quality – (see Chapter 4 – 4.3, 4.3.1).
- Defensible – (see Chapter 5).
- Reproducible – (see Chapter 5).
- Representative – (see Chapter 5-Table 5-20 and Chapter 6 – Figures 6 - 1& 6-2, Tables 6-1& 6-2)
- Useful – (see Chapter 5 – Table 5-20 and Chapter 6 – Figures 6-1& 6-2, Tables 6-1& 6-2)

4.2 The Research Sampling Plan

4.2.1 Visiting the River

Before collecting samples from the control survey, the River was visited twice for reconnaissance purposes. The first of these visits was on 13th of April 2000 to observe the sample sites used in previous studies, (Duty, 1995), and to determine possible sample sites for this study.

After that visit, the Map Room at Sheffield Public Library was visited to gather relevant information on the history of the river and on whether there was significant change in the course of river during the time period. Maps for the whole district between years 1875 and 1949 were checked. It was found for example that, on map for Staveley (surveyed in 1949) the river course changed between New Whittington and Staveley works.

A suitable scale base-map was obtained for the whole river (maps reference: Dove Dale, 111-119-120). This was used to determine the present target sites of research. The choice of sites was based on their historical environmental significance. These were as near as possible to those used in earlier studies.

The second visit was on the 9th of November 2000. The area was substantially flooded over most of the river flood plain. This included some places such as Woodhouse, where the ground level is 52 to 53 metres above sea level and had never been flooded since 1955 (before the flood control barriers were established). At Clay Cross, the surrounding area was completely flooded. At

Old and New Whittington, the river surface was 4 metres above the normal and the floodwater was covering all the land around the river. This visit was to inspect the sample sites and to make observations about their conditions and to provide individual site descriptions.

4.2.2 Sample Locations

The selection of the sampling sites was governed by two distinct factors:

a) To match, as close as possible, those locations of sites used in previous research studies along the Rother in order that comparisons of results could be made.

b) To gain safe access to the riverbank to enable subsurface samples to be obtained from the flood plain alluvium. [It is to be noted that several sections of the river channel have been canalised as part of the flood control process thereby making it very difficult to get down to water level.]

The samples were collected in two phases as follows:

a) The first phase on December 4th.2000 following a flood episode in the previous November so that former bedload sediments discharged to the banktop and beyond, could be collected. These were targeted because of recorded high values of heavy metals by previous researches.

b) The first phase samples were analysed and the results indicated some amelioration of the metal values. Therefore if became essential to investigate the migration of the metals downstream. A second phase of sampling was organized.

c) The second phase was on 21st November 2002, again following a major flood episode, providing a second opportunity to collect former bedload sediments.

Full details of the sample sites, depths at which samples were collected and their locations are presented in Tables 4.1 and 4.2 and on Map 4.1.

No	Depth	Location Name	Grid Ref.
1	120mm	Tupton	400 661
2	200mm		
3	355mm		
4	S.S		
5	120mm	Whittington Moor 1	392 740
6	200mm		
7	S.S		
8	173mm	Whittington Moor 2.	393 742
9	120mm		
10	S.S	Staveley	431 751
11	1m		
12	1.5m		
13	2m		
14	650mm	Hague	443 773
15	S.S		
16	S.S hollow		

Table 4-1 <u>First phase site description and sub- samples sites</u>

No.	Depth	Location Name	Grid Ref.
1	200mm	Renishaw	439 793
2	1 m		
3	200mm		
4	200mm	Killamarsh	448 812
5	600mm		
6	300mm	Beighton	446 838
7	1.3m		
8	200mm	Catcliffe	424 880
9	1.20m		
10	200mm	Rotherham	426 918
11	1m		
12	100mm	Don 1	447 941
13	300mm		
14	600mm		
15	1200mm		
16	1500mm		
17	100mm	Don 2	446 941
18	300mm		
19	600mm		
20	1200mm		
21	1500mm		

Table 4-2 <u>Second phase site description and sub-samples sites.</u>

Figure 4-1 a map showing the samples at first and second phases.

4.2.3 Sample Collection:

The surface soil samples were collected from the superficial deposits from the riverbank after the flood episode, using a plastic trowel and then placed into sterile glass jars and sealed *(BTF-625, 500mg capacity).*

Subsurface samples were collected using a shell auger, driven into the alluvium at measured depths from the surface. The soil was transferred to sterile glass jars and sealed, as before, to prevent cross contamination. The auger was cleaned between collecting each sample.

The depth chosen for sample collection were to reflect on zones of deposition of the alluvium. An upper layer 0-150 mm, and below the major root zones of plans; 150-300 mm to reflect on minor changes in lithology in medium term and below 500 mm to reflect on the earliest period of deposition.

The samples from Don 1 and Don 2 were collected from a deeper borehole which had been driven through built up embankment materials overlying the original floodplain sediments. Further illustration of the site location and depths is given in Figures 5.2 and 5.4.

The sample jars were labeled indicating the site location and the depth of collection. Following transfer to the laboratory the samples were also given Lab Numbers to permit tracking, during the processing, in the laboratory.

4.2.4 Drying and Grinding:

The soil samples were kept in their containers and dried. It was suggested that the best way to dry samples in an oven at 40°C – 45°C to avoid chemical and physical changes. The drying room was separate from grinding room which was equipped with Pascall® Engineering Ltd. mechanical pestle mill and Nederman EK 3000 dust extraction. The grinding machine was cleaned between processing samples to avoid contamination. After grinding, the samples were screened through a 2-mm (10-mesh) sieve to give what is commonly referred to as the 2-mm fine earth and which is used for most routine soil analysis. Samples were quartered to reduce the volume of the samples to increase the accuracy as possible.

4.2.5 Sample Preparation for Analysis:

Making sample dissolution one of the most common operations in analytical chemistry because most quantitative analytical techniques require that samples be introduced in liquid form. In order to determine the heavy metals by two different quantitative analytical techniques, it was necessary to dissolute the samples before introducing them to the instruments. Clean apparatus was used for each sample prepared.

It decided to use the (microwave digestion method) USA EPA (method 3051). In this method the samples were digested in closed Advanced Composite Vessels (Teflon® PFA) for microwave heating (CEM- MDS 2000 microwave unit, CEM microwave technology Ltd. 2 Middleslade, Buckingham industrial Park, Buckingham, MK18 1WA), the parameters of the microwave oven are presented in table 4.3.

The use of the closed digestion vessels (described above) is to obtain the high pressures and temperatures necessary for digestion. The elevated pressure in closed reaction vessels heated by microwaves ensure complete oxidation of organic matter and minimizes losses of analyte ions. The process is more efficient than 'open vessel' digestion processes by enhancing the solubility of the analyte ions. Increases the reaction rate in the organic syntheses and the product yield. Control of the pressure and temperature during the closed vessel work is critical to the efficiency, reproducibility, and above all, safety of the procedure (Barfield, 2001).

By using this technique, it was possible to perform faster, more controlled dissolutions with no difficulty in a safe manner.

4.2.6 Summary of Method:

The samples were digested, by using the method described above. After cooling and filtering, the vessel contents were diluted to volume (50ml) and analyzed. Blank samples were prepared to match the digestion acid mixture of the samples. All the sample preparations were done at the Sheffield Hallam University School of Sport and Leisure Management laboratories before set them to analysis.

Method 3051	**Step 1**	**Step2**
Sample Wt. 1g	-	-
Microwave power %	50	100
Pressure PSI	20	85
Time	10	20
Time at pressure	5	10
Fan %	100	100

Table 4-3 **the parameter of the microwave oven**

4.3 Sample Analysis:

The two techniques used in this study were Inductively Coupled Plasma (ICP) and Atomic Absorption (AA). All previous investigations in the Rother used AA technique and it was important to have results from the current investigation for comparison.

The selection of the more sophisticated ICP technique was used. This providing a comparison to the results from the AA.

The determination of the heavy metals was made using two different techniques; Inductively Coupled Plasma (ICP) at School of Science and Mathematics - Division of Chemistry and Atomic Absorption (AA) at School of Sport and Leisure Management. The analysis included metals (Cd, Cu, Hg, Pb, Ni, and Zn). The same sample solutions were used for both techniques.

The first phase samples from five sites as shown in (Table 4-1), were analysed by using both techniques in order to determine the metals (Cd, Cu, Hg, Pb, Ni, and Zn) concentrations. All the results obtained from both techniques were acceptable except cadmium data, which was very high in (ICP) and did not match the data of AA. The Certified Reference Material (CRM) No. (GBW07401) and (GBW07411) was analysed to find out and determine which technique was more accurate.

The cadmium results of (CRM) obtained from (AA) were acceptable whereas the (ICP) results were very high. In fact, they were twice as high as the expected values. As a result of this mismatch between (AA) and (ICP), the (CRM) analysis was done for a second time by both instruments. The results obtained from (ICP) were not as satisfactory as the (AA) results; the (ICP) results were still very high. Therefore, it was decided to accept the AA cadmium results and discard the (ICP) cadmium ones. However, all the other metals analysis results obtained from (ICP) were included. These cadmium results may be due to the sensitivity of the (ICP). It could be that the (ICP) was not adjusted and therefore it merged elements that were similar to cadmium during the analysis, which could have led to the high concentration of the cadmium.

The second phase samples are shown in (Table 4-2). The Atomic Absorption and (ICP) techniques produced analyses for all metals other than Cadmium, which were elements (Zn, Cu, Ni, Hg, Pb) in close agreement between each technique.

In the early stage of method development, atomic absorption produced analysis figures that corresponded more closely to the certified values for the (CRM) than did (ICP). Further method development of the (ICP) analysis parameters produced cadmium analysis in close agreement with those determined by (AA). The results were more accurate, which could be that the (ICP) was adjusted in the second stage.

4.3.1 Mercury Analysis:

The initial digestion method and (ICP) analysis parameter produced unacceptably high values for the CRM's. Consequently, the technique was changed to vapour generation (ICP/MS). The process reduces mercury ions to metally mercury whose vapour is partitioned from the digest solution and swept on a steam of inert carrier gas (argon) into the (ICP) torch. Hence the mercury is separated from any potentially chemical and spectral interferonts; thereby producing a more accurate analysis.

Having refined the methodology for mercury analysis, all samples from phase one and two were re-analysed by this technique. Analyses produced by this technique are presented in Chapter 5 of this study.

4.4 Atomic Absorption Spectrometry (AAS):

In this technique (Frangi and Richard, 1997), electromagnetic energy (from a hollow cathode lamp) specific to the element been analyses in used to excite ground state atoms (in a flame) of that element. The resulting reduction in transmitted energy is measured as absorption. The degree of absorption is proportional to the population of the ground state atoms in the flame.

Sample solutions are introduced to the flame via a capillary tube fitted to the burner unit.

4.4.1 Instrumental Parameters Used:

Element	**Wavelength Λ nm**	**Spectral band pass nm**	**Optimum working range mg/ml**	**Lamp current**	**Fuel**	**Support**	**Flame stoichio-metry**
Cu	324.7	0.5	2-8	3.5m A	Acetylen	Air	Oxidizing
Ni	232.0	0.2	3-12	3.5m A	Acetylen	Air	Oxidizing
Zn	213.9	1.0	0.4-1.6	5m A	Acetylen	Air	Oxidizing
Pb	283.3	0.5	10-40	EDL	Acetylen	Air	Oxidizing

Table 4-4 Atomic Absorption Spectrometry parameters.

4.5 Inductively Coupled Plasma ICP:

Of all the various plasma devices used for elemental analysis during the past 25 years, the inductively coupled plasma (ICP) (Manz *et al.,* 1998) has had the most significant impact on the field of atomic spectroscopy.

The ICPs instrument is comprised of four fundamental parts: (ICP) source, optics and spectrometer, sample introduction, and data analysis. Samples are typically introduced into the centre of the plasma as aerosols

4.5.1 ICP Properties:

As all the analytical chemistry instruments, Inductively Coupled Plasma (ICP) has limitations along with its advantages. The advantages and disadvantages are displayed in (Table 4.5).

Advantages	**Disadvantages**
Rapid, simultaneous, multi element analysis.	*Spectral interferences.*
Low detection limits (ppb or less for some elements).	*Matrix effects from concomitant species.*
Relatively small interelement matrix effects.	*Matrix effects from solvent.*
Wide liner dynamic range (up to 5 or 6 orders of magnitude).	*Difficulty in analyzing solids without dissolution.*
High precision (0.5% - 5%).	*Inefficient sample introduction.*
Applicable for analysis of gases, liquids, or solids.	*Detection limits too high for some applications.*
	Drift and insufficient precision for some applications.

Table 4-5 Inductively Coupled Plasma ICP properties.

The methods covering sample collection, preparation and chemical analyses are described. Protocols for different methods of analysis are debated and justification is presented for the methods selected.

CHAPTER 5 : RESULTS AND THEIR INTERPERTATION.

5. Results.

The data presented in this chapter is set out in both tables and graphs. The sample data are arranged in two sections; Phase One, and Phase Two in the study. Sample data are presented for each of the sample sites along the River Rother. The results are interpreted and the significant values are highlighted.

5.1 Presentation of Tables and Figures

The following pages contain tables and figures that describe the sample sites location and the data obtained from the chemical analyses. These pages are:

Table 5-1 that explains the first phase samples and contains field site number; location of the sample, laboratory sample number and the depth of the each sample were taken from each site.

Figure 5-1 is a map of the River Rother showing the location of first phase sample sites between Tupton and Hague.

Figure 5-2 is a sketch plan showing how first phase samples were taken from each site.

Table 5-2 is a table containing the total heavy metals chemical analyses from first phase samples.

Table 5-3 presents the data table of the first phase surface samples between Tupton and Hague; a graph shows lead, zinc, nickel, and copper concentrations of surface samples and a graph shows cadmium and mercury concentration. The graphs were presented separately because the cadmium and mercury were very low compared to the lead, zinc, nickel, and copper so they would be not clear if presented at the same scale on the graph.

Tables from 5-4 to 5-8 are showing individual sites of Tupton, Whittington Moor 1 and 2, Staveley and Hague in succession. Each main table contain two sub-tables showing sub-samples of each site, samples description, grid reference, land use, ecological description, depth of samples and the total concentrations of Pb, Zn, Ni, Cu, Cd, and Hg.

Table 5-9 is explaining the sample sites of second phase and their location. It contains field site number; location of the sample, laboratory sample number and the depth of each sample where taken from each site.

Figure 5-3 is a map of the River Rother showing the location of second phase samples between Renishaw and Rotherham.

Figure 5-4 is a sketch plan showing how second phase samples were taken from each site.

Table 5-10 is a table containing the total heavy metals chemical analysis from second phase samples.

Table 5-11 shows the data table of the second phase surface samples between Renishaw and Rotherham; a graph shows lead, zinc, nickel, and copper concentrations of surface samples and a graph shows cadmium and mercury concentration.

Tables from 5-12 to 5-18 are showing individual sites of Renishaw, Killamarsh, Beighton, Catcliffe, Rotherham and Don 1 and 2 sequentially. Each main table contain two sub-tables showing sub-samples of each site, samples description, grid reference, land use, ecological description, depth of samples and the total concentrations of Pb, Zn, Ni, Cu, Cd, and Hg.

Table 5-1 Sample Sites Used for Phase I Analyses:

Field site No	Location	Lab sample No.	Depth
1	Tupton	1A 1B 1C 1D	120 mm (S.S) 200mm 355mm Surface.
2	Whittington Moor 1	2B 2C 2D	120mm 200mm Surface sample
3	Whittington Moor 2	3A 3B	173mm 120mm (Gap)
4	Staveley	4D 4B 4C 4A	Surface sample 1m 1.5m 2m
5	Hague	5A 5B 5C	650mm Doe Lea Surface sample Surface sample hollow

Figure 5-1 A map show the sample sites between Tupton and Hague

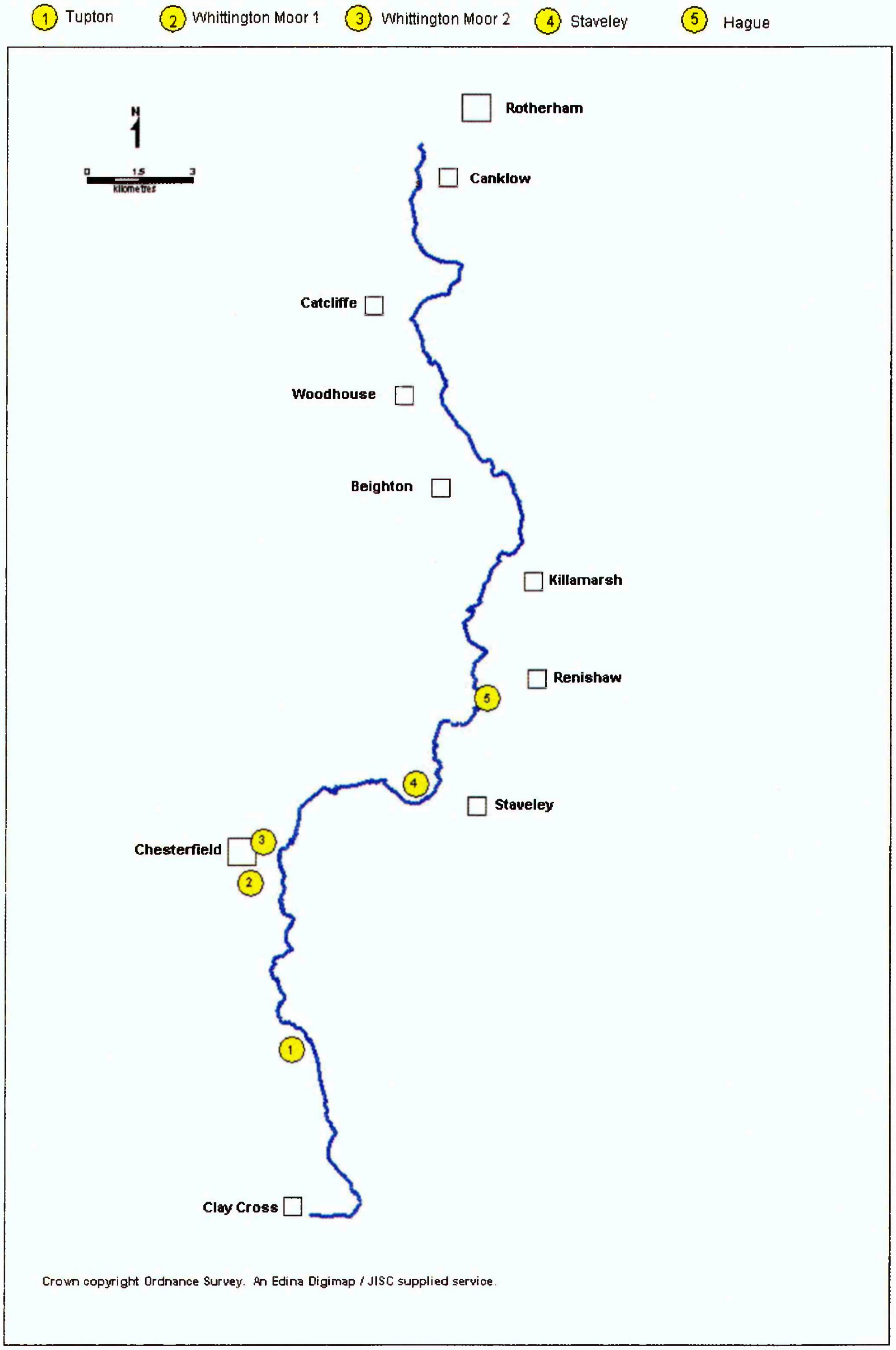


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Figure 5-2 Sketch plan for sites 1-5 of phase 1 sample sites.

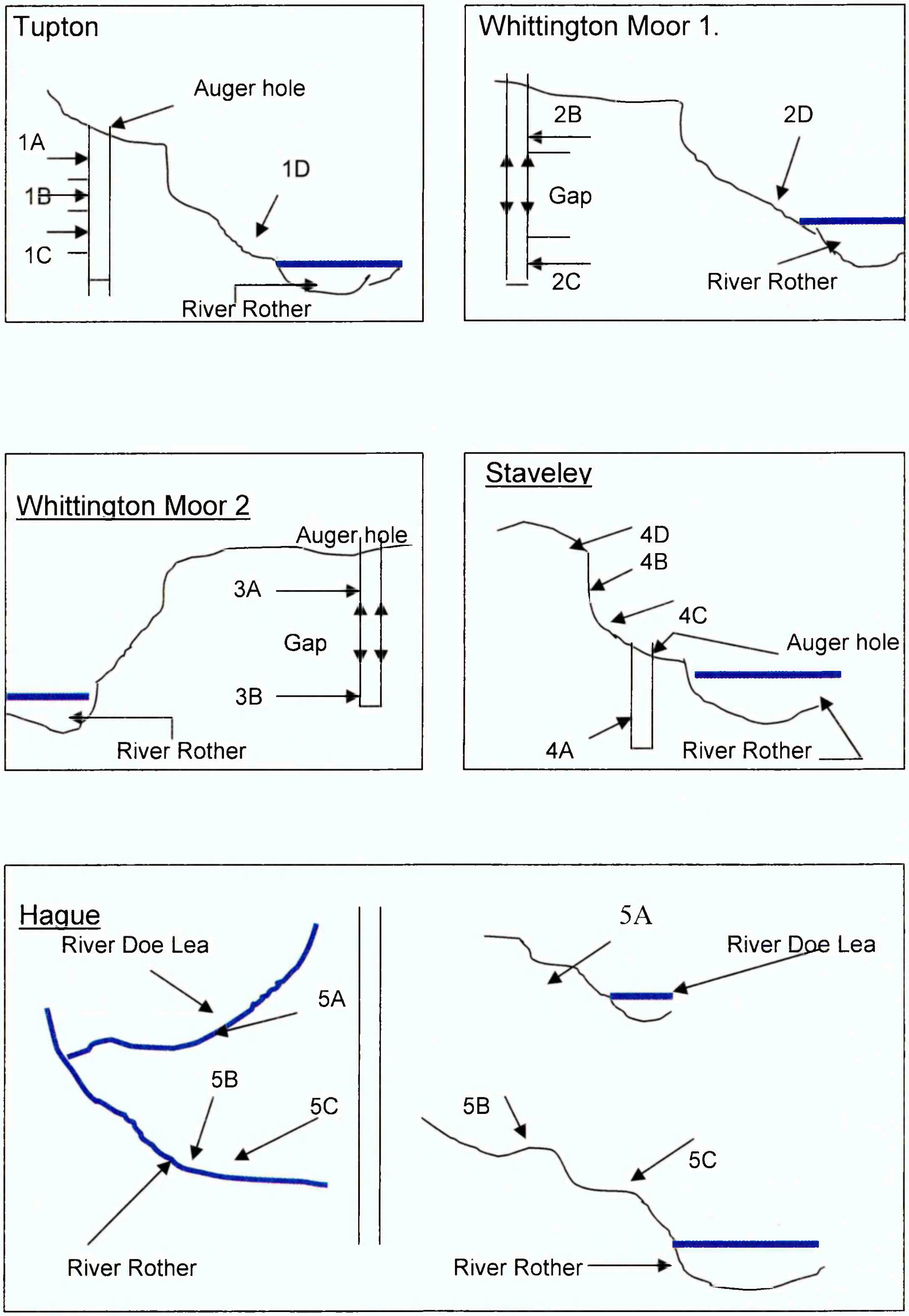


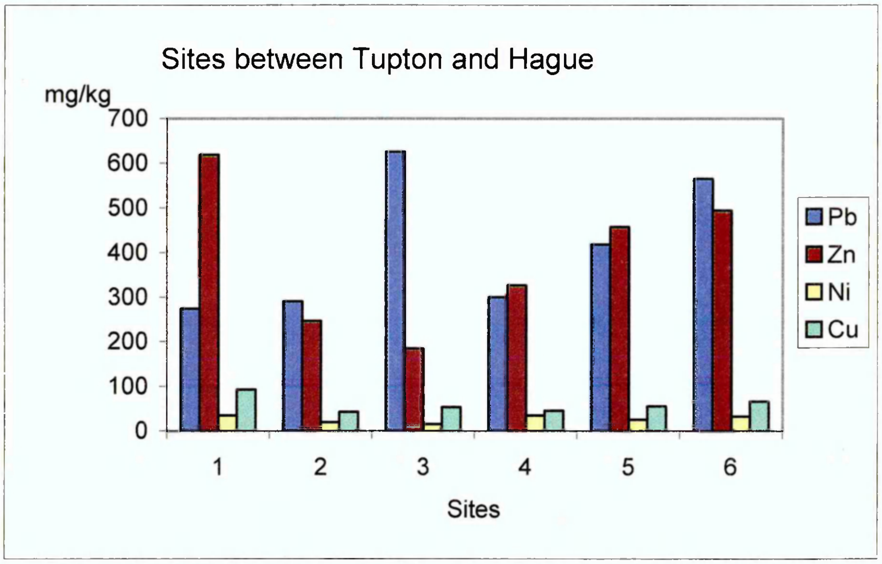
Table 5-2: Table containing total chemical analysis data from phase 1 study:

No.	Site	Lab No.	Pb mg/kg	Zn mg/kg	Ni mg/kg	Cu mg/kg	Cd mg/kg	Hg mg/kg
1	Tupton	1A	274	619	35	93	3	0.37
2		1B	125	219	21	48	1	ND
3		1C	68	252	42	29	0	ND
4		1D	250	719	21	78	2	0.44
5	Whittington 1	2B	291	247	20	43	1	ND
6		2C	333	293	29	52	2	0.84
7		2D	398	481	16	78	1	0.90
8	Whittington 2	3A	625	185	16	54	1	0.13
9		3B	695	158	32	34	1	ND
10	Staveley	4D	300	327	35	46	1	0.68
11		4B	344	370	36	66	0	0.49
12		4C	396	340	42	71	1	ND
13		4A	297	360	30	58	1	0.82
14	Hague	5A	102	217	30	44	1	0.26
15		5B	418	457	26	56	1	1.15
16		5C	565	494	33	67	2	0.51

The following tables (5.2 – 5.7) contain data from each individual sample sites.

Table 5-3 Table of data and illustrative graphs showing the heavy metal concentrations (mg/kg) in floodplain soils of the phase 1 surface samples between Tupton and Hague.

Site	Pb mg/kg	Zn mg/kg	Ni mg/mg	Cu mg/kg	Cd mg/kg	Hg mg/kg
Tupton	274	619	35	93	3	0.37
Whittington Moor 1	398	78	16	481	1	0.90
Whittington Moor 2	625	185	16	54	1	0.13
Staveley	300	327	35	46	1	0.68
Hague1	418	457	26	56	1	1.15
Hague 2 hollow	565	494	33	67	2	0.51



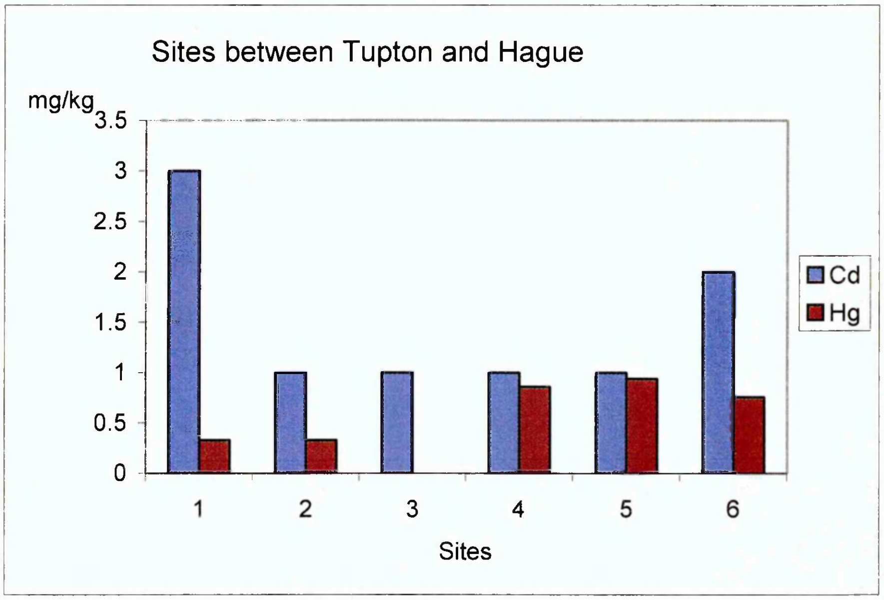


Table 5-4 Site No. 1 Tupton.

No	Sample description	Grid Ref.	Land Use	Ecological Description
1	Clay loam	400 661	Riverbank, 20m W. from old Railway trackbed leading to a former colliery site	Tall herbs covering the river bank
2	Mottled clay			
3	Brown clay			
4	Bulked sample from low terrace.			

No	Depth	Pb mg/kg	Zn mg/kg	Ni mg/kg	Cu mg/kg	Cd mg/kg	Hg mg/kg
1-1A	120 mm	274	619	35	93	3	0.37
2-1B	200 mm	125	219	21	48	1	ND
3-1C	355 mm	68	252	42	29	0	ND
4-1D	S.S	250	719	21	78	2	0.44

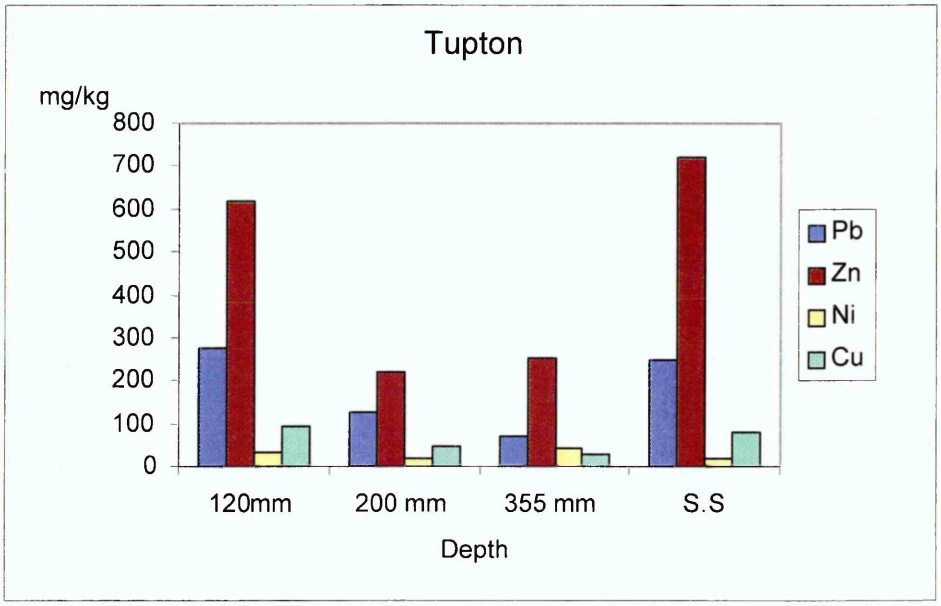


Table 5-5 Site No. 2 Whittington Moor 1

No	Sample description	Grid Ref.	Land Use	Ecological Description
1	Sandy loam	392 740	Riverbank adjacent to old pasture	River margin with occasional shrubs.
2	Clay alluvium			
3	Bulked sample.			

No	Depth	Pb mg/kg	Zn mg/kg	Ni mg/kg	Cu mg/kg	Cd mg/kg	Hg mg/kg
1-2B	120 mm	291	247	20	43	2	0.84
2-2C	200 mm	333	293	29	52	1	ND
3-2D	S.S	398	481	16	78	1	0.90

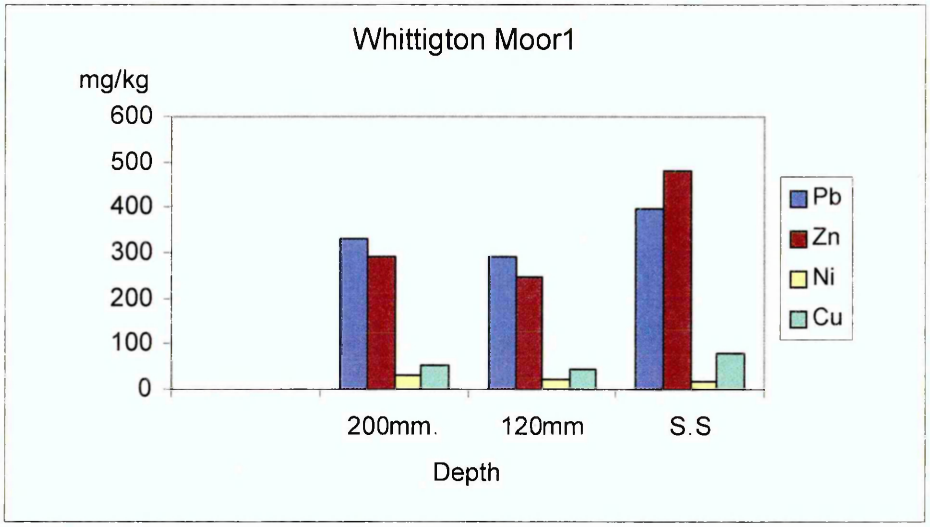


Table 5-6 Site No. 3- Whittington Moor 2

No	Sample description	Grid Ref.	Land Use	Ecological Description
1	Brown clay loam	393 742	On floodplain 6m from river channel, Old pasture.	Floodplain grassland creeping thistle
2	Clay alluvium			

No	Depth	Pb mg/kg	Zn mg/kg	Ni mg/kg	Cu mg/kg	Cd mg/kg	Hg mg/kg
1-3A	173 mm	625	185	16	54	1	0.13
(Gap)	-	-	-	-	-	-	-
2-3B	120 mm	695	158	32	34	1	ND

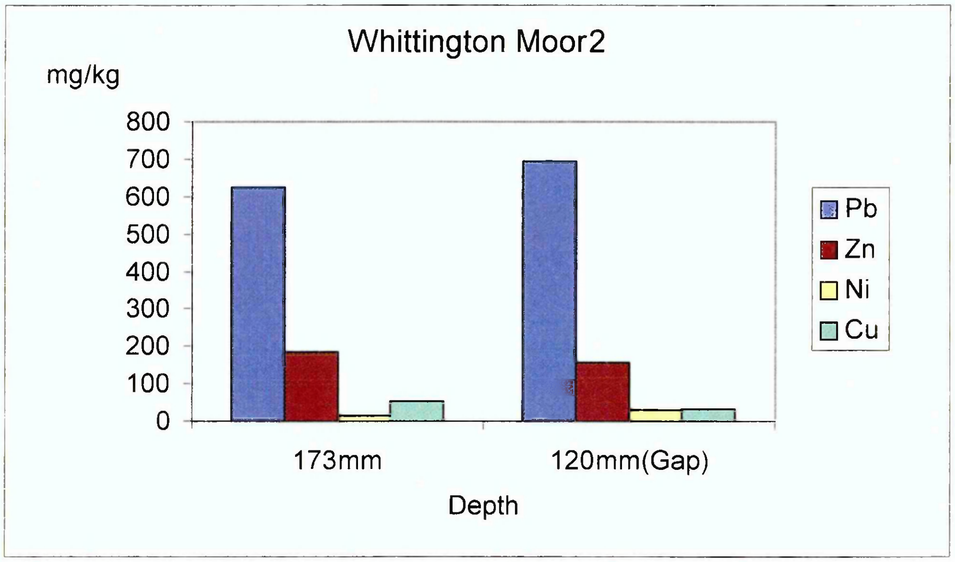


Table 5-7 Site No. 4 - Staveley.

No	Sample description	Grid Ref.	Land Use	Ecological Description
1	Auger sample from low terrace.	431751	Riverbank adjacent to grazed pasture. about 40m N of Staveley Works.	Tall herbs along top of the river bank.
2	Clay alluvium			
3	Clay alluvium			
4	Bulk sample alluvium.			

No	Depth	Pb mg/kg	Zn mg/kg	Ni mg/kg	Cu mg/kg	Cd mg/kg	Hg mg/kg
1-4D	200 mm	300	327	35	46	1	0.68
2-4B	1 m	344	370	36	66	0	0.49
3-4C	1.5 m	396	340	42	71	1	ND
4-4A	2 m	297	360	30	58	1	0.82

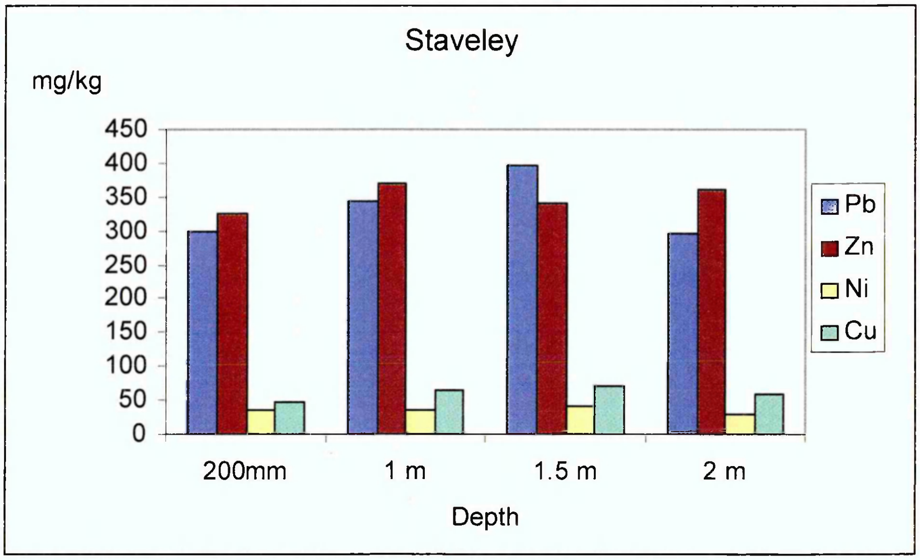


Table 5-8 Site No. 5 - Hague.

No	Sample description	Grid Ref.	Land Use	Ecological Description
1	Rother floodplain near confluence with the Doe Lea	443 773	Wasteland between the Doe Lea and the Rother. Railway bridge and embankment some 50m to the E.	Wetland meadow, some pools still remaining after flood of 4-7/11/00
2	floodplain			
3	Bulk surface sample.			

No	Depth	Pb mg/kg	Zn mg/kg	Ni mg/kg	Cu mg/kg	Cd mg/kg	Hg mg/kg
1-5A	650mm DoeLea	102	217	30	44	1	0.26
2-5B	S. S.	418	457	26	56	1	1.15
3-5C	S. S. hollow	565	494	33	67	2	0.51

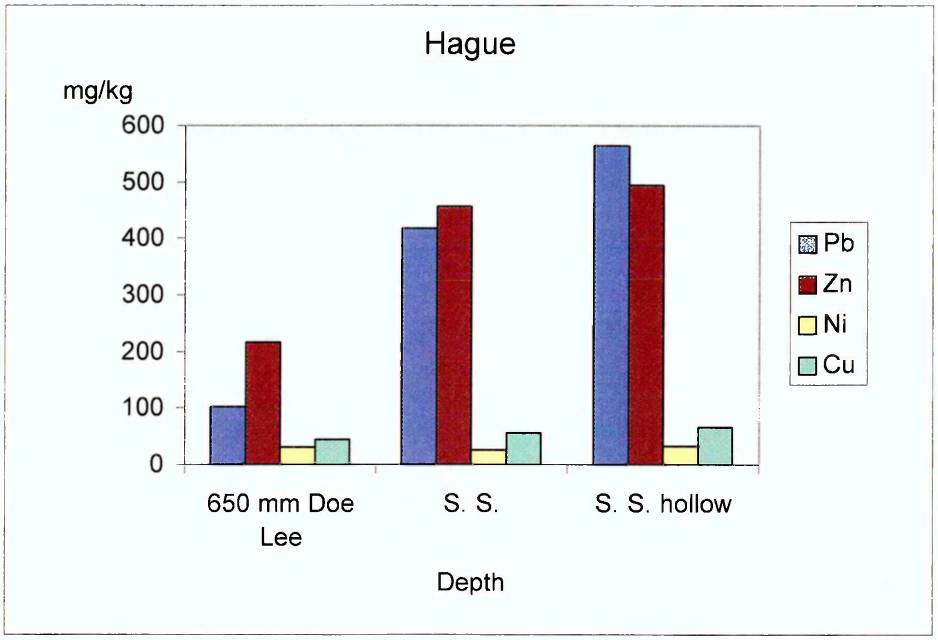


Table 5-9 Sample sites used for phase 2 analyses:

Field site No	Location	Lab sample No.	Depth
1	Renishaw	27 A	200mm
		27B	1m
		27C (Con.)	200mm
2	Killamarsh	29A	200mm
		29B	600mm
3	Beighton	32 A	300mm
		32B	1.3m
4	Catcliffe	37A	200mm
		37B	1.2m
5	Rotherham	44A	200mm
		44B	1m
6	Don 1	BH1- LAB1	100mm
		BH1- LAB2	300mm
		BH1- LAB3	600mm
		BH1- LAB4	1.2m
		BH1- LAB5	1.5m
7	Don 2	BH2- LAB6	100mm
		BH2- LAB7	300mm
		BH2- LAB8	600mm
		BH2- LAB9	1.2m
		BH2- LAB10	1.5m

Figure 5-3 A map show the sample sites between Renishaw and Rotherham.

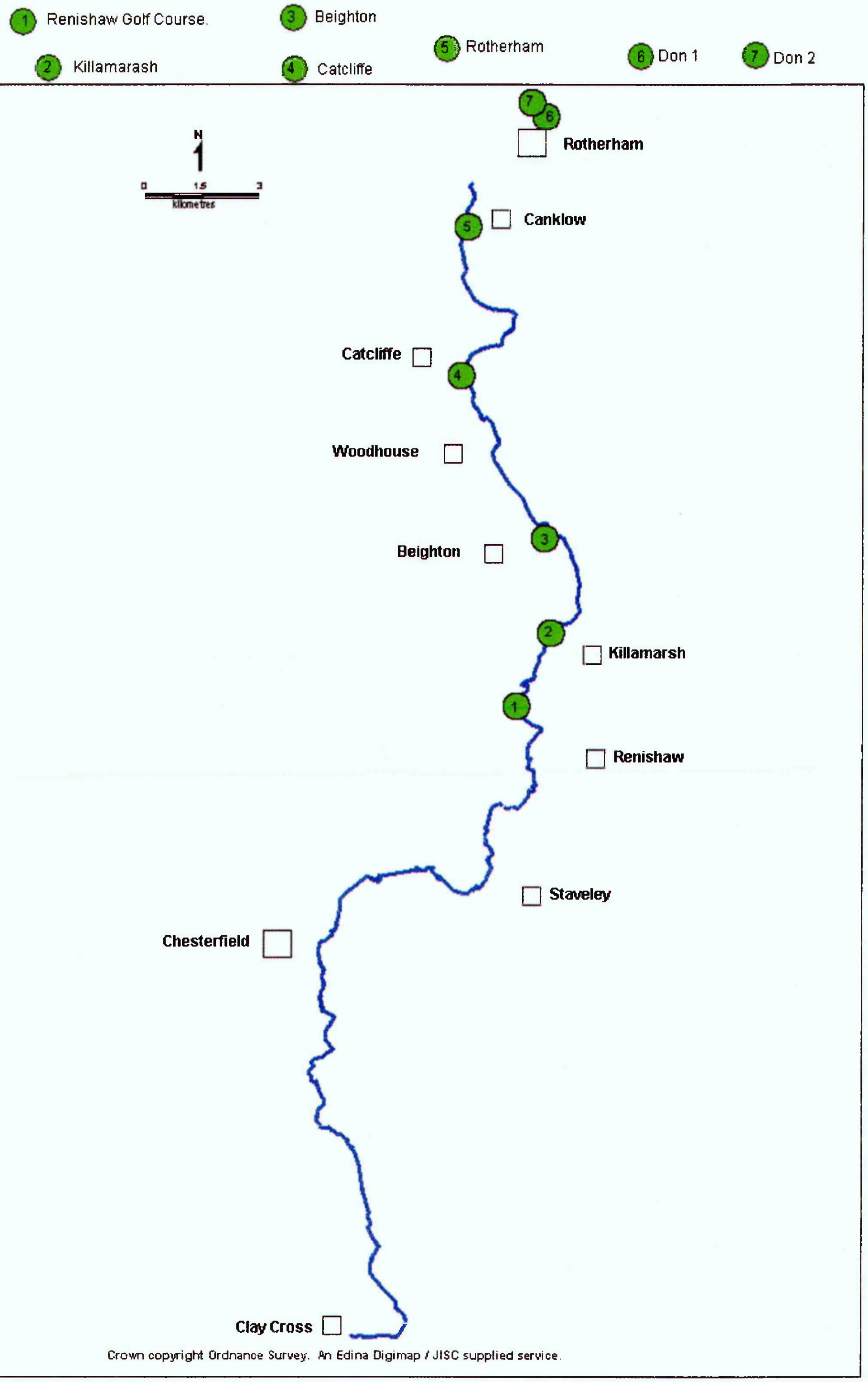


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Figure 5-4 Sketch plan for sites 1-5 of phase 2 sample sites.

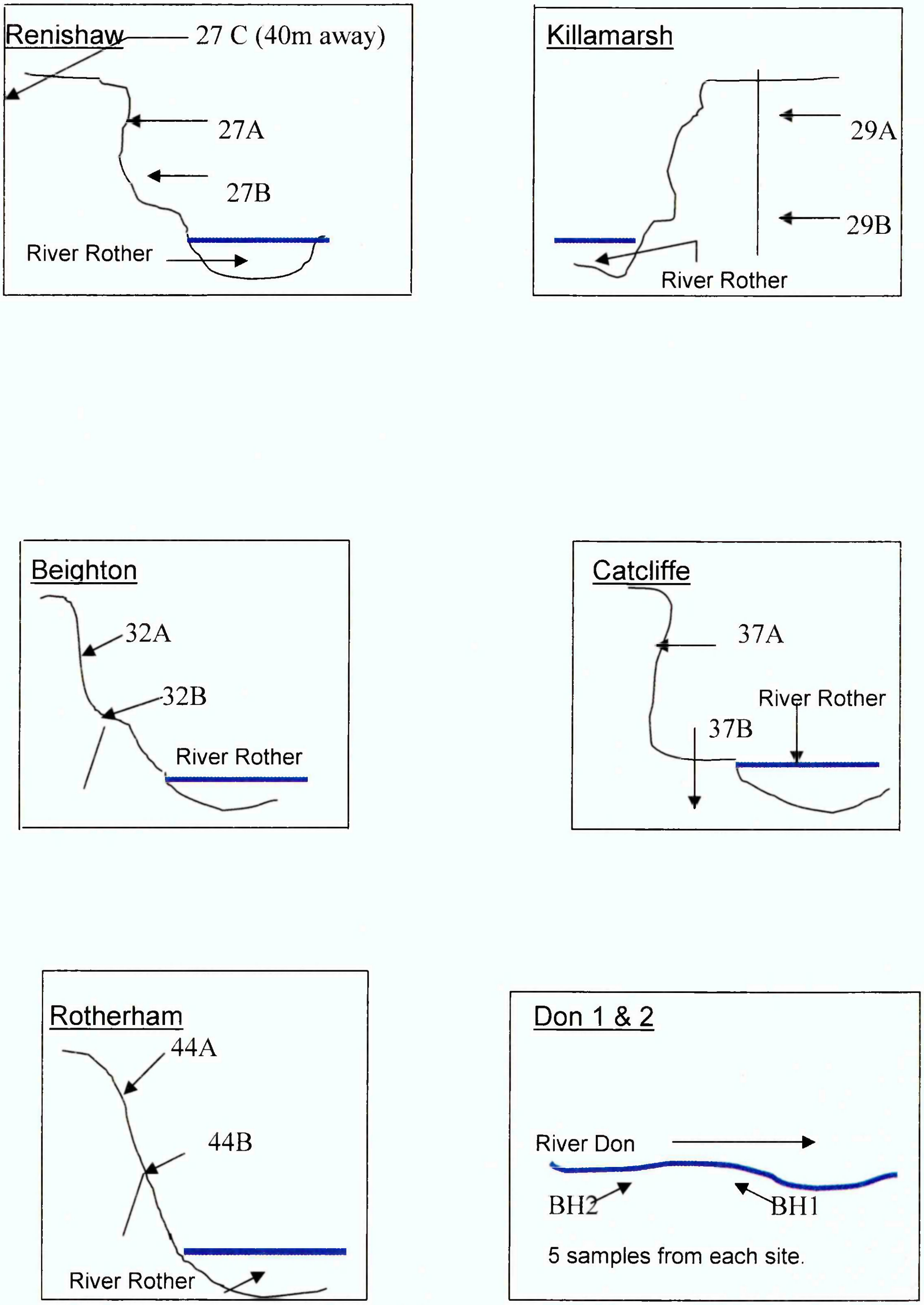


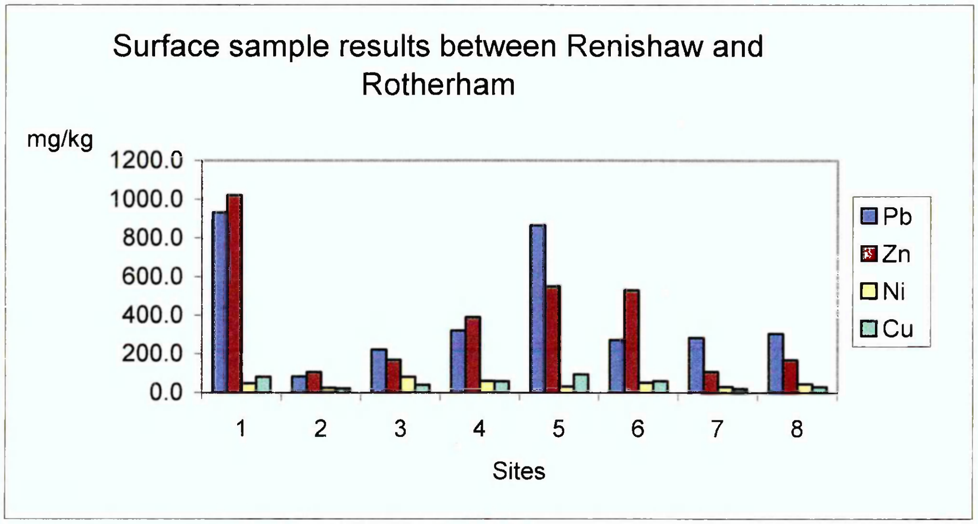
Table 5-10 This table contain total chemical analysis data from phase 2 study.

No	Site.	Lab No.	Pb mg/kg	Zn mg/kg	Ni mg/kg	Cu mg/kg	Cd mg/kg	Hg mg/kg
1	Renishaw	27A	932.1	1021.4	48.9	83.4	2.1	10.70
2		27B	418.8	268.6	65.6	43.3	0.8	2.52
3		27C	83.8	108.4	26.4	24.0	0.4	0.33
4	Killamarash	29A	223.7	169.9	82.6	40.9	0.5	0.60
5		29B	219.3	181.9	87.1	44.1	1.5	0.51
6	Beighton	32A	322.1	391.4	60.9	59.0	0.9	6.12
7		32B	411.4	571.8	56.3	65.4	2.2	6.74
8	Catcliffe	37A	865.6	550.8	32.7	95.7	1.2	16.77
9		37B	404.3	580.6	59.9	82.8	2.1	7.04
10	Rotherham	44A	273.6	531.1	52.3	60.8	4.1	3.48
11		44B	840.3	1512.2	72.3	120.2	4.2	15.56
12	Don 1	BH1-LAB1	285.8	109.0	32.2	22.0	0.4	ND
13		LAB2	246.6	173.7	36.1	57.1	0.9	0.70
14		LAB3	28.3	76.8	44.8	71.3	0.9	ND
15		LAB4	195.1	276.4	53.3	132.1	1.1	ND
16		LAB5	282.3	733.3	73.7	706.5	2.5	0.29
17	Don 2	BH2-LAB6	306.7	170.4	46.8	32.2	0.5	ND
18		LAB7	338.5	514.6	401.5	331.6	1.3	0.06
19		LAB8	31.8	60.5	49.0	85.0	0.6	ND
20		LAB9	358.8	1289.9	87.7	352.9	1.2	ND
21		LAB10	899.9	1441.2	145.5	2918.8	3.1	3.37

The following tables (5.11 –5.18) contain data from each individual sample sites.

Table 5-11 A table of data and illustrative graphs showing the heavy metals concentration (mg/kg) in floodplain soils of the phase 2 surface samples between Renishaw and Rotherham.

No.	Sites	Pb mg/kg	Zn mg/kg	Ni mg/kg	Cu mg/kg	Cd mg/kg	Hg mg/kg
1	Renishaw	932	1021	49	83	2.1	10.70
2		83	108	26	24	0.4	0.33
3	Killamarash	223	169	83	41	0.5	0.60
4	Beighton	322	391	61	59	0.9	6.12
5	Catcliffe	865	551	33	96	1.2	16.77
6	Rotherham	273	531	52	61	4.1	3.48
7	Don 1	285	109	32	22	0.4	ND
8	Don2	306	170	47	32	0.5	ND



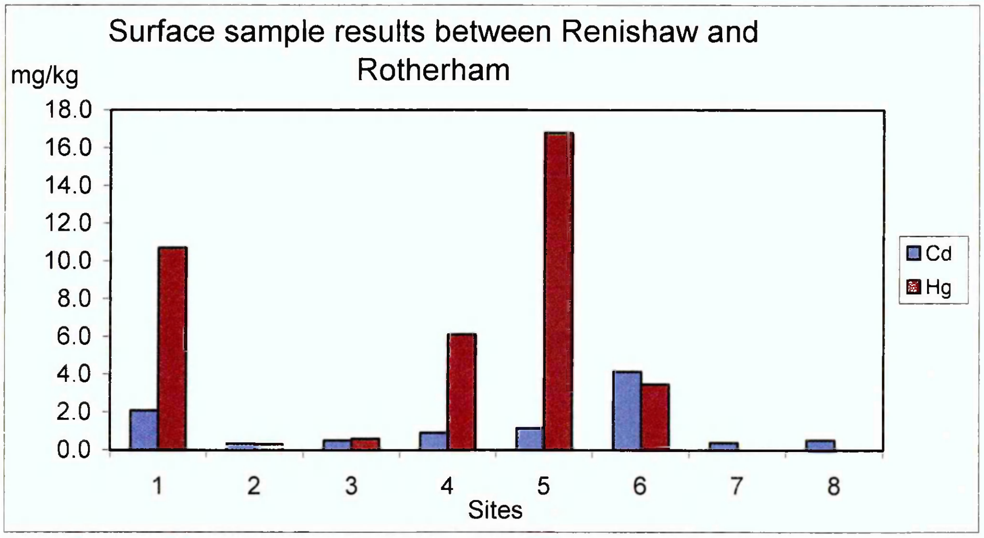


Table 5-12 Site No. 1 - Renishaw.

No	Sample desc.	Land Use	Ecological desc.
1	River Bank adjacent to the footbridge over the river. Brown alluvial soil with fragments of sandstone at the base	Riverbank and grazing land on the W side of the channel. Golf course on E side of the channel.	Area of acid grassland on former floodplain of the river
2			
3			

No.	Depth	Pb mg/kg	Zn mg/kg	Ni mg/kg	Cu mg/kg	Cd mg/kg	Hg mg/kg
1-27A	200mm	932.1	1021.4	48.9	83.4	2.1	10.70
2-27B	1 m	418.8	268.6	65.6	43.3	0.8	2.52
3-27C*	200mm	83.8	108.4	26.4	24.0	0.4	0.33

*Control Sample collected some 40m north of the River Rother.

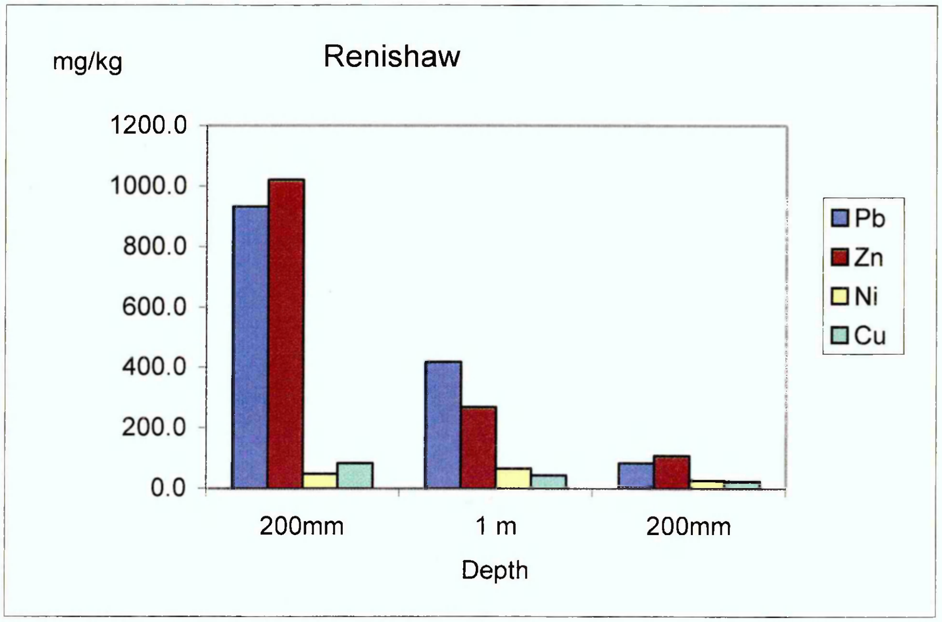


Table 5-13Site No. 2 - Killamarsh.

No	Sample desc.	Land Use	Ecological desc.
1	Dark brown clayey alluvium with rootlets.	Pasture. Land 20m S of road bridge (B6058).	Large Poplar with grass Sward beneath.
2	Brown, clayey alluvium with occasional blebs of ochre		

No.	Depth	Pb mg/kg	Zn mg/kg	Ni mg/kg	Cu mg/kg	Cd mg/kg	Hg mg/kg
1-29A	200 mm	223.7	169.9	82.6	40.9	7.78	0.60
2-29B	600 mm	219.3	190.1	87.1	44.1	7.66	0.51

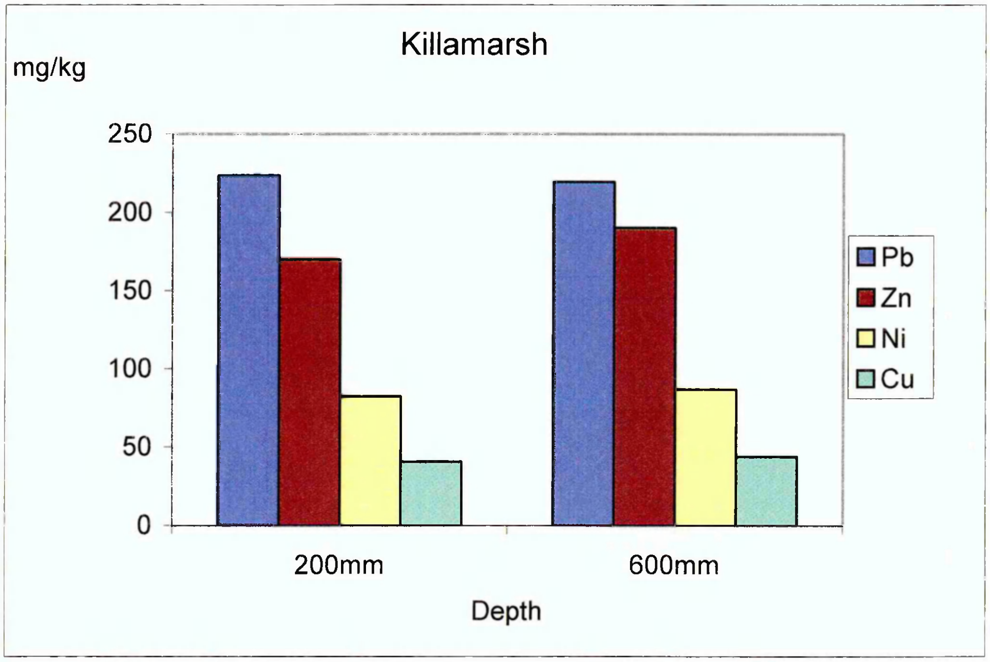


Table 5-14 Site No. 3 - Beighton.

No	Sample desc.	Land Use	Ecological desc.
1	Pale brown clayey alluvium with rootlets.	Waste land between river and railway line along E boundary.	Tall herbs with rank grasses
2	Dark brown clayey alluvium with framents of greenish sandstone.		

No.	Depth	Pb mg/kg	Zn mg/kg	Ni mg/kg	Cu mg/kg	Cd mg/kg	Hg mg/kg
1-32A	300 mm	322.1	391.4	60.9	59	7.79	6.12
2-32B	1.3m	411.4	571.0	56.3	65.4	9.65	6.74

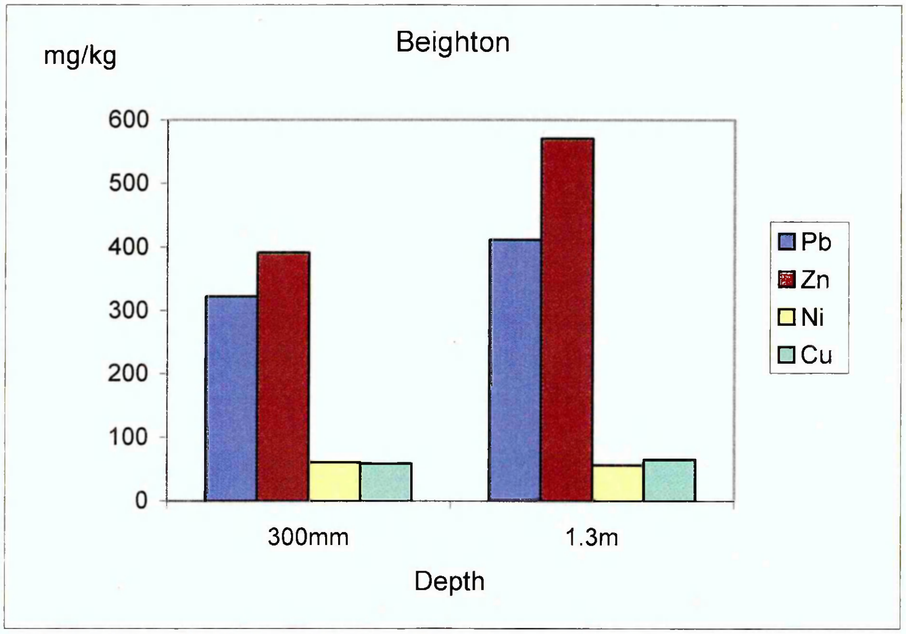


Table 5-15 Site No.4 - Catcliffe.

No	Sample desc.	Land Use	Ecological desc.
1	Pale brown clayey alluvium with rootlets	Riverbank adjacent to scrub woodland. 600m N of Orgreave Coking works.	Tall herbs plus rank grasses.
2	Dark brown alluvium with fragments of sandstone and shale.		

No.	Depth	Pb mg/kg	Zn mg/kg	Ni mg/kg	Cu mg/kg	Cd mg/kg	Hg mg/kg
1-37A	200 mm	865.6	550.8	32.7	95.7	1.2	16.77
2-37B	1.20m	404.3	580.6	59.9	82.8	2.1	7.04

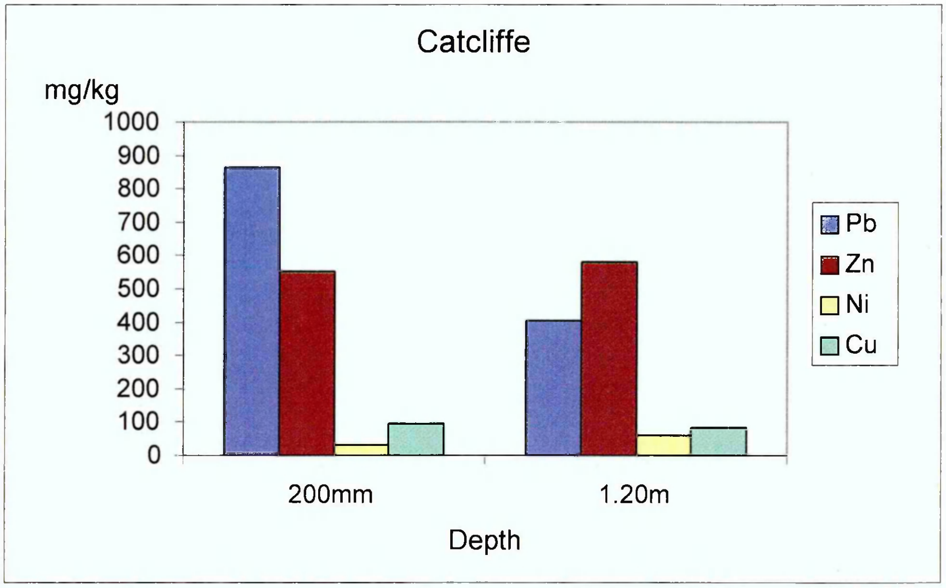


Table 5-16 Site No. 5 - Rotherham.

No	Sample desc.	Land Use	Ecological desc.
1	Pale brown clayey alluvium with rootlets.	Riverbank adjacent to recreational space 20m E of Ring Road.	Tall herbs plus rank grasses and bramble
2	Dark brown alluvium with fragments of sandstone.		

No.	Depth	Pb mg/kg	Zn mg/kg	Ni mg/kg	Cu mg/kg	Cd mg/kg	Hg mg/kg
1-44A	200 mm	273.6	531.1	52.3	60.8	4.1	3.48
2-44B	1m	840.3	1512.2	72.3	120.2	4.2	15.56

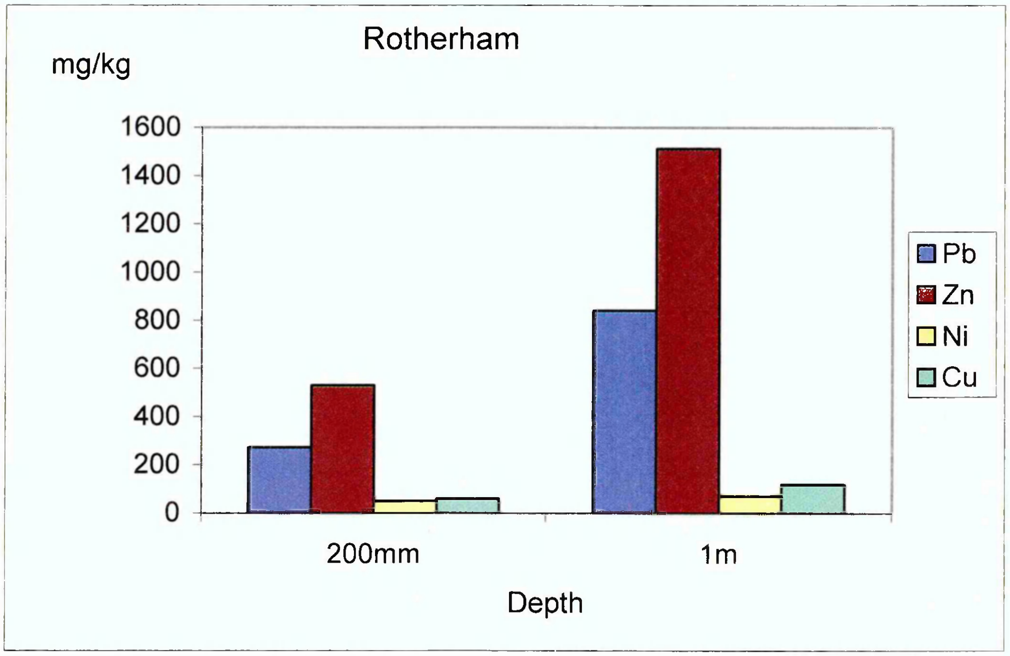


Table 5-17 Site No. 6 - Don 1.

No	Sample desc.	Land Use	Ecological desc.
1	Dark brown alluvium with fragments of sandstone. Layers of ash and cinder	Grass border to works site. Land built up from tipped wastes.	Managed grassland.
2			
3			
4			
5			

No.	Depth	Pb mg/kg	Zn mg/kg	Ni mg/kg	Cu mg/kg	Cd mg/kg	Hg mg/kg
1- BH1- LAB1	100 mm	285.8	109	32.2	22	0.4	ND
2- BH1- LAB2	300 mm	246.6	173.7	36.1	57.1	0.9	ND
3- BH1- LAB3	600 mm	28.3	76.8	44.8	71.3	0,9	ND
4- BH1- LAB4	1200 mm	195.1	276.4	53.3	132.1	1.1	ND
5- BH1- LAB5	1500 mm	182.3	733.3	73.7	706.5	2.5	0.29

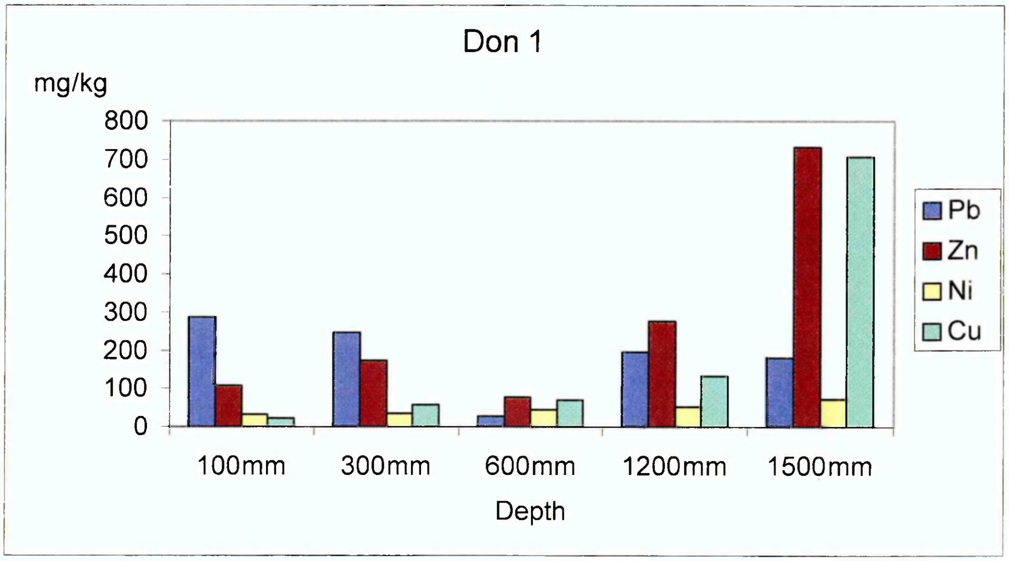
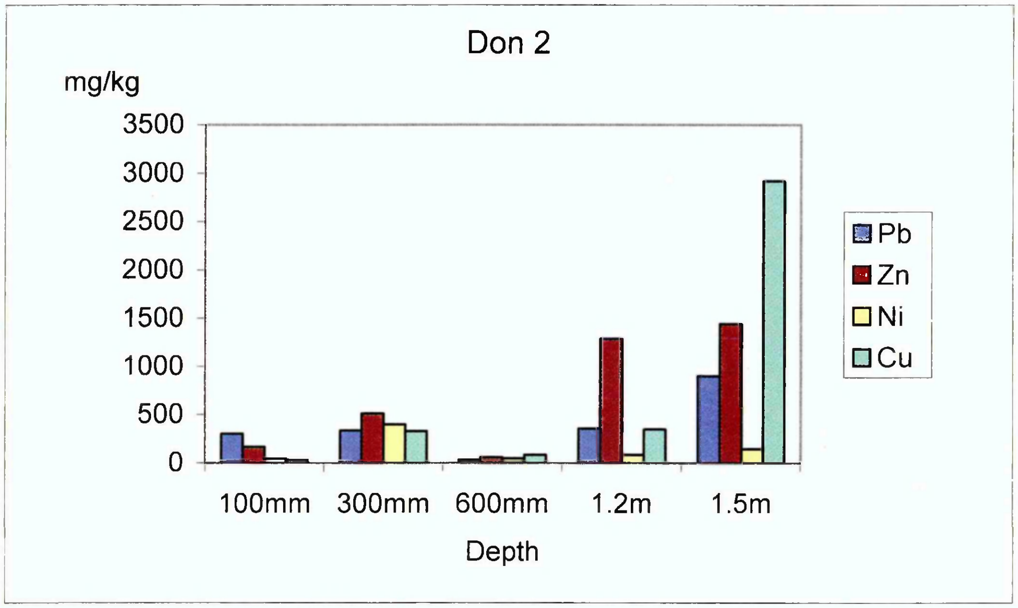


Table 5-18 Site No. 7 - Don 2.

No	Sample desc.	Land Use	Ecological desc.
1	Dark brown alluvium with fragments of sandstone. Layers of ash and cinder	Grass border to works site. Land built up from tipped wastes.	Managed grassland.
2			
3			
4			
5			

No.	Sample No.	Depth	Pb mg/kg	Zn mg/kg	Ni mg/kg	Cu mg/kg	Cd mg/kg	Hg mg/kg
1	BH2- LAB6	100 mm	306.7	170.4	46.8	32.2	0.5	ND
2	LAB7	300 mm	338.5	514.6	401.5	331.6	1.3	0.06
3	LAB8	600 mm	31.8	60.5	49	85	0.6	ND
4	LAB9	1200 mm	358.8	1289.9	87.7	352.9	1.2	ND
5	LAB10	1500 mm	899.9	1441.2	145.5	2918.8	3.1	3.37



5.2 Interpretation of Results

The results, presented in 5.1, are critically reviewed and their significance noted in preparation for the discussion in Chapter 6. The results are presented in site order from south to north along the River Rother (Table 5 -20).

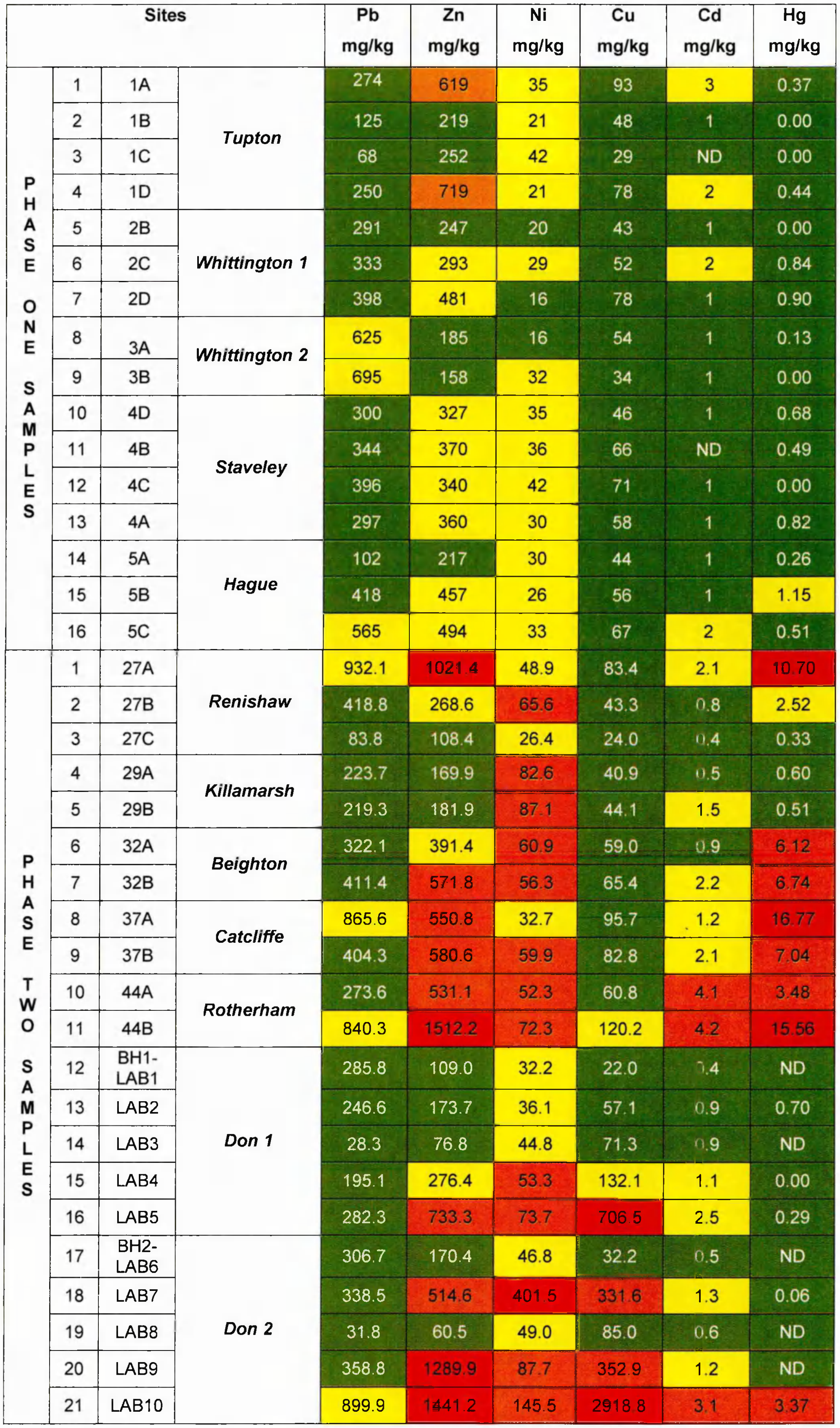
5.2.1 Levels of contaminations

The results are scrutinised and discussed, firstly against the Kelly Indices (Table 5-19 and Appendix 1) to provide an indication of the level of contamination and secondly against the New Dutch List (Table 5-21 and Appendix 3) to illustrate where action would be required if the land were to be re-developed at some date in the future.

Metal	Uncontaminated	Slight Contamination	Contaminated	Heavy Contamination
Lead	0-500	500 – 1000	1000 - 2000	2000 - 10000
Zinc	0 - 250	250 - 500	500 - 1000	1000 - 5000
Nickel	0 - 20	20 - 50	50 - 200	200 - 1000
Copper	0 - 100	100 - 200	200 - 500	500 - 2500
Cadmium	0 - 1	1 to 3	3 to 10	10 to 50
Mercury	0 - 1	1 – 3	3 – 10	10 to 50

Table 5-19 Kelly Indicators of contamination :(**All values given as mg/kg air-dried soil)**

Comparison of the results with the Kelly Indices (Table 5-19) are shown, in colour, to emphasise the general levels of contamination and to highlight those samples where heavy contamination is clearly evident.



Sites				Pb mg/kg	Zn mg/kg	Ni mg/kg	Cu mg/kg	Cd mg/kg	Hg mg/kg
PHASE ONE SAMPLES	1	1A	*Tupton*	274	619	35	93	3	0.37
	2	1B		125	219	21	48	1	0.00
	3	1C		68	252	42	29	ND	0.00
	4	1D		250	719	21	78	2	0.44
	5	2B	*Whittington 1*	291	247	20	43	1	0.00
	6	2C		333	293	29	52	2	0.84
	7	2D		398	481	16	78	1	0.90
	8	3A	*Whittington 2*	625	185	16	54	1	0.13
	9	3B		695	158	32	34	1	0.00
	10	4D	*Staveley*	300	327	35	46	1	0.68
	11	4B		344	370	36	66	ND	0.49
	12	4C		396	340	42	71	1	0.00
	13	4A		297	360	30	58	1	0.82
	14	5A	*Hague*	102	217	30	44	1	0.26
	15	5B		418	457	26	56	1	1.15
	16	5C		565	494	33	67	2	0.51
PHASE TWO SAMPLES	1	27A	*Renishaw*	932.1	1021.4	48.9	83.4	2.1	10.70
	2	27B		418.8	268.6	65.6	43.3	0.8	2.52
	3	27C		83.8	108.4	26.4	24.0	0.4	0.33
	4	29A	*Killamarsh*	223.7	169.9	82.6	40.9	0.5	0.60
	5	29B		219.3	181.9	87.1	44.1	1.5	0.51
	6	32A	*Beighton*	322.1	391.4	60.9	59.0	0.9	6.12
	7	32B		411.4	571.8	56.3	65.4	2.2	6.74
	8	37A	*Catcliffe*	865.6	550.8	32.7	95.7	1.2	16.77
	9	37B		404.3	580.6	59.9	82.8	2.1	7.04
	10	44A	*Rotherham*	273.6	531.1	52.3	60.8	4.1	3.48
	11	44B		840.3	1512.2	72.3	120.2	4.2	15.56
	12	BH1-LAB1	*Don 1*	285.8	109.0	32.2	22.0	0.4	ND
	13	LAB2		246.6	173.7	36.1	57.1	0.9	0.70
	14	LAB3		28.3	76.8	44.8	71.3	0.9	ND
	15	LAB4		195.1	276.4	53.3	132.1	1.1	0.00
	16	LAB5		282.3	733.3	73.7	706.5	2.5	0.29
	17	BH2-LAB6	*Don 2*	306.7	170.4	46.8	32.2	0.5	ND
	18	LAB7		338.5	514.6	401.5	331.6	1.3	0.06
	19	LAB8		31.8	60.5	49.0	85.0	0.6	ND
	20	LAB9		358.8	1289.9	87.7	352.9	1.2	ND
	21	LAB10		899.9	1441.2	145.5	2918.8	3.1	3.37

Table 5- 20 Results of phase I samples before upstream flooding and phase Π samples following major flood.

The table (5 - 20) illustrates the levels of contamination, compared to the Kelly Indices, showing that of total 222 samples, 57% are uncontaminated; 25% are slight contaminated; 13.5% are contaminated but only 4.5% are heavily contaminated.

Apart from the two samples collected near the surface at Tupton, the remainder show no or slight contamination. This may be a reflection upon natural river processes having moved the contaminants downstream. The pattern illustrated by the phase two samples clearly indicates heavy contamination by Zn and Hg around Renishaw and a major zone of contamination with Zn, Ni, and Hg between Beighton and Rotherhom. The high levels found in the Don samples are as a result of the tipping of wastes from former foundries and steelworks along the floodplain to raise the land above normal flood levels in preparation for the development of the trading estate.

Contaminant	**Soil sediment** *(Mg/kg dry weight)*		**Ground water** *(µg/l)*	
Metals	*Optimum*	*Action*	*Optimum*	*Action*
Cadmium	0.8	12	0.4	6
Copper	36	190	15	75
Lead	85	530	15	75
Nickel	35	210	15	75
Mercury	0.3	10	0.05	0.3
Zinc	140	720	65	800

Table 5-21 The new Dutch list of trigger values of heavy metals.

5.2.2 Trigger values of contamination

In the context of developing formally contaminated land along the flood plain of the River Rother comparison of the results obtained (Table 5-20) needs to be compared with the trigger values as set out in the "New Dutch List" (Table 5-21 and Appendix 3), for levels where amelioration would be required. Each site is discussed in turn.

I) Tupton Site

The samples of this site were taken from different depths as shown previously. There were two surface samples (1A and 1D). These particular samples were indicating high levels in Zn but were below the action level of 720 mg/kg. Otherwise all samples from different depths were in the range that count not polluted.

II) Whittington Moor 1

All samples from this site was indicating an acceptable range according to the new Dutch list trigger values for contaminants.

III) Whittington Moor 2

The Zn, Ni, Cu, Cd, and Hg scored low concentration levels, which were in the acceptable range. Pb values were high in both surface samples and above the trigger values of 530 mg/kg (Dutch list).

IV) Staveley

All samples from different depths indicated low concentrations of Pb, Zn Ni, Cu, Cd, and Hg. All were well below trigger values.

V) Hague

All samples in this site from different depths, which were taken from the flood plain of the Doe Lea, were within the acceptable ranges for Pb, Zn, Ni, Cu, Cd, and Hg concentrations. On the contrary, sample 5C from beside the Rother indicated acceptable concentrations levels for elements Zn, Ni, Cu, Cd, and Hg, while the Pb value was higher yet well below the trigger value of 530 mg/kg (Dutch list).

VI) Renishaw

Sample 27 B and sample 27C, which is a control sample for this site, indicated acceptable levels of heavy metals recorded. Whereas the other surface sample, 27A indicated high levels compared to the control sample and well below the trigger values. Sample 27A, however, recorded levels of Pb, Zn and Hg above the trigger values while Levels of Cu, Cd and Ni the acceptable range below the trigger values. The level of Hg was exceptionally high and indicates the position of the upper part of the contaminant plume.

VII) Killamarsh

This site recorded acceptable values of the heavy metals in all samples from different depths according to the new Dutch list trigger values for heavy metals.

VIII) Beighton

All samples from this site at different depths recorded acceptable values of the heavy metals according to the new Dutch list. Elevated levels of the Hg were noted, even though they were below the trigger values.

IX) Catcliffe

At this site, surface sample 37A recorded high levels of Hg and Pb well above trigger values. Other samples from different depths recorded acceptable levels of heavy metals. The recorded concentration of Hg at this site was the highest value of all samples collected along the River Rother and represents the position of the lower plume as it migrates towards Rotherham and the confluence with the River Don.

X) Rotherham

In the surface sample 44A, levels of heavy metals indicated acceptable values, according to the new Dutch list. The sample 44B from 1m depth, recorded acceptable values of Ni, Cu and Cd. but the values of Pb, Zn and Hg were well above the trigger values (Dutch list) indicating some earlier period of gross pollution near this site.

XI) Don 1

All samples from different depths in this site recorded acceptable values of heavy metals according to the new Dutch list. However, the sample (LAB5), with a depth of 1.5 m recorded values of Zn and Cu above the trigger values of 720 mg/kg respectively indicating the presence of some metals at depth.

XII) Don 2

The surface sample and other samples from different depths in this site, indicate acceptable values of heavy metals except sample (LAB10), and sample (LAB9). These recorded values above trigger levels for Pb and more emphatically for Zn corroborating the suggestion that metal wastes have been deposited at some earlier time through anthropogenic activity around this site.

CHAPTER 6 : DISCUSSION

6. Discussion:

6.1 Introduction:

The results presented in Chapter 5 are showing the concentrations of heavy metals from
different depths at different sites along the flood plain of the River Rother.

Consideration of the previous studies along the River Rother confirms that it is difficult to compare the earlier results with those of the present study. Most of the previous studies have focussed upon the determination of mercury levels in bed-load sediments. The differences of methodologies and strategies that were followed also make comparison difficult. Table 6-1 shows the results obtained from different sources for comparative purposes. Table (6-1) shows the results of the studies made in 1983 by Doyle,1988 by Murfin, 1991 by Gunn, 1995 by Duty and 2001 by Barfield in addition to this current research. Most of the previous studies did focus on specific sites, such as Staveley, which had a history of industries causing contamination.

The results of the present study, presented in Table 5-20 (page 101), provide an excellent illustration of the levels of contamination when compared to the Kelly's Indices. The greater number of samples are not contaminated but there distinct zones of contamination evident, one around Renishaw and Killamarsh and the other further downstream between Beighton and Rotherham (Table 6-2 and Figure 6-1). Within these two zones the metals causing the contamination are nickel, mercury and zinc in the upper zone and cadmium, nickel, mercury and zinc in the lower zone. The probable sources of this contamination were the former metal-working industries as well as the processing of chemicals, many derived from local coal, at sites upstream of Renishaw. Periodic flood episodes have added contaminated bed-load to the surface of the floodplain and identified in samples 27A. 29A, 37A and 44A.

The heavy contamination identified in the Don borehole samples is due to an entirely different set of circumstances. In order to raise the level of the floodplain to a height above normal flood levels the tipping of furnace ash and cinder was encouraged from local metal working factories. This has left a legacy of a cocktail of cadmium, copper, nickel, mercury and zinc at various depths within the fill material.

Scrutiny of the results displayed in Table 6-1 further validates the presence of the contamination plume which is slowly migrating downstream and is illustrated by the values for mercury (Figure. 6-2)

Murfin indicated the presence of the plume between Whittington and Hague in 1988.

By 1995, Duty indicated that the plume had split, with one part moving downstream faster than the other. He located the upper plume between Hague and Renishaw and the lower one between Beighton and Catcliffe. These correlate very well with the upper and lower zones respectively, demonstrated in Table 5-20. The present study, using the surface, post-flood samples indicates some further migration with the upper plume around Renishaw and the lower one leaving Beighton for Catcliffe. The significance of these observations supports the idea of the river cleansing itself through natural hydrological processes causing the offending metal pollutants to migrate to the River Don.

The natural hydrological processes of active erosion, transportation and deposition occur primarily when the river is in spate and therefore discharge is higher. Under these circumstances materials from the bed-load and the river bank are picked up and carried downstream until such time and the energy levels in the river channel fall and enable deposition to take place. This may be beyond the river bank on to the floodplain or within the river channel itself. This sequence of processes is repeated during each flood episode thus causing the contaminated soils to migrate downstream towards the River Don.

Furthemore, this chapter discusses the significance of selected values of the metals at each site in relation to the contamination of the environment and its potential after-use by reference to the Dutch list standards (Table 5-21) and those set out by DEFRA (Table 6-3). The tables of trigger values, as presented in the New Dutch List and DEFRA, are used in the current study because they are the most up-to-date tables used by the Planning Authorities. While the Dutch List caters, not only for metal contamination but a wider range of other types of contaminants found in land to be used for future development for industrial, domestic or recreational uses. The DEFRA scale has been designed specifically for reclamation to agricultural use of former contaminated land especially where sewage sludge is to be used in the amelioration process.

Table 6-1 Comparative results obtained from different studies in the River Rother catchment:

Site	Doyle **1983** Sediment mg/kg			Murfin **1988** mg/kg *	Gunn **1991**. Soil samples- mg/kg			Duty **1995** mg/kg*	Barfield **2001** mg/kg*		B. Ahmed **2002** Soil samples					
	Hg	**Cd**	**Ni**	**Hg**	**Pb**	**Zn**	**Cd**	**Hg**	**Hg**	**Hg[1]**	**Pb**	**Zn**	**Ni**	**Cu**	**Cd**	**Hg**
Tupton	-	-	-	0.075	-	-	-	0.11			274	619	35	93	3	0.37
Wittington1	-	-	-	**0.838**	-	-	-	0.055			398	78	16	481	1	0.90
Wittington2	-	-	-	**0.506**	-	-	-	0.113			625	185	16	54	1	0.13
Staveley	50.0	2.427	43.7	-	-	-	-	0.041			300	327	35	46	1	0.68
Hague	-	-	-	**0.825**	-	-	-	**7.257**			418	457	26	56	1	1.15
Renishaw	-	-	-	0.15	-	-	-	**1.062**			932.1	1021.4	48.9	83.4	2.1	**10.70**
Killamarsh	-	-	-	0.131	444.7	184	0.49	0.068			83.8	108.4	26.4	24.0	0.4	0.60
Beighton	-	-	-	0.045	1185	2421	4.98	**1.282**			223.7	169.9	82.6	40.9	0.5	**6.12**
Catcliffe	-	-	-	4.15	-	-	-	**6.36**	1.28	0.5/ 2	322.1	391.4	60.9	59.0	0.9	**16.77**
Rotherham	-	-	-	0.08	-	-	-	0.938	0.55		865.6	550.8	32.7	95.7	1.2	**3.48**
Don 1	-	-	-	-	-	-	-	-			273.6	531.1	52.3	60.8	4.1	0.00
Don 2	-	-	-	-	-	-	-	-			285.8	109.0	32.2	22.0	0.4	0.00

* Sediment samples.

[1] Rotherham Environmental Health results {0.5 mg/kg (sediment sample) and 2 mg/kg (flood sediment from riverbank).

Table 6-2 Indicative levels of contamination for Lead and Zinc.

Site	Tupton	Wh1	Wh2	Staveley	Hague1	Hague2	Renishaw	Killamarsh	Beighton	Catcliffe	Rotherham	Don1	Don2
Pb	274	398	625	300	418	565	932	232	322	865	273	285	306
Zn	619	78	185	327	457	494	1021	169	391	551	531	109	170

Figure 6-1 Graph to illustrate the position of the two contamination zones along the River Rother.

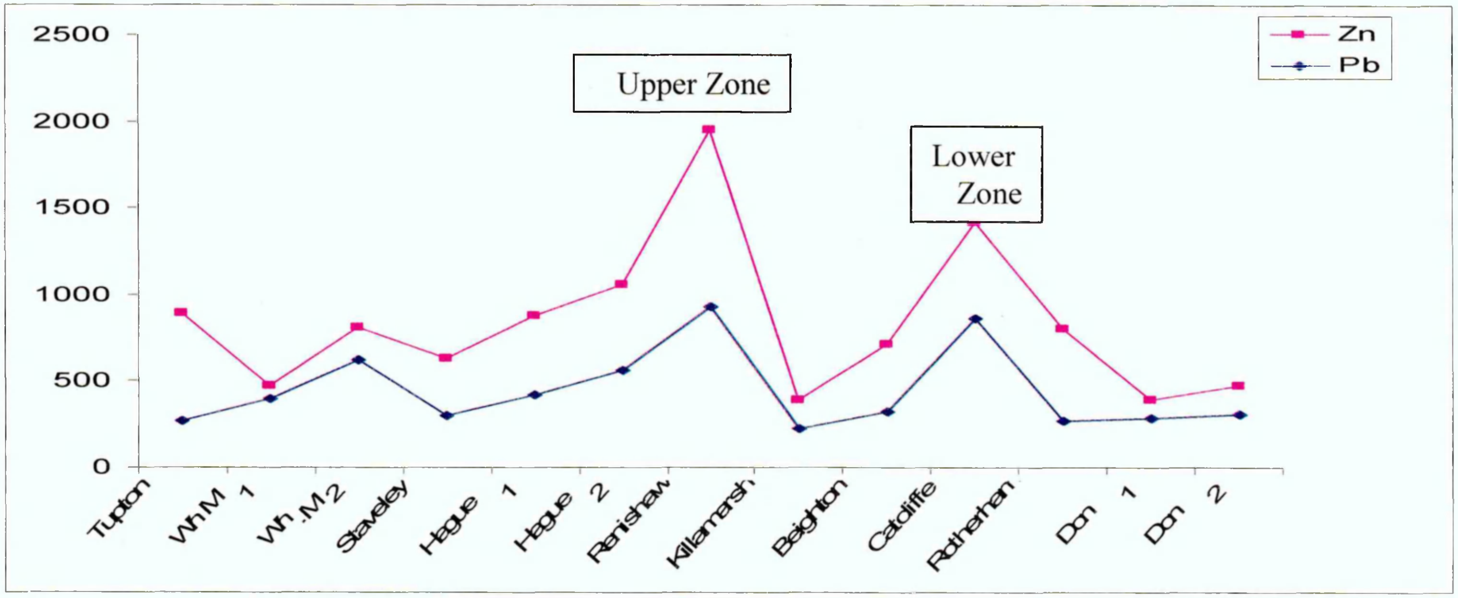
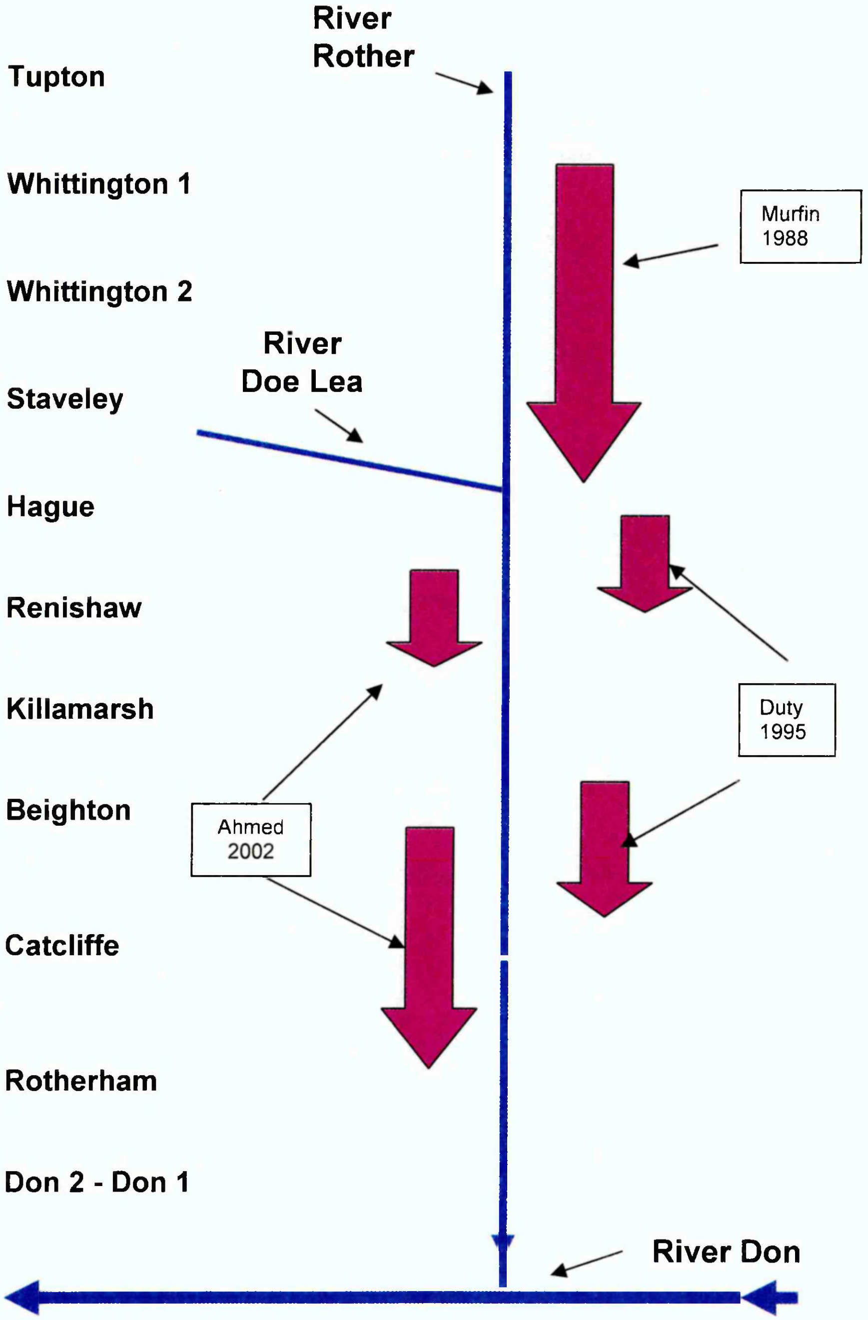


Figure 6-2 Migration of Mercury Contaminant plume downstream along the River Rother catchment based in values in Table 6- 1.



NOTE: The contamination plume identified by Murfin 1988, above Staveley, divides into two smaller plumes at Hague and below Beighton, according to Duty (1995)

The present study indicates that the two smaller plumes are migrating downstream, with upper one around Renishaw and the lower one approaching Catciffe from Beighton.

Standards		**Pb mg/kg**	**Zn mg/kg**	**Ni mg/kg**	**Cu mg/kg**	**Cd mg/kg**	**Hg mg/kg**
*DEFRA**	PH 5 - 5.5	300	200	50	80	3	1
	pH 5.5 – 6		200	60	100		
	pH 6 - 7		200	75	135		
	pH >7		300	110	200		

Table 6-3 **The DEFRA Standards.** *(* for more details see appendix No.5)*

6.2 The DEFRA Standards

To discuss the results for contaminated land to be re-used for agriculture it is necessary to refer to the DEFRA guideline threshold values for action prior to it being used for crops or livestock.

MERCURY

Mercury is one of the most poisonous elements to many animals and man. Soil concentration of mercury should not be greater than 1mg/kg of dry soil or 10mg/kg respectively for DEFRA and Dutch List values.

According to the Department of the Environment, Food and Rural Affairs DEFRA (1998) standards, the threshold values are higher than the maximum permissible and advisable concentrations of potentially toxic elements in soils. The DEFRA standard value of 1mg/kg is the maximum permissible concentration.

It is obvious from the mercury results that the upstream sites (Tupton, Whittington Moor 1&2 and Staveley) have become cleaner and safe from mercury. In other words, the cleansing of the river sediments has progressed naturally, over time, supported by some separate reclamation activities at specific hot spots along the valley such as Coalite Company, Avenue Works and Ireland Colliery.

The highest value recorded was 16.77mg/kg in the surface sample at Catcliffe and a high value in the 1.2m sample was 7.04mg/kg. This is most likely to be linked to the discharges from the former Orgreave Coke Works in times past. The high values of the surface sample was interesting as the material was collected immediately after a major flood event thereby illustrating the potential for heavy metal migration downstream during spate events.

Renishaw, Beighton and Rotherham sites were recording values of 10/70mg/kg, 6.12mg/kg and 3.48mg/kg in succession. The value at Renishaw may be as a result of the discharges from the former collieries at Renishaw and Barrowhill and linked to the discharges from the Staveley works during the 1900's. The value recorded at Beighton may be caused by the dischrges from the former Beigjhton Brookhouse Colliery. Upstream of Hague the value of 1.15mg/kg was recorded which is above the permissible DEFRA standard and may well be related to former discharges from Staveley Chemicals. The higher values of mercury referred to support the idea of a former Mercury plume having split thus enabling the two sections to migrate at different rates downstream (See figure 6-2).

CADMIUM

Cadmium is often found along with geological deposits of lead and zinc particularly when the latter elements have been mined. In this case, the high concentration of lead and zinc will have much greater effect than the cadmium The effect of cadmium is greater at low pH values. For example, grazing cattle ingesting cadmium suffer from a build up of the cadmium in liver and kidney tissues. The guideline concentration of 3mg/kg of cadmium in soil is set to protect the food supply for animals and man, whereas, plant growth is not affected at this level (DEFRA, 1998).

The threshold value of 3mg/kg set by DEFRA was only exceeded at Rotherham with a surface value of 4.1mg/kg and 4.2mg/kg at 1m depth. The Dutch List value of 12mg/kg was not exceeded in any of the samples. Only in the borehole sample of Don 2 was a value of 3.1mg/kg obtained but this was at a depth of 1.5m. The high values at the Rotherham site could be attributable to the nearby plant re-processing steel slags while the levels at Don 2 would be from the tipped furnace wastes as part of the eraly landfill operation.

LEAD

The existence of lead in soil with a pH greater than 6.0 is not normally toxic to plants however eating soil contaminated herbage could be dangerous to livestock. The chemical and physical form of the lead affects its absorption rate and translocation in the various plants. Thus in a soil contaminated by over 300mg/kg dry soil would the level in the vegetation exceed the DEFRA standard of 1mg/kg. However care must be taken during harvesting to ensure that the crop is not contaminated with soil (DEFRA, 1998).

Comparison of the analysed samples with the DEFRA threshold value show that six of the fourteen surface samples were below threshold and eight were above therefore they would require further investigation.

ZINC

For the re-use of a site its past history of occupation and activity is important to determine whether contamination is likely. Some plants are not susceptible to high concentrations of zinc, depending upon the pH of the soils eg. some plants growing of former mine-spoil. DEFRA set a threshold value of 1000mg/kg for zinc at a pH of 6.0 for the growing of Clover and productive grass species. Zinc derived from industrial wastes, sewage sludge or atmospheric deposition is more available to plants thus sensitive species may be affected by values around 300mg/kg in slightly alkaline soils (between pH 6.0 to 7.0) (DEFRA, 1998). The recommended threshold values by DEFRA for soils whose pH is between 5.0 & 7.0 is 200mg/kg and 300mg/kg for soils where the pH is above 7.0

An examination of the results obtained in this study show that nine samples gave values above the DEFRA thresholds, they were at: Tupton (619mg/kg), Whittington Moor 1 (481mg/kg), Staveley (327mg/kg), Hague (457mg/kg), Renishaw (1021.4mg/kg), Catcliffe (550.8mg/kg), Beighton (391.4mg/kg) and at

Rotherham (531.1mg/kg). However it is most likely that none of the soils have a pH above neutral.

NICKEL

Nickel is phytotoxic and therefore in order to protect against damage to both crops and animals DEFRA has set a threshold value of 75mg/kg for dry soil where the pH is between 6.0 –7.0 and is receiving sewage sludge to help with amelioration.. Variation in the pH value of the soils would attract different values as follows :-

pH value	Threshold value
5.0 – 5.5	50 mg/kg
5.5 – 6.0	60 mg/kg
6.0 – 7.0	75 mg/kg
above 7.0	110 mg/kg

In comparison with the DEFRA threshold values only three samples gave values above threshold, and they are : at Killamarsh (82.6 mg/kg)*, at Beighton (60.9 mg/kg)* and at Rotherham (52.3 mg/kg)*. It is important to note that the soil pH values, marked with an asterix (*) are not known and therefore the significance of the values is difficult to determine.

COPPER

Although copper is an essential plant micro-nutrient it can be phytotoxic in high concentrations. At a soil pH of 6.0 or above, a total soil concentration of copper from geological sources of up to 500 mg/kg dry soil would allow the growth of productive grasses, however sensitive species of grasses or Clover may be affected at values of 250 mg/kg. Cattle are more likely to suffer from copper deficiencies than higher concentrations (DEFRA, 1998). DEFRA quotes the following threshold values at the different ranges of pH:-

pH values	Threshold values
5.0 – 5.5	80 mg/kg
5.5 – 6.0	100 mg/kg
6.0 – 7.0	135 mg/kg
above 7.0	200 mg/kg

6.3 The New Dutch List.

This standard is based on the publication of intervention values and target values for soil quality standards issued by the Ministry of Housing, Spatial Planning and Environment, Department of Soil Protection, The Netherlands. These are the standards which are used as guideline target values for contaminants in soils which are being processed for some future change in land use of the site. For heavy metals they are the target values above which action has to be taken to reduce the levels present in the soils.

MERCURY

The threshold value set by the New Dutch List for mercury is 10 mg/kg in dry soil. It is noted that all the samples in phase 1 are free of mercury contamination. However, in phase 2 samples those collected from Renishaw (10.7 mg/kg), Catcliffe (16.77 mg/kg) and Rotherham (15.56 mg/kg) are heavily contaminated by mercury. It is significant that these three sites are all downstream of Staveley and the tributary, the Doe Lea, which may have been a former hot-spot for mercury contamination.

CADMIUM

All samples from the sites in phases 1 & 2 are free of cadmium contamination when compared to the New Dutch List which presents a threshold value of 12 mg/kg in dry soils.

COPPER

The only samples, when compared to the New Dutch List Threshold value of 130 mg/kg, showing signs of contamination are found in the boreholes at Don 1 and Don 2.. At a depth of 1.5m in Don 1 the value is 706.5 mg/kg while in Don 2 values of 331.6 mg/kg at 300mm; 352.9 mg/kg at 1200mm and 2918.8 mg/kg at 1500mm were obtained It is noted that these high levels are at depth and not in surface sample therefore they must be attributed to the tipped wastes used to build up the level of the land prior to its development.

NICKEL

The threshold value given in the New Dutch List for Nickel is 210 mg/kg in dry soil. Values recorded from the present study have only one value above threshold at Don 2 with a value of 401.5 mg/kg at a depth of 300mm. Again, this must be attributed to the tipped wastes and not from river contamination.

ZINC

The New Dutch List threshold value for zinc is 720 mg/kg in dry soil. Most of the samples from the current study are free of zinc contamination except from Renshaw (1021.4 mg/kg), Rotherham (1512.2 mg/kg) , Don 1 (733.3 mg/kg) and Don 2 (1289.9 mg/kg & 1441.2 mg/kg). Only the high value at Renishaw is in a surface sample, the remainder are at various depths within the floodplain. It is most likely that these values reflect past anthopogenic activities.

LEAD

The New Dutch List threshold value for lead is 530 mg/kg in dry soil. Comparing the findings from the present study show that some of the sites are free while others are mildly contaminated by lead. The sites with values higher that the threshold are Whittington 2 (625 & 695 mg/kg respectively), Hague (565 mg/kg), Renishaw (932.1 mg/kg), Catcliffe (865.6 mg/kg), Rotherham (840 mg/kg) and

Don 2 (899.9 mg/kg). Explanation of these values shows a mix of recent spate events and earlier anthopogenic activities.

6.4 Recommendations

Recommendations have to be set in the context of the floodplain land being required by the Environment Agency for flood protection. At several sites along the river adjustable flood barriers have been installed to pond back the flood waters during any flood episode and to release them in a controlled manner so as to prevent flooding of the towns of Rotherham and Doncaster downstream. However, some of the land could be used temporarily for conservation, animal grazing and recreation purposes. Professional guidance on the ways to clean-up contaminated land has developed considerably over the past twenty years such that most derelict sites can now be made safe for re-use.

6.4.1 Clean Up Technology

Overviews of clean up technologies, introduced by by Denner and Bentley (1991) and Armishaw *et al* (1992 & 1993), described five generic treatment categories. These categories derived from the work into waste treatment processes that they had undertaken at Warren Spring Laboratory (Syms, 1997). "The systems they identified were:

- Biological system of soil treatment, which depends on the biological transformation or mineralization of contaminants to less toxic states. Biological processes can also be used to fix and accumulate contaminants in harvestable biomass.
- Chemical systems in soil treatment are used to destroy, fix or neutralize toxic compounds. Chemical processes do not necessarily destroy contaminants. Chemical processes of fixation have been grouped with solidification for convenience since solidification-based processes tend to be associated with stabilization processes and vice versa.

- Physical systems in soil treatment are used to remove contaminants from the soil matrix, concentrating them in process residues requiring further treatment or safe disposal.
- Solidification systems are those which encapsulate the waste in a monolithic solid or high structural integrity. Solidification may or may not be accompanied by the destruction or stabilization of contaminants in the solid mass.
- Thermal systems are those based on incineration, gasification or pyrolysis at elevated temperature.

Within each of these generic categories there are numerous different types of treatment, some of which may be commercially available, whilst others are only at the experimental or pilot study stages" (Syms, 1997,p.104).

Of the different types of technical treatment systems outlined above there are other classifications according to the form of the contamination and the nature of the site (see Appendix No. 6).

6.4.2 Re-use of the contaminated sites

Bearing in mind the constraints of the use of the floodplain land set out in section 6.4 (p. 119) the land is unlikely to be used for housing but certainly can be used for recreational use. Some small areas at the margin of the floodplain can and are being used for commercial purposes, eg at Avenue site, south of Tupton, at Staveley, at Holbrook and at Rotherham particularly around the Don 1 & Don 2.site.

Those sites destined for recreational use can be for either passive or active use. The active sites are catering for a number of leisure activities including sports, equestrian activities, sailing, fishing and general walking. The passive sites are being given over to wildlife conservation where active management is increasing the biodiversity of the areas involved. All of these after-uses are in-line with the proposals set out in the River Rother Wildlife Strategy (Anon, 1994)

In this context the levels of contamination only become an issue where people are to be involved in some form of active recreation. Areas such as the former colliery sites at Poolsbrook and Rother Valley Country Park have been treated and landscaped to enable different sports to take place such as golf, cycling, horse riding, fishing and other water sports (rowing, sailing, canoeing, wind-surfing and jet-ski racing) within the confines of the floodplain. Other areas have been created to encourage increased birdlife and so become a focus for more passive recreation. However, some sites have been earmarked for more intensive conservation management where the regimes applied are to increase the biodiversity of the sites. Excellent examples exist at Holbrook and at the Woodhouse Washlands where education becomes a key element in the recreation pastime. As part of the management regimes applied to these sites grazing animals, cattle and or sheep, are being employed to keep the vegetation under control and thereby increase the floristic diversity. The levels of contamination reported in Chapter 5 will have little impact on these types of activities.

In all cases no major programme of amelioration has had to be carried out in order to achieve the re-use objectives. There is some concern that temporary contamination of parts of these floodplain areas may occur following flood events. Under such circumstances intervention may be required in the short term in order to protect the users of the recreational areas involved. This may mean restricted access for a period of time, physical removal of the offending contaminated waste if possible or some form of *in situ* treatment to ameliorate the contamination. To date this has not had to happen.

There are a few sites which are heavily contaminated and which are currently being cleaned up under the auspices of the Regional Development Agencies (RDA's), namely the East Midlands Development Agency (EMDA) and the Yorkshire and the Humber Development Agency (Yorkshire Forward). In the south of the catchment, Avenue Coke works is being cleaned up using a range of technologies to remove coal tar derivatives and other metal contamination so that the site may have a mixed enterprise of commercial and recreational use. Similarly the Orgreave Coke works, near Catcliffe, has been mined by opencast methods to provide deep holes, lined with welded, geotextile liners to accept contaminated waste from around the site and the former works. This material to be buried, more than 200m deep, in a safe manner before being back-filled and landscaped for both commercial and recreational use. This programme will provide a new section of river channel and adjacent areas for conservation and passive recreation while at the margin of the floodplain new land for commercial development will be created.

Along the length of the River Rother, parts of the flood plain can and have been used for the grazing of horses and store cattle but not on an intensive scale. As previously mentioned some of these areas are now being targeted for more intensive management regimes to improve the biodiversity quality to meet the targets of the various Biodiversity Action Plans (BAP's). This enables floodplain land to be upgraded to maintain its floristic quality and to still ensure that it is available as part of the flood defences required by the Environment Agency to protect habitation further downstream. It is most unlikely; therefore, that planning permissions will be granted for housing but encouragement will be given to establishing an attractive, green, well -managed fluvial landscape along the course of the River Rother.

CHAPTER 7: CONCLUSION

7. Conclusion

The rapid increase in technological ability that resulted from the Industrial Revolution lead to gross pollution of the area around the water courses. This led to an increase in legal constraints on Industry and the control of the discharge of noxious and toxic metals from them.

The River Rother was one of the watercourses in Derbyshire that was badly contaminated by those early industries. Therefore, it became essential to work on the closure of the major industrial sites that caused the pollution in order to reduce the sources of contamination.

The introduction of legislation to reduce contamination of the environment has caused a major reduction in the output of heavy metals. In fact, the legislation has been effective in reducing excessive, toxic discharges from many industrial sources. Similarly the demise of many of the older industries such as forges, mines and coke works was witnessed as they became less efficient and were closed as part of the changing economy. The increase in the production of electricity from natural gas led to a decrease in the demand for coal followed by the closure of most of the collieries, many of which were over 100 years old.

The introduction of smoke-free zones in major conurbations was the final blow to the use of coal, for both factory and domestic use, leading to further closures of uneconomic mines.

Changes in technologies, away from coal-based chemical industries, increased the rate of which polluting effluents were being replaced. This has caused a decrease in some metals but has shown increases in others, such as mercury.

Latterly, the changes in legislation introducing environmental controls have further reduced the discharges of all effluents, including metals, into the environment. This is clearly evident along the valley of the River Rother.

The current investigation has revealed varied levels of contamination by heavy metals in the soils of the Rother floodplain. Fortunately most of the heaviest pollution is buried at depth within the floodplain soils but may at some future date be exhumed by the erosive action of the river.

Most of the surface samples yielded low contamination values where few sites would require active amelioration in order to use the sites for some other kind of development. As stated earlier (Section 6.4.2, p. 120) most of the floodplain land will be retained as part of the flood control system in place on the Rother. Thus re-use of the land for passive recreation and/or conservation would not require any major clean-up. The buried contamination will only be exposed through natural erosive processes by the river or by anthropogenic activity involving some form of excavation should either of these events happen then time will be required to allow for the natural cleansing processes to take place. A detailed assessment would be required in order to determine whether some form of intervention would be desirable and cost-effective, The study has clearly demonstrated that, at present, there are two plumes of contamination (Figures 6-1 & 6-2) which are slowly migrating downstream under the influence of natural fluvial processes, including flood events. Eventually these will reach the River Don leaving the Rother relatively clear of metal contamination. This scenario is one which is reported from other river catchments in the Amazon (Marice, 1999) and in Russia (Roeva & Ispravnikova, 1999) where, over time the cleaning processes actively reduce the influence of the contaminants.

While detailed ecological studies were not an integral part of the current investigation observations were made around the sampling sites at the time of the sample collection. There was no evidence of the vegetation under stress from the various levels of contamination. Most of the surface vegetation covering the flood plain was in a healthy condition and where conservation management techniques are being practised the floristic composition is increasing eg. Woodhouse Washlands... Increasing the range of habitats by creating ponds has also increased the diversity of species associated with them including insects, birds and small mammals. It must therefore be concluded that the levels of metal contamination are not hindering the increasing biodiversity of the floodplain lands.

The political change towards the environment in more recent times has provided funds to the Regional Development Agencies for the reclamation of 'brownfield sites'. Major colliery sites and Industrial complexes involving coke works that were a main source of pollution in the area have been reclaimed in order to reuse them for several different purposes. Sites have been reclaimed for active recreational use such as Rother Valley Country Park and Poolsbrook Country Park or transformed into a mix of recreational and industrial space, such as Avenue Coke Works, Holbrook and Orgreave.

The clean up technologies have performed an efficient role to restore the contaminated sites and bring them within the acceptable range for reuse However, where "hot-spots" do occur risk assessment has to be carried out in order to safeguard any workers given the responsibility to clean up the site prior to its re-use.

The findings of this research indicate that the past legacy of industrialization leading to various degrees of contamination by heavy metals will not have a detrimental effect upon the future use of the lands along the Rother floodplain. Where the heavier levels of contamination are evident then clean-up intervention has speeded up the rate of recovery, not only for commercial use but also for improving the biodiversity through selected conservation management regimes which will encourage greater use of the Rother corridor for recreation purposes. It is clear from the creation of the Rother Valley Country Park and Poolsbrook Country Park that these former degraded areas can become attractive sites and part of the leisure and tourism map (Anon, 1988)

While this study has focused on heavy metal contamination the author is aware that the flood-plain sediments may still be contaminated with other organic, coal-derived substances such as coal-tar and poly Aromatic Hydrocarbons (PAH's). It was known that from the chemical works around Staveley, contaminants such as Poly Chlorinated Biphenyls (PCB's) and Dioxins were released into the environment.

Any future use of land on the valley floor should require additional surveys to be undertaken before permission is granted by the planning authority.

7.1 Limitations:

Constraints were imposed upon the research investigation in order to keep it within the parameters required for a higher degree at Masters Level. These are:-

1- Time scale is limited in which to accomplish all the work required.

2- The investigations covered just the twelve named sites, and this means the majority of the land that is expected to be contaminated has not been investigated yet.

3- The study focused on just six metals. In fact, there could be other metals present which need to be investigated.

4- Due to the past history of the land, contamination by organic compounds is likely, e.g. Dioxins, PAH's & PCB's which need investigating

5. Habitat surveys were not undertaken as part of the current investigation due to time and level of expertise.

7.2 Recommendations for further studies:

According to the limitations in this study, further investigations are recommended:

1- As this study covered a limited number of sites along the Rother, a study that covers new sites is recommended.

2- Investigations into other metals could be carried out that may provide new information concerning the sites and the potential levels of contamination

3- It would be interesting to investigate levels of the toxic form of mercury, methylmercury along the course of the River Rother

4- It would be an advantage to have a full ecological survey of the Rother catchment in order to have greater insight into the impacts of the different levels and different types of contamination left as a legacy from the industrial past along the valley.

Much of the analysis of the six metals from samples at different depths within the floodplain, at twelve discreet sites has provided a clear indication that various parts of the river catchment are contaminated. However, it is not so severe as to prevent the growth of vegetation or present a possible hazard to people engaged in leisure pursuits along the valley. Overtime it is likely that the river corridor will become an attractive area for conservation, interspersed with sites for more active recreation as part of the broader leisure landscape.

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Map Referencing

The following maps, produced by the Ordnance Survey have been used in this study:

Sheet XII. 4, Derbyshire, 1: 25 000,1897.

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Appendices

Appendices

Appendix No.1

Kelly Indices (Former GLC) Guidelines for Contaminated Soils specifically developed for gasworks sites in London: Suggested Range of Values (mg/kg on air-dried soils, except for pH)

Parameter	Uncontaminated	Slight Contamination	Contaminated	Heavy Contamination	Unusually Heavy Contamination
pH (acid)	6-7	5-6	4-5	2-4	< 2
pH (alkaline)	7-8	8-9	9-10	10-12	> 12
Antimony	0-30	30-50	50-100	100-500	> 500
Arsenic	0-30	30-50	50-100	100-500	> 500
Boron (available)	0-2	2-5	5-50	50-250	> 250
Barium	0-500	500-1000	1000-2000	2000-1.0%	> 1.0%
Beryllium	0-5	5-10	10-20	20-50	> 50
Cadmium	0-1	1-3	3-10	10-50	> 50
Chromium	0-100	100-200	200-50	500-2500	> 2500
Copper (available)	0-100	100-200	200-500	500-2500	> 2500
Cyanide (free)	0-1	1-5	5-50	50-100	> 100
Cyanide	0-5	5-25	25-250	250-500	> 500
Ferricyanide	0-100	100-500	500-1000	1000-5000	> 5000
Lead	0-500	500-1000	1000-2000	200-10,000	> 10,000
Lead (available)	0-200	200-500	500-1000	1000-5000	> 5000
Mercury	0-1	1-3	3-10	10-50	> 50
Manganese	0-500	500-1000	1000-2000	2000-10,000	> 10,000
Magnesium	0-500	500-1000	1000-2000	2000-1.0%	> 1.0%
Nickel (available)	0-20	20-50	50-200	200-1000	> 1000
PAHs (Coal Tar)	0-500	500-1000	1000-2000	2000-1.0%	> 1.0%
Phenol	0-2	2-5	5-50	50-250	> 250
Selenium	0-1	1-3	3-10	10-50	> 50
Sulphate	0-2000	2000-5000	5000-1.0%	1.0%-5.0%	> 5.0%
Sulphur	0-100	100-500	500-1000	1000-5000	> 5000

(free)					
Sulphide	0-10	10-20	20-100	100-500	> 500
Thiocyanate	0-10	10-50	50-100	100-500	> 500
Toluene extract	0-5000	5000-1.0%	1.0-5.0%	5.0-25.0%	> 25.0%
Vanadium	0-100	100-200	200-500	500-2500	> 2500
Zinc (available)	0-250	250-500	500-1000	1000-5000	> 5000
Zinc (equivalent)	0-250	250-500	500-2000	2000-1.0%	> 1.0%

Guidelines for classification of contaminated soils - suggested range of values (parts per million) on air dried soils

Note - added to guidelines after publication of ICRCL 59/83:

Source: Site investigation and materials problems, Proc. Conference on Reclamation of Contaminated Land, Eastbourne, UK, October 1979 (Society of the Chemical Industry, London 1980).

Appendix No.2

ICRCL 59/83 Trigger Concentrations

Contaminant	Planned Use	Trigger Values (mg / kg air-dried soil)	
Group A (may pose hazards to health)		Threshold	Action
Arsenic	Domestic gardens, allotments	10	-
	Parks, playing fields, open space	40	-
Cadmium	Domestic gardens, allotments	3	-
	Parks, playing fields, open space	15	-
Chromium (hexavalent) (1)	Domestic gardens, allotments	25	-
	Parks, playing fields, open space	No Limit	No Limit
Chromium (total)	Domestic gardens, allotments	600	-
	Parks, playing fields, open space	1,000	-
Lead	Domestic gardens, allotments	500	-
	Parks, playing fields, open space	2,000	-
Mercury	Domestic gardens, allotments	1	-
	Parks, playing fields, open space	20	-
Selenium	Domestic gardens, allotments	3	-
	Parks, playing fields, open space	6	-
Group B (Phytotoxic - but not normally hazardous to health)		Threshold	Action
Boron (water-soluble) (3)	Any uses where plants are grown (2) (6)	3	-
Copper (4) (5)	Any uses where plants are grown (2) (6)	130	-
Nickel (4) (5)	Any uses where plants are grown (2) (6)	70	-
Zinc (4) (5)	Any uses where plants are grown (2) (6)	300	-
Group C - (Organic contaminants)		Threshold	Action
Polyaromatic hydrocarbons (7) (8)	Domestic gardens, allotments, play areas	50	500
	Landscaped areas, buildings, hard cover	1,000	10,000
Phenols	Domestic gardens, allotments,	5	200
	Landscaped areas, buildings, hard cover	5	1,000
Cyanide (free)	Domestic gardens, allotments, landscaped areas	25	500
	Buildings, hard cover	100	500
Cyanide (complex)	Domestic gardens, allotments	250	1,000
	Landscaped areas	250	5,000
	Buildings, hard cover	250	No Limit
Thiocyanate	All proposed uses	50	No Limit

Sulphate	Domestic gardens, allotments, landscaped areas	2,000	10,000
	Buildings (9)	2,000	50,000
	Hard cover	2,000	No Limit
Sulphide	All proposed uses	250	1,000
Sulphur	All proposed uses	5,000	20,000
Acidity	Domestic gardens, allotments, landscaped areas	pH<5	pH<3
	Buildings, hard cover	No Limit	No Limit

Notes :-

No limit - The contaminant does not expose a particular hazard for this use.

1. Soluble hexavalent Chromium extracted by 0.1m HCL at 37 ° ; solution adjusted to pH 1.0 if alkaline substances present.
2. Pure rainwater is slightly acidic, with a pH of about 6.5 (due to dissolved Carbon Dioxide). The soil pH value is assumed to be about 6.5, and should be maintained at this value. If the pH falls the toxic effects of uptake of these elements will be increased.
3. Determined by the standard ADAS method (soluble in hot water).
4. Total concentration (extractable by $HN0_3/HCl0_4$.
5. The phytotoxic effects of Copper, Nickel and Zinc may be additive. The trigger values given here are those applicable to the 'worst-case', phytotoxic effects may occur at these concentrations on acid sandy soils. In neutral (pH=7) or alkaline soils, phytotoxic effects are unlikely at these concentrations.
6. Grass is more resistant than most other plants to phytotoxic effects, hence its growth may not be adversely affected at these conditions.
7. Used as a marker for Coal Tar. See CIRIA, 1988 Annex 1.
8. See CIRIA, 1988 for details of analytical methods.
9. See BRE Digest 250 : 'Concrete in sulphate-bearing soils and groundwater.

Appendix No.3

The New Dutchlist

Contaminant	**Soil Sediment** (mg/kg dry weight)		**Groundwater** (µg/l)	
Metals	optimum	action	optimum	action
Arsenic				
29	55	10	60	
Barium	200	625	50	625
Cadmium	0.8	12	0.4	6
Chromium	100	380	1	30
Cobalt	20	240	20	100
Copper	36	190	15	75
Lead	85	530	15	75
Molybdenum	10	200	5	300
Nickel	35	210	15	75
Mercury	0.3	10	0.05	0.3
Zinc	140	720	65	800
Cyanides	optimum	action	optimum	action
Free	1	20	5	1500
Complex (pH<5) (1)	5	650	10	1500
Complex (pH>5) (1)	5	50	10	1500
Thiocyanate	-	-	20	1500
Aromatics	optimum	action	optimum	action
Benzene	0.05[d]	2	0.2	30
Ethylbenzene	0.05[d]	50	0.2	150
Phenol	0.05[d]	40	0.2	2000
Toluene	0.05[d]	130	0.2	1000
Xylene	0.05[d]	25	0.2	70
Cresol	-	5[d]	-	200
Catechin	-	20	-	1250
Resorein	-	10	-	600
Hydroquinone	-	10	-	800
Polycyclic Aromatic Hydrocarbons (PAH)	optimum	action	optimum	action
Anthracene	-	-	0.02	5
Benzo(a)pyrene	- -	-	0.001	0.5
Fluoroanthrene	- -	-	0.005	1

Naphtalene	-	-	0.1	70
Phenanthrene	-	-	0.03	5
Benzo(a)anthracene	-	-	0.002	0.5
Chrysene	-	-	0.002	0.05
Benzo(a)fluoranthrene	-	-	0.003	0.5
Benzo(k)fluoranthrene	-	-	0.001	0.05
Benzo(g,h,i)perylene	-	-	0.0002	0.05
Indenol(1,2,3-c,d)pyrene	- -	-	0.0004	0.05
Total PAH (2) (10)	1	40	-	-
Chlorinated Hydrocarbons	optimum	action	optimum	action
1,2 Dichloroethane	-	4	0.01[d]	400
Dichloromethane	[d]	20	0.01[d]	1000
Tetrachloromethane	0.001	1	0.01[d]	10
Tetrachloroethane	0.01	4	0.01[d]	40
Trichloromethane	0.001	10	0.01[d]	400
Trichloroethene	0.001	60	0.01[d]	500
Vinylchloride	-	0.1	-	0.7
Monochlorobenzene	[d]	-	0.01[d]	180
Dichlorobenzol (total)	0.01	-	0.01[d]	50
Trichlorobenzol (total)	0.01	-	0.01[d]	10
Tetrachlorobenzol (total)	0.01	-	0.01[d]	2.5
Pentachlorobenzene	0.0035	-	0.01[d]	1
Hexachlorobenzene	0.0025	-	0.01[d]	0.5
Chlorobenzenes (3) (10)	-	30	-	-
Monochlorophenol	0.0025	-	0.25	100
Dichlorophenol	0.003	-	0.08	30
Trichlorophenol	0.001	-	0.025	10
Tetrachlorophenol	0.001	-	0.01	10
Pentachlorophenol	0.002	5	0.02	3
Chlorophenols (total) (4) (10)	-	10	-	-
Chloronapthylene	-	10	-	6
PolyChloroBiphenyls (total)(5) (10)	0.02	1	0.01	0.01[d]
Pesticides	optimum	action	optimum	action
DDT/DDD/DDE (total) (6)	0.0025	4	[d]	0.01
Aldrin	0.0025	-	[d]	-
Dieldrin	0.0005	-	0.02ng/l	-
Endrin	0.001	[d]	-	-
Drins (total)	-	4	-	0.1

alpha HCH	0.0025	-	[d]	-
beta HCH	0.001	-	[d]	-
gamma HCH	0.05 µg/l	-	0.2 ng/l	-
HCH combined (7)	-	2	-	1
Carbaryl	-	5	0.01[d]	0.1
Carbofuran	-	2	0.01[d]	0.1
Maneb	-	35	[d]	0.1
Atrazin	0.05 µg/l	6	0.0075	150
Miscellaneous	optimum	action	optimum	action
Tetrahydrofuran	0.1	0.4	0.5	1
Pyridine	0.1	1	0.5	3
Tetrahydrothiophene	0.1	90	0.5	30
Cyclohexanone	0.1	270	0.5	15000
Styrene	0.1	100	0.5	300
Mineral Oil (9)	50	5000	50	600
Phthalates (total)	0.1	60	0.5	5

Notes :-

Values are for a Standard Dutch Soil (10% organic matter and 25% dry content)
[d] = Detection Limit.

1. Acidity: pH (0.01M $CaCl_2$) The 90 percentile of the measured value is used to determine the pH value.
2. PAH (total of 10) is the total of Anthracene, Benzo(a)anthracene, Benzo(a)fluoranthrene, Benzo(g,h,i)perylene, Benzo(k)fluoranthrene, Chrysene, Fluoroanthrene, Indenol(1,2,3-c,d)pyrene, Naphtalene, Phenanthrene.
3. Chlorobenzenes are the total of all chlorobenzenes (mono-, di-, tri- ,tetra-, penta- and hexachlorobenzene).
4. Chlorophenols are the total of all chlorophenols (mono-, di-, tri- ,tetra-, pentachlorohenols).
5. The action value for PCB's (Polychlorinatedbiphenyls) is the total of PCB's 28,52,101, 118, 153, 180. The target value refers to the total excluding PCB 118.
6. DDT/DDD/DDE is the total of DDT, DDD, DDE.
7. Drins is the total of Aldrin + Dieldrin + Endrin.
8. HCH combined is the total of alpha, beta, gamma and delta HCH.
9. Mineral Oil is the sum of all alkanes (both straight and branch-chain) When contamination is due to mixtures (eg petrol or heating oil), then the content of aromatic and/or polycyclic aromatic hydrocarbons must also be determined.
10. The total values for PAH's, chlorophenols and chlorobenzenes in the soil/sediment apply to the total concentration of the compound belonging to the relevant category. If contamination is due to only one compound of a category, the value used is the intervention value of that compound. Where there are two or more compounds the value for the total of these compounds applies. For soil/sediment the effects are directly additive. In the case of groundwater effects are indirect and are expresses as a fraction of the individual values before being summed.

Appendix No.4

Netherlands Standards for Soil Contamination

- Level **A** acts as a reference value. This level may be regarded as an indicative level above which there is demonstrable pollution and below which there is no demonstrable pollution.
- Level **B** is an assessment value. Pollutants above the B level should be investigated more thoroughly. The question asked is: To what extent are the nature, location and concentration of the pollutant(s) of such a nature that is possible to speak of a risk of exposure to man or the environment.
- Level **C** is to be regarded as the t assessment value above which the pollutant(s) should generally be treated.

Present in: Component / concentration	Soil (mg / kg dry matter)			Groundwater (µ / l)		
	A	B	C	A	B	C
1. Metals						
Cr	100	250	800	20	50	200
Co	20	50	300	20	50	200
Ni	50	100	500	20	50	200
Cu	50	100	500	20	50	200
Zn	200	500	3000	50	200	800
As	20	30	50	10	30	100
Mo	10	40	200	5	20	100
Cd	1	5	20	1	2.5	10
Sn	20	50	300	10	30	150
Ba	200	400	2000	50	100	500
Hg	0.5	2	10	0.2	0.5	2
Pb	50	150	600	20	50	200

Appendix No.5

DEFRA standard

Maximum permissible and advisable concentrations of Potentially Toxic Elements (PTES) in soil application of sewage sludge to agricultural land and maximum annual rates of addition (Ministry of Agriculture, Fisheries and Food, 1998).

Maximum permissible concentrations of PTE					Maximum permissible
	pH[1] 5.0 -5.5	pH[1] 5.5 – 6.0	pH 6.0 –7.0	pH[2] > 7.0	Over a 10- year period (Kg/ha)[3]
Zn	200	200*	200*	300*	15
Cu	80	100	135	200	7.5
Ni	50	60	75	110	3
For pH 5.0 and above					
Cd	3				0.15
Pb	300				15
Hg	1				0.1

*These parameters are not subject to the previsions of Directive 86/27/EEC.

[1]- For soil in the pH ranges 5.0 –5.5 and 5.5 – 6.0 the permitted concentrations for lead, zinc, copper and nickel are provisional and will be reviewed when current research into their effects on certain crops and livestock is completed.

[2]- the increased permissible PTE concentrations in soil of pH greater than 7.0 apply only to soils containing more than 5% calcium carbonate.

[3]- the annul rate of application of PTE to any site shall be determined by averaging over the ten-year period ending with the year of calculation.

*- These zinc concentrations are advisable limits as given in *The Code of Practice for Agricultural Use of Sewage Sludge (revised, 1996).*

Appendix No.6

Suitability of treatment methods according to media and contaminant types.

Treatment method	Media types	Contaminant types
Excavate and dispose of to landfill	All soil types	Most contaminants, with the exception of PCBs and perhaps cyanides. Care should be taken to prevent exceeding loading rates, especially for cyanides, phenolics, heavy metals, arsenic, mercury, selenium and antimony.
Clean cover and containment	All soil types, but liners and/ or barriers required in permeable soils and rock.	Most contaminants, but subject to the same qualifications as for landfill. Some liners may also be prone to acid attack from contaminants and systems will need to be installed for the collection and disposal of leachate.
Bioremediation	Most soil types but a high content of natural organic material may assist the process.	Spent halogenated and non-halogenated solvents, compounds from the manufacture of chlorinated aliphatic hydrocarbons, wastes from the use and manufacture of phenols and benzenes, wastes from metal plating and cleaning industries, petro-chemical products and wastes.
Oxidation	Liquids only	Volatile Organic Compounds, organic pesticides, heavy metals, metalloids and cyanides.
Ultra-violet oxidation	Liquids only	Organic compounds.
Chemical reduction	Liquids and slurried soils	Organics including paraquat and PCBs, metals including chromium, selenium, lead, silver.
Chemical dechlorination	Liquids, sand, silt, clay, in sludges and soils.	Volatile halogenated hydrocarbons, PCBs, and organochlorine pesticides.
Chemical extraction	Liquids, sand, silt, clay	Organic and metal contaminants.

Continued.

Treatment method	Media types	Contaminant types
Supercritical fluid extraction	Sand, silt, clay, in soils and sludges	Polynuclear Aromatic Hydrocarbons, PCBs, DDT and VOCs.
Electrochemical	Liquids only	PCBs and metals.
Neutralisation	Liquids, sand, silt, clay	Organic, inorganic and metallic contaminants.
Precipitation	Liquids, sand, silt, clay	Organic, inorganic and metallic contaminants.
Soils washing	Most soil types but more successful on coarse, sandy soils.	Heavy metals, PAHs, PCBs, cyanides, non-ferrous metals.
Steam stripping	All soils but best suited to water-unsaturated soils.	VOCs and some SVCs, volatile inorganics including hydrogen sulphide and ammonia.
Soil vapour extraction/air venting	Sand, silt and peat, best suited to water-unsaturated soils.	VOCs and SVCs, hydrocarbon mixtures including petrol, jet fuel, diesel, kerosene and heavy napthas.
Electro-remediation	Clays, peat and fine sand, can be used for soils with a relatively high water content.	Heavy metals, including arsenic, cadmium, cobalt, chromium, mercury, manganese, molybdenum, nickel, lead, antimony and zinc.
Solidification	Silt and clay, some methods may be effective on other soil types.	Organic and inorganic contaminants.
Thermal	Sand, silt, peat, clays present handling problems.	Organic and inorganic compounds.