Identifying sediment sources in the tees catchment

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Nelson, Tracy Jane (2003) *Identifying sediment sources in the tees catchment*, Durham theses, Durham University. Available at Durham E-Theses Online: http://etheses.dur.ac.uk/3684/

Identifying Sediment Sources in the Tees Catchment

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Submitted for the degree of Doctor of Philosophy
University of Durham
School of Engineering
2003

Abstract

The main objective of this research is to identify the sources of suspended sediments in the River Tees. Earlier work in the Tees has focused on the extent of heavy metal concentrations in the river sediments as a result of mining in the upper catchment, but this is the first time that an attempt has been made to fingerprint the sources of suspended sediment.

The idea of identifying sediment sources by fingerprinting was similar to that used by other authors, i.e. attempting to determine a distinctive chemical fingerprint for the different landuse, geology or subcatchments in the Tees. Field sediment samples were collected from potential source areas throughout the catchment and suspended sediment samples were collected from strategic points on the River Tees and its main tributaries. The samples were prepared using a sequential extraction procedure before analysis by ICP-AES.

The samples were then subjected to several statistical procedures to determine which metals could classify the samples between the different source groups. Principal Components Analysis was the most successful tool for allowing interpretation of different sediment sources, identifying three possible sources for sediment. These were the upstream bed and bank sediments, samples collected from the Leven catchment and the third source, which appeared to be the middle catchment agricultural areas. The data was subjected to a two-stage statistical analysis, as used by previous authors, but the data failed to provide a reliable fingerprint for use in a mixing model.

Water samples collected along with suspended sediment showed distinct differences between the upper catchment and the lower tributaries, with samples from the lower Tees showing a degree of mixing. An attempt to use a mixing model failed, possibly owing to the small number of samples.

Acknowledgements

I would like to thank my supervisors Dr Mark Dyer, Dr Alan Selby and Dr Sue White for their guidance, time and patience reading through my work. Dr Stephen Anderton was invaluable both with fieldwork and checking my first few chapters. I would like to thank Dr Fred Worrall for his help with principal component analysis and interpretation of the chemical data. I would also like to thank Julian Wright for helping me analyse the samples on the ICP machine.

I would also like to thank Bernie, Steve, Claire Novis and Catherine Poulton for their help in the field. I am also very grateful to all those who provided me with data, including the Environment Agency, Cranfield Institute of Technology and the British Geological Survey. I would like to thank Trevor Nancarrow, Michael Wilson for their much-needed help with computer problems. I would also like to thank Karl Pedersen (Durham ITS) for his help with GIS and Julie Carter for her invaluable help with SPSS and the mixing model.

I would like to thank EPSRC for funding me for this work.

And finally I would like to thank Chris for his patience and understanding.

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Declaration

The material contained within this thesis has never previously been submitted for a degree in this or any other university, and, if it is based on joint research, work done by other than the author is noted.

Statement of Copyright

Chapter 1 Introduction

In recent years the impoundment of river estuaries by the construction of barrages has become a popular strategy for the development and redevelopment of estuarine areas. The Tees barrage on the River Tees at Stockton, Northeast England was built in 1991 for a variety of reasons:

- To regenerate the depressed urban area
- To improve the water quality
- To improve aesthetics by covering unsightly mud-flats
- To provide amenity use

According to Burt (1996) barrages are designed to modify or totally prevent the progression of the tide up an estuary or inlet. The Tees Barrage is of the total exclusion type and therefore prevents the polluting waters from the lower industrial section moving upstream. All barrage systems suffer from sedimentation as, by their nature, they act as sediment traps in the same manner as reservoirs. Sediment accumulation has severe impacts on the function of the impoundment:

- Infilling of the impounded area causes a loss of amenity value and navigation, as boat and leisure craft movement becomes restricted.
- Increased likelihood of flooding of upstream areas.
- Increased management costs due to the requirement for dredging.
- Decreased water quality as high sediment loads store adsorptive pollutants (e.g. heavy metals), cause oxygen depletion and provide a nutrient source internal to the impoundment leading to eutrophication.

The Tees barrage has proved very successful with large improvements in water quality, which have seen the return of salmon to the river. The impounded area has also proved very popular with water sports from a National canoe slalom to water-skiing, sailing and rowing. The area surrounding the impoundment has been extensively re-developed, bringing large amounts of investment to a previously derelict area.

Barrages also have negative impacts on the estuaries on which they are built due to the complete blocking of the river channel. Navigation up the river is interrupted, but may be overcome by the installation of locks alongside the barrage. The barrage also obstructs migratory fish, so fish passes/ladders have to be incorporated into the barrage system. The fish pass on the Tees has not proved successful (Environment Agency, personal communication) with the fish needing to be passed through the navigation lock in order to proceed upstream. The entrapment of sediment and nutrients behind the barrage and the reduced water flow could also have implications on the wildlife that inhabit the area downstream.

The River Tees has been described as a 'flashy river' (Environment Agency, 1996) as, owing to the characteristics of the catchment, water level can rise and fall very quickly. Large amounts of sediment are transported, especially during large flood events. It is still unknown whether all eroded sediment reaches the impoundment, or if it is deposited upstream. Once sediment reaches the impounded area research has yet to determine if the barrage will silt up and, if so, how long it will take. The partial exclusion barrage on the River Wansbeck in Northumberland has a severe siltation problem after 25 years of operation, reducing its amenity use and causing water quality problems. The Wansbeck has been subjected to algal blooms in summer months (Worrall & McIntyre, 1998). The Wansbeck is a partial exclusion system with 30% of tides overtopping the barrier. It is thought that the saline water causes flocculation of sediment particles, therefore increasing the rate of sediment deposition (ongoing work - Wright & Worrall, 2001), a problem that should not be encountered on the Tees.

The barrage gates on the Tees Barrage can be lowered and raised during floods. It is intended that this action will scour away sediment deposited upstream of the barrage into the estuary. A report by HR Wallingford (1991) used calibrated mathematical models to simulate upstream siltation after construction of the barrage. Researchers at HR Wallingford estimated the annual sediment load transported by the Tees would be 35,000 tonnes, over 90% of which was estimated to be carried when river flow exceeded $50m^3/s$ at Low Moor, the furthest downstream gauging station at the old tidal limit. The results from the HR Wallingford report predicted that a 1-year return period flood would remove 75-80% of the annual siltation upstream of the barrage via the sluicing action through the gates.

The subject of this research study is to identify the areas producing the sediment load transported to the barrage. By identifying the sources of sediment, the problem of reducing barrage sedimentation by ameliorative work upstream can be assessed. The problem therefore is to understand the sediment budget of the Tees barrage and to develop a long-term, efficient strategy for its management.

The high sediment load carried by the Tees is likely to be supplied from fields, banks and riverbeds upstream of the barrage. The removal of sediment from its source has a detrimental effect on that location. Removal from riverbanks will cause undermining and eventual collapse. The retreat of the riverbank detracts from the value and usefulness of the land; it can also undermine nearby structures. Large bank collapses/slips into the river could block the channel - this can lead to localised flooding in the area and will provide a large sediment source. Riverbanks in vulnerable areas can be protected and strengthened in many ways including the use of gabions and netting.

Runoff from fields into the river can cause long term problems for farmers as the soil is slowly washed away, taking with it valuable nutrients. This will lead to a drop in crop yield and possibly increase the use of fertilisers. Runoff from agricultural land containing fertilisers also presents an environmental risk. In rivers this can cause excessive algal growth, reducing oxygen in the water and therefore killing fish or other flora and fauna. The correct management of farmland next to rivers will reduce the sediment loss from fields and therefore the sediment budget of the river. These management procedures involve simple techniques such as:

- Not leaving soil bare in the wettest seasons of the year
- Not ploughing too close to the river
- Introduction of grass buffer strips next to rivers to catch runoff and bind soil together, hence making the bank more stable

Large amounts of sediment are also removed from urban areas during wet periods. The nature of covered ground e.g. tarmac and stone pavements reduces the infiltration of rainwater and increases runoff. The increased runoff and flow velocity increase the amount of sediment that can be transported.

1.2 The SIMBA Project (Sustainability in Managed BArrages)

The SIMBA project is a 3yr EPSRC (Engineering and Physical Sciences Research Council) funded joint venture between the School of Engineering and the Department of Geological Sciences, Durham University and the Civil Engineering Department at Glasgow University into the sustainability of managed barrages. The research concentrates on the effects of barrages on the rivers Tees and Wansbeck in North East England and the Tawe in Swansea, Wales. The work in the School of Engineering centres on the sediment transport and budget of the rivers Tees and Wansbeck, with emphasis on determining the sediment sources in the river Tees catchment. The Department of Geological Sciences deals with the water quality and impoundment studies. Their work covers the Tees, Wansbeck and Tawe. Data collected by the Durham departments is to be used by Glasgow to construct a water flow and sediment transport model of the Tees from Low Moor to the barrage. This model will predict areas of erosion and sedimentation in the river channel.

This work complements the SIMBA project by determining the origin of the sediment load carried by the River Tees. Knowledge of the location of the sediment source areas can be used both to improve the predictive models of sediment yield and to implement effective erosion control measures.

1.3 Aims and Objectives

The objective of this research is to identify the origin of suspended sediment transported in the River Tees catchment. The method chosen to do this is chemical fingerprinting. The idea is to determine a distinctive chemical fingerprint for the sediment from major subcatchments / geological groups and land uses in the Tees catchment. This will be done by analysing soil and riverbank samples from all areas of the catchment for the major elements. Non parametric statistical procedures will be used to identify and establish discernible differences between different subcatchments/ geological and landuse groups. The sediment samples will be collected from potential sediment source areas for catchment characterisation. Suspended sediment samples and overbank samples will also be collected during and after flooding events.

Principal Component Analysis, a multivariate technique, will be performed on the data. The component factor plots allow the visual interpretation of relationships between sediment source groups and suspended sediment. When several key determinants have been identified (preferably with different environmental controls) they will be used to construct an 'end member mixing model'. A computer model will mix various percentages of the key determinants from different subcatchments/landuses and calculate the outcome of the various mixes. This model will then be used to 'unmix' the suspended sediment samples analysed, thus statistically identifying sediment sources.

The analysis of suspended sediment data should allow identification of areas producing the majority of sediment during a flood event. An assessment will be made to determine if this changes between events. For each flood event, knowledge of the hydrograph for each flow gauging point will be studied along with rainfall data. The aim is to identify how closely linked is the suspended sediment signature to hydrological data. Do areas of the catchment supplying the largest percentage of the total water flow in the catchment also transport the highest volumes of sediment? With this data it is possible to assess whether each tributary always has the same sediment signature. If not, the variation may be related to the timing of sample collection during the floodwave or differing sediment sources contributing to the suspended load.

Water samples will be collected alongside suspended sediment samples during each flood. An attempt will also be made to fingerprint the water chemistries of different tributaries with the aim of identifying main water sources from their chemical signature. This provides another means of studying whether sediment and water sources are the same for some, all or none of the floods. If the water data allow, an end-member mixing model will also be constructed for water chemistry - can we determine if the main water sources are also the main sediment sources?

To determine the past history of sedimentation, grab samples will be taken from the barrage impoundment. The chemistry of the bed sediment can also be unmixed by the model, to determine relative proportions of sources.

1.4 Thesis Outline

This thesis is organised into eight chapters. Chapter 2 is a review of sediment transport, supply and yield. Methods commonly used to identify sediment sources are discussed along with previous research in the Tees area. Chapter 3 describes the research area in detail and how the data was collected. Chapter 4 outlines the methods for sample preparation and analytical methods chosen for data interpretation. Chapter 5 covers the use of the 2-stage statistical analysis and mixing model used by previous authors (Collins et al 1997a), general chemistry of the samples analysed, looking at general trends and explanations. Chapter 6 uses ANOVA (analysis of variance statistical technique) to select elements capable of differentiating between different source groups; these elements are then subjected to Principal Components Analysis (PCA). PCA is a multivariate analysis technique and is used to identify sediment sources in the Tees catchment. Chapter 7 again uses PCA, but this time it is conducted on the whole dataset, not just those selected by their analysis of variance. Chapter 8 focuses on the results of PCA analysis on the river water samples taken and finally, Chapter 9 discusses the results from the earlier chapters and draws conclusions from them. Recommendations for further study are also made.

Chapter 2 Literature Review

2.1 Introduction

The discussion of factors influencing sediment detachment and transport in this chapter is specifically aimed at suspended sediment. This refers to sediment with a particle size of 63microns and below (Knighton, 1984). There has been a lot of research into sediment transport in rivers, from the detachment of particles to transport out of the river mouth. This part of the sediment profile contributes approximately 70% of total sediment load delivered to the world's oceans (Knighton, 1984). In the lower reaches of most British rivers, fluvial transport is dominated by suspended material, which represents 90-95% of total load (Newson, 1986). Walling & Webb (1987) found that this fraction represented over 95% of the suspended sediment load in the Exe basin, UK. Most river studies aim to calculate the annual suspended sediment budget and its relationship to discharge. The sediment yield from a catchment is an indirect and imprecise measure of soil erosion (Meade, 1982).

Sedimentation of eroded sediments deposited by river flow can cause various problems including loss of capacity in reservoirs and behind barrages. Sediment erosion can also destroy fields, undermine buildings, walls and roads (Butcher et al, 1993). Erosion causes loss of productive topsoil, organic matter, nutrients and water storage capacity. Up to fifty percent of the annual rainfall can be lost from eroded slopes owing to decreased infiltration and high surface runoff. The downstream effects include increased flood peaks and sediment loads (Kithiia, 1997).

Sediment source evaluation is the topic of many research projects; knowledge of sediment sources allows the development of practical tools for effective, source-focused drainage basin management (deBoer & Crosby, 1995). The determination of sediment delivery and sediment budgets has been an area of concern for many years (Walling, 1983; Trimble, 1995). Increased interest in recent years has focused on identifying the origin of the sediment and its properties. It has been discovered that the movement and behaviour of many contaminants is often closely related to that of the suspended sediment load (Russell et al, 2001; Owens et al, 2001; Foster & Charlesworth, 1996; Dawson & Macklin, 1988). Pollutants such as heavy metals and organic material adhere to the sediment particles. Deposition of these sediments has the potential to build up large stores of contaminants (Macklin et al, 1997; Marron, 1992). The growing interest in sources, fate and transport of contaminants in river systems reflects the increase in our awareness of their impacts (Foster & Charlesworth, 1996). Schumm (1977) developed an idealised model of sediment movement in a river basin. He proposed that the upper catchment was the place of sediment production, whilst the middle catchment was an area of transport and deposition occurred in the lower part of the catchment. Although useful in general terms such an idealised system is simplistic in many catchments.

2.2 Erosion Processes

The predominant processes that determine erosion rates are infiltration, runoff, detachment, transport by raindrops and overland flow and deposition. The two factors controlling the erosion potential are rainfall erosivity and soil erodibility.

2.2.1 Erosivity

Erosivity is the potential ability of rain to cause erosion and is a function of the physical characteristics of rainfall (Hudson, 1981). Rainsplash is the most important detaching agent; the amount of soil moved is related to the drop velocity, diameter and rainfall rate (mm per hour). Wischmeier & Smith (1958) showed that the kinetic energy of rain was the factor most closely related to erosion. The best measure of erosivity of rainfall is called the EI index and is the product of rainfall energy and the greatest average intensity in any 30-minute period during a storm (Hudson, 1981). A crucial assumption in calculating rainfall erosivity is that it is assumed to be proportional to soil erosion (Yu, B, 1985).

Surface erosion by rainfall and overland flow is characteristic of agricultural lands (Mitchell, 1991) and is the primary force behind the detachment and removal of sediment. The principal effect of raindrops is to detach the soil and the main effect of surface flow is to transport the detached particles away from the site of erosion (Carson and Kirkby, 1972). Each raindrop creates a miniature crater and the impact scatters hundreds of dislodged particles. On a sloping surface most of the particles will fall back slightly downslope of the impact (Ritter, 1978). In each downpour thousands of millions of raindrops can strike great areas of soil with velocities up to 30kmhr^{-1} (Duff, 1993). Detached soil particles can lead to sealing of the soil surface; this happens when the particles block small holes and pores in the surface. Raindrops hitting the ground also have a compaction effect; this sealing of the soil surface can lead to lower infiltration rates and increased surface runoff (Hudson, 1981).

2.2.2 Erodibility

The erodibility of a soil is the vulnerability or susceptibility of the soil to detachment and transport by erosion (Hudson, 1981). Erodibility is a function of the physical and chemical characteristics of the soil and its management (Parteniades, 1971). The soil structure, texture and silt/clay ratio determines the soil's detachability and transportability along with the permeability, depth and organic content (Lal & Elliot, 1994). Soil chemistry and texture exerts a great influence on the soil's ability to absorb and transmit water and the detachability of its particles for erosion.

The particle size of a soil strongly affects the hydrological characteristics. A clayey soil has strong electrostatic charges, which hold the particles together and allow little infiltration, therefore generating more runoff. Slow infiltration leads to greater runoff; faster runoff means more energy, which may then have the power to erode the clay soil. A sandy soil has larger pore sizes than clay soils and will therefore allow more infiltration, which leads to less runoff and less erosive power. Sandy soils are more easily detached than silty soils but less easily transported (Lal & Elliot, 1994). Silty soils allow some infiltration, but also generate runoff. Silty soils do not have the strong bonding ions found in clays and therefore the runoff can lead to erosion of the surface. The balance between infiltration and runoff determines the erosion of the surface material. The conditions proceeding the rainfall event need to be taken into consideration as they can greatly affect the response of the soil.

2.3 Methods of Erosion

There are three main sources of sediment in the water profile. Firstly there is that from hillslopes (which reaches the river from overland flow) or by being deposited directly into the river (i.e. by landslide). Secondly there is that from the bed and banks of the river, whilst finally there is the autochthonous material. Either particulate organic matter or particulate inorganic matter (Arnell, 2002) forms this material in the water body itself. This latter material is not a direct method of erosion and therefore will not be considered further.

2.3.1 Sheet and rill erosion

High intensity rain on a shallow slope angle allows a surface covering of water to form. This is known as overland, sheet, flood or interill flow and occurs when the precipitation is greater than the infiltration (Petts & Foster, 1985). When overland flow encounters uneven surfaces (e.g. tillage lines, topographic variations, stones, and clumps of grass) rills are formed (Schumann, 1998; Ritter, 1978). Rills are rivulets where the water is concentrated into lines of runoff. Erosion can occur within the rills and these may be deepened with each rainfall event. When the rills are too deep to be traversed by normal ploughing methods they are known as gullies (Ahnert, 1996). Gullies are usually associated with accelerated erosion and therefore with landscape instability (Morgan, 1995).

2.3.2 Mass movements

Weathering continually supplies rock waste, which falls or creeps or is washed by rain into the nearest stream. The river carries away debris provided to it and also creates more by eroding its own channel. The river widens by undercutting its banks, especially on the outer side of meanders (downcutting and lateral cutting). Mass movements are of three primary types - slides, flows and heaves. They can occur alone, but generally are all involved to some extent in most natural slope failures (Ritter, 1978). The mode of transport depends on the relationship between the physical properties of the material and the stresses produced within the system. The movement is a downslope migration of debris under the force of gravity and is usually classified by its speed and water content and is illustrated in Figure 2.1 below.

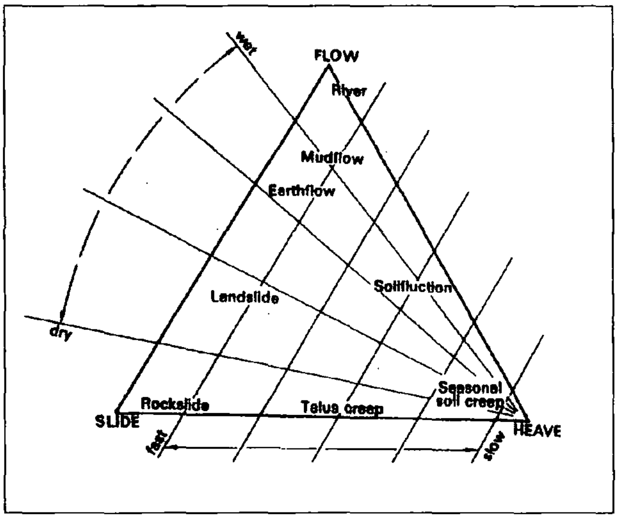


Figure 2.1 Classification of mass movements (from Carson & Kirkby 1972)

A landslide is rapid and can affect large volumes of sediment, which usually disintegrate during movement (Duff, 1993). Landslides normally occur because of a lack of support at the base of the slope i.e. the toe has been undercut. The slide involves fracture along a slide plane, which may reach down to bedrock. The slide usually leaves a deep sided scar (Morgan, 1995). Landslides may occur preferentially where there are bedding, cleavage planes or fault fractures dipping towards a valley. Landslides generally occur during exceptional weather conditions with a low recurrence interval (Young, 1973).

Landslips and slumps are slower than slides and normally retain some coherence and structure. Slips generally occur due to an increase in bulk density and therefore mass, plus a reduction in normal force and friction, possibly because of an increase in water content. Slumps often leave spoon shaped shear planes (Duff, 1993). Mudflows generally occur on steep slopes where there is a large proportion of fine material; they are triggered by heavy rainfall events. In true flows, the movement within the displaced mass closely resembles that of a viscous liquid. Flows are often the final event in a slide, distinction between the two is usually unclear (Ritter, 1978). Flows generally have no defined shear zones and failure is spread throughout the mass, with maximum shear at the base.

The effects of an extreme event can be long lasting and give rise to high soil losses for a number of years. Landslide and slips can be rapid, violent events depending on their size, speed and devastation (Dikau et al, 1996). A slide in the Italian Alps at Vaiont Dam in 1963 moved 250 million cubic metres of material. This material displaced the water in the reservoir killing over 2500 people living in the valley below.

Creep is the downslope movement of unconsolidated material at an annual rate of 1-2cm per year (Ahnert, 1996). It is the sum of innumerable tiny displacements of particles under the force of gravity. Heave is instrumental in the process of creep and is caused by expansion and contraction relative to the slope surface (Ritter, 1978). It causes downslope movement by heaving normal to the slope surface with downward movement being more vertical due to gravity. No continuous external stresses are applied, movement occurs under gravity when the cohesion and frictional resistance of the material are lowered. The process occurs in the upper few metres of soils and its effects decrease rapidly with depth (Ritter, 1978). Heaving occurs because of various climatic factors such as freeze-thaw, thermal expansion & contraction and wetting and drying.

Soil can also be eroded from within the soil layer when rainfall infiltrates a porous unconsolidated upper soil and flows along a lower denser soil. This interflow is generally more concentrated along preferred paths within the soil structure, due to changes in soil level, texture etc. If the soil is cohesive enough pipes develop (hollow tubes/spaces) which can vary from a few millimetres to a metre in diameter and allow fine material to be washed away (Selby, 1993). Pipes are often found in peat covered slopes in upland parts of the UK (Thompson & Oldfield, 1986).

2.3.2 Bank failure Mechanisms

Bank erosion is one of the principal means of sediment supply to rivers (Knighton 1984). Mechanisms of bank failure are complex and related to forces of erosion, size and geometry, the structure of the bank and bank material properties (Schumm, 1977). Bank failures can provide large volumes of sediment. There are two groups of processes acting on riverbanks. Firstly there is sub aerial/sub aqueous weakening and weathering of the banks which reduces strength and decreases bank stability. Secondly there is fluvial entrainment by the river water itself.

Where the river bank is steep, a fissure or weakness in the sediment may cause whole sections of the bank to collapse - known as block failure. The riverbank can also fail by deep or shallow rotational slips which is one of the most recognised methods of bank failure (Thorne, 1998). It generally occurs in cohesive soils where there is a deep seated failure along a curved surface. This leads to a mass of slab that is back tilting towards the bank.

Rotational slips are often caused by erosion of the toe and hence steepening of the bank, as shown in Figure 2.2 (a). Water erosion at the foot of the bank produces an overhang, as the lower part of the bank is removed and the upper section remains, often bound by vegetation. Eventually this overhang of sediment collapses due to tension stresses and is known as cantilever failure (Thorne 1998). This type of bank erosion is cyclic – the base is undercut and then the top fails, which is also shown in Figure 2.2 (b).

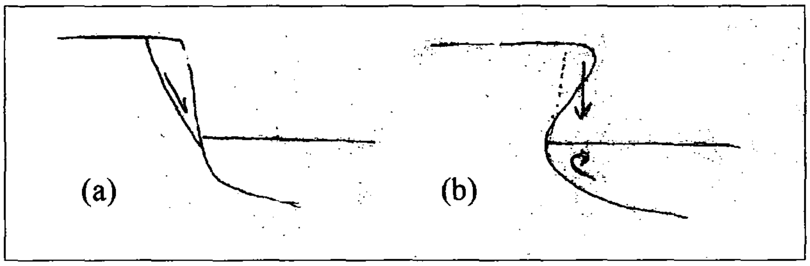


Figure 2.2 Types of bank erosion

Fluvial entrainment is the removal of debris by scouring of the riverbed and bank. Fluvial entrainment is achieved by a variety of methods:

- Hydraulic process - The mechanical loosening, lifting and removal of material by flowing water is achieved by the force provided by turbulent eddies in the river.
- Corrasion – The wearing away of bank sides and riverbeds with the aid of debris from boulders to silt which are in transit.
- Attrition – The wear and tear suffered by transporting materials. The particles are broken down, smoother and rounded. The smaller particles are then easily carried away.

2.4 Anthropogenic Influences

2.4.1 Human influences which accelerate erosion

The change from natural vegetation to agricultural land can increase soil erosion rates by an order of magnitude or more (Walling, 1999). Research has emphasised clear relationships between forest cutting and increased runoff (Ward & Robinson, 1990). The ploughing of agricultural land leads to exposed surfaces at harvest time, which leaves the soil vulnerable to erosion. Cultivation and ploughing alters the soil structure, whilst compaction by machines reduces the infiltration capacity (Robinson et al, 2000). The crops planted and seasonal timing can significantly affect the amount of runoff produced, the biggest effect of agricultural practices being found to be field drains (Robinson et al, 2000). The dredging of river banks/beds and the removal of weeds can also induce within channel erosion (Hasholt, 1988). Areas disturbed by construction activity can increase soil erosion rates by 2 – 40,000 times the pre-construction rates (Harbor, 1999). Mining can increase the amount of sediment transported for centuries after mine closure owing to the erosion of spoil heaps (Macklin et al, 1997; Marron, 1992). Froehlich & Walling (1997) found that roads provided the majority of suspended sediment carried by streams in a catchment in Poland.

2.4.2 Human efforts to reduce sediment erosion

Trimble & Lund (1982) showed that conservation schemes significantly reduced erosion and sedimentation rates in a $360km^2$ catchment. The management practices used included contour ploughing, contour stripping, long rotation, crop-residue management, cover crops, improved fertilisation and controlled grazing. Extensive soil and water management (and also a shift towards a drier climate) have seen a reduction in the runoff and sediment yield in the Yellow River at Longmen, China (Walling, 1999). The high erosion rates were associated with the thick loess deposits and a decline of approximately 50% has been achieved during the period of record. Afforestation can reduce the runoff and therefore potential for erosion, but it takes many years to reach maturity and in the first few years runoff may increase (Arnell, 2002) but after several years the flow is severely reduced and reduced to zero when the plantation reaches maturity.

2.5 Controls on sediment movement in the river

Sediment transported in a river can be divided into three categories, which are based on the grain size of the particles (Knighton, 1984). Washload consists of the fine particles that are easily washed away by flow and are always in suspension with a constant concentration anywhere in a cross-section. The suspended bed sediment load is generally the coarse material in suspension and the concentration generally increases with flow velocity and depth. Bedload (or contact load) refers to the transport of sediment particles that maintain contact with the bed. The amount of sediment carried by water is difficult to calculate, as a point sample cannot give an exact sediment concentration of the full river section. Also, the relationship between discharge and suspended sediment is non-linear (as generally there are different concentrations on falling and rising limbs) and is variable over time (Arnell, 2002).

When calculating sediment loads in rivers the estimates are seldom thought to be better than ± 25 percent (Ferguson, 1987). More recently, Webb et al (1997) found that simple rating curves gave a level of accuracy of -57% to +29% of the true value at the 95% confidence level. The sediment load of a river is the total weight of solid material in unit time, passing a cross-section of the river at the place of observation. This load includes all material in solution, all suspended sediment and bedload. The bedload is very difficult to measure and is generally taken to be no more than ten percent of the suspended sediment load (Duff, 1993). Ward (1984) describes four methods of measuring bedload - channel and bed material measurement, bed load samplers, slot traps and tracers.

The suspended sediment load of a river is routinely measured in only a few places around the world and is often carried out as part of a specific monitoring project. It is generally achieved using a fixed sampler at a point in the river which takes samples of river water at set times or accumulative flow (after a set volume of flow has passed the measurement point), or using a proxy variable such as turbidity. Suspended sediment is measured by the SIMBA project team at sites on the Tees and Wansbeck Rivers (Anderton et al, 2000) using both automatic samplers and turbidity sensors; the LOIS research project also collected data this way (Leeks et al, 1997).

The measured concentration of sediment in the stream is plotted against the flow to construct a rating curve (Phillips et al, 1999). To achieve the most accurate rating curves the recorded data should cover long periods of time whist sampling the full spectrum of river conditions. If a good rating curve can be constructed for a river the sediment concentration for any particular flow rate can be estimated. A commonly used research approach is to continuously measure the turbidity of the water and relate this to suspended sediment content (Wass et al, 1997; Wass & Leeks, 1999). Where a river is continuously monitored, the summing up of daily flow and sediment loads can give an estimate of the annual sediment load of the river.

The river channel itself can govern the amount and movement of sediment and is defined by its slope, cross section and pattern (e.g. straight, braided or meandering); all of which affect the transport of sediment within the channel. The size or form of a channel is determined primarily by discharge, mean velocity, slope gradient, width, mean depth, load and 'roughness' of the bed (Duff, 1993). Roughness is a coefficient like friction, which expresses the resistance to flow and depends on the size of debris, the sediment in the river and irregularities of the riverbed.

According to Schumm (1977) the slope or gradient of a channel is controlled by the hydrological and geological characteristics of the drainage basin. The gradient of a channel normally decreases downstream with a corresponding increase in discharge and a decrease in sediment size (Lane, 1955). For most rivers the wetted perimeter is directly dependant on discharge, and the water surface width and depth increase with mean annual discharge in a downstream direction (Leopold & Maddock, 1953). Lacey (1930) found that the shape of a channel reflects the size of the sediment load carried; rivers with a high proportion of coarse sediment tend to have a high width/depth ratio, whilst those carrying fine sediment tend to be narrow and deep in cross section. The shape of the channel is also affected by variations of resistance in the bank material and the flood peak characteristics.

Meandering and braiding occur when a straight river becomes unstable and needs to reduce its energy to regain the balance between discharge, slope and sediment load. Meandering lengthens the river and therefore reduces its gradient. Meandering rivers generally maintain a steady width because erosion and widening on one side is balanced by deposition and narrowing on the other. The meander length is correlated with discharge and a straight channel will start to meander beyond a certain threshold slope for a given discharge. Parts of the Lower Tees River meander downstream of the Skerne confluence.

Excess energy can also be dissipated by dividing into interlacing networks of tributaries with islands of shingle and sands between; this type of river is termed braided. Braided rivers are generally wide and shallow with the floor and outer banks generally consisting of the river's own deposits. They normally occur at high stream powers, have low sinuosity and range from coarse gravel to sand. This type of river is common in the upper Tees streams such as Langdon, Harwood and Hudeshope. Braided rivers migrate freely in an environment of unrestricted bank erosion. These rivers are typically unstable and sensitive to changes in discharge and sediment load. They require a high-energy environment because the friction is increased by the wide, shallow floor and rough bed.

The river transports the debris in a river by various methods. The smaller particles are carried in suspension whilst the larger ones move along by either saltation (jumping) or sliding and rolling along the riverbed, and are controlled by velocity and turbulence (Arnell, 2002). The fine material is the first to be moved when the discharge increases and the concentration is usually controlled by the amount of material supplied (Arnell, 2002). The proportion of fine to coarse deposited material tends to decrease upstream, as clearly shown in the Tees catchment from walkover surveys and is a well-known phenomenon (Ashmore et al, 2000). This can be altered due to coarse debris from tributaries, landslides/slumping of the banks.

The transport capacity of a river increases very rapidly as discharge and velocity increase, the maximum load carried being proportional to the 3rd – 4th power of velocity (Duff, 1993). Any irregularities in the channel can provoke energy loss (Knighton, 1984) as the velocity of flow is related to flow resistance (interaction between fluid flow and channel boundary). In stable flow conditions the Manning equation can be used to calculate channel resistance to flow with values of n to account for surface roughness in the channel (Dingman, 1984). The bankfull discharge provides the means of comparing one river and another or one river at different places. When a river floods (reaches bankfull and overflows it) the width of a river may be increased by slumping and caving in of the channel sides.

2.6 Sediment Delivery Concept

Not all sediment eroded in the catchment reaches the river network (Walling, 1983; Atkinson, 1991; Baldwin & White, 1991; Trimble 1999). The sediment is deposited on slopes, either temporarily until the next storm event or permanently. This deposition of eroded sediment increases with increasing basin size (Walling, 1983). The sediment delivery ratio is a measure of the amount of eroded sediment in the catchment reaching the basin outlet and is calculated from:

$$\frac{\text{Sediment yield at basin outlet (t km}^{2}\text{ yr}^{-1}\text{)}}{\text{Gross erosion within the basin (t km}^{2}\text{ yr}^{-1}\text{)}}$$

The sediment delivery ratio is a simple concept, which is extremely difficult to apply (Baldwin & White, 1991). A large amount of the existing knowledge of sediment budgets is based on theory and inference rather than direct empirical evidence (Walling, 1999). There is no simple relationship between gross erosion and sediment delivery as it is controlled by a number of factors such as annual and seasonal distribution of rainfall and also the sediment storage in the basin. The delivery ratio can be used to account for all sediment deposition between the erosion source and the catchment outlet (Atkinson, 1991).

Sediment delivery ratios can vary greatly from year to year in the same basin. Some catchments have shown sediment delivery ratios over 100 percent which is due to the remobilization of stored sediment in rivers (Walling, 1983). This leads to inherent difficulties in determining the sediment erosion, transport and delivery ratio. Atkinson (1991) deals with some methods of estimating the delivery ratio.

There are two conditions that may limit the rate of sediment transport – the transport capacity of the stream and the availability of materials in the watershed (Julien, 1995). If the river is transport limited there is plenty of sediment being supplied to the river but it does not have the energy to transport. These rivers may show high concentrations of sediment with a small increase in discharge, whilst the sediment load may be high throughout the rainfall event. Supply limited streams are characterised by lower concentrations and high variability. Sediment transport is limited by the supply of sediment, usually from the catchment, which varies with the location and intensity of rainstorms on the catchment, seasonal variation in temperature, weathering, vegetation and type of precipitation (rain / snow). Sediment transport is very variable and the majority of the annual budget can be concentrated into a few days, Walling & Webb (1996) found that 90% of the long term sediment yield was transported in 5% of the time.

Trimble (1976; 1983; 1995; 1997; 1999) studied the effects of severe soil erosion in the late nineteenth century and early twentieth century in Coon Creek, Wisconsin, USA. He found that only a small portion of eroded soil was transported out of the area by rivers and the rest accumulated as alluvium in the valleys. When improved landuse practices were introduced in the middle twentieth century the sediment yields did not decline as expected, due to the re-mobilisation of alluvium. Figure 2.3 shows the estimated sources and sinks in the Coon Creek valley for three different periods, from Trimble (1999). Golubev (1982) found that only 10 percent of the gross soil erosion from the upper tributaries entered the main river in the Oka basin in central USSR. Sixty percent of eroded sediment was deposited on the lower parts of slopes whilst the remaining 30 percent was deposited in minor streams. Hadley & Shown (1976) showed that for a 124.8km^2 basin in NW Colorado USA only 30 percent of the sediment eroded in small tributaries entered the main river and only 30 percent of this reached the basin outlet.

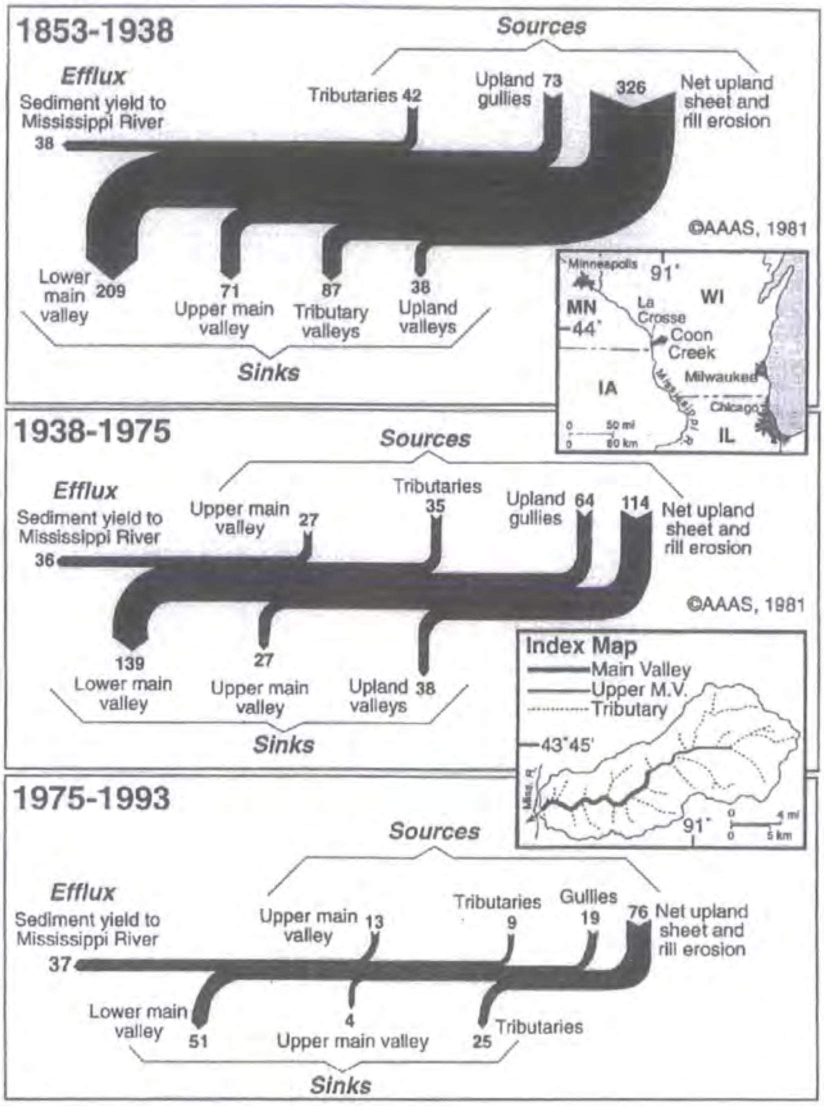


Figure 2.3 Sources and sinks in the Coon Creek

2.7 Geomorphic Factors Controlling Erosion and Transport of Sediment

Climate is an important independent control on both hydrology and geomorphological evolution of a catchment (Kirkby, 1993). As a result the shape and form of a river depends primarily on the climate and the geology. The climate dictates the amount and intensity of rainfall the slopes receive whilst the underlying geological structure determines the varied resistance to erosion offered by the rocks encountered (Duff, 1993). The physical characteristics of the catchment greatly influence the erosion location, patterns, processes and the likelihood of the eroded particles being transported to a watercourse. Research has concentrated on many of the variables to determine the relationship with erosion potential (Wischmeier & Smith, 1958). The variables can have a profound effect on sediment erosion, particularly when combined. Catchment characteristics commonly accounted for in equations and considered to influence the erosion potential are discussed further:

2.7.1 Geology

Geology plays a part in determining the size of a river catchment, the size and number of channels and the drainage density. The channels that the rivers carve for themselves are in response to the dip of the geological strata and the weaknesses in the rocks themselves (Duff, 1993). The geological structure of an area dictates its topographical characteristics, whilst petrological characteristics will determine the chemistry and grain size of the soil, which the weathering of the rocks will provide. In turn the chemistry and size of the soil particles play a huge role in the likelihood of being eroded. With similar climate and topography, basins underlain by sedimentary rocks or low-grade metamorphics have higher rates of erosion and suspended sediment loads than regions of crystalline rocks or highly soluble rocks (Ritter, 1978; Corbel, 1964).

2.7.2 Climate

Rainfall is the biggest single most important natural variable when determining sediment erosion and transport (Ekern, 1950). It is the intense, prolonged rainfall events that break loose the surface particles and cause surfaces/slopes to become so waterlogged/heavy that they fail. After detachment, rainfall provides the energy needed to transport the soil particles away from the erosion site, causing sediment to be deposited elsewhere and creating a new surface for erosion. Landslips and slides caused by heavy rainfall are particularly large providers of sediment into the system often giving a 'chocolatey appearance' to nearby water courses (Carling, 1986).

The more prolonged the rainfall attack the further the sediment is transported from its source. The riverbanks fill up and then flood the surrounding area, tapping into new sources and causing collapses of weak riverbanks. With greater runoff comes greater sediment transport.

2.7.3 Soil

The soil type plays an important part in its erosion. Different soils erode at different rates when the other factors that affect erosion are the same (Mitchell & Bubenzer, 1980). The physical, chemical and organic components of a soil play an important role in determining the soil's erodibility. The primary control is the grain size; the particles of a fine sand are more easily detached than those of a clay soil, but the clay particles are more easily transported (Hudson, 1995). The chemical composition of the soil plays a role in determining the aggregate strength i.e. how easily the soil particles are broken down.

Organic matter is important in maintaining soil aggregates as it provides a moist soil which is permeable (Kirkby, 1980). The high permeability and aggregate strength of the organic soil minimises the risk of overland flow. The loss of organic matter depends primarily on the vegetation cover and its management, organic depletion leads to lower infiltration capacity and increased overland flow (Kirkby, 1980).

2.7.4 Landuse

Naden & Cooper (1999) found that landuse was the main control of suspended sediment in 62 catchments ranging from 5 to 380 km^2 in the Yorkshire region. The landuse of an area greatly affects the timing, speed and volume of runoff and the erodibility of soils. Urban catchments have the fastest runoff rates, owing to large areas of impermeable cover and man made water channels. The falling precipitation is caught and transferred through a drainage system, which is designed to route it to a nearby stream as quickly as possible. This can lead to a rapid build up of overland flow below urban areas, which can be accentuated by steep slopes (Ward & Robinson, 1990).

Changing the landuse from natural vegetation/forest to cultivated land can increase soil erosion rates by an order of magnitude (Walling, 1999). The major effect of deforestation is to increase the total amount of runoff (Bosch & Hewlett, 1982) as the peak flows are increased and minor precipitation events have a bigger effect. The storage capacity of vegetation clearly influences the proportion of precipitation that reaches the soil surface (Arnell, 2002). A heavily vegetated area will also retain a higher percentage of runoff in its soils, owing to the binding affects of the soil and retention of runoff. Heavily vegetated areas also intercept a large amount of the precipitation on the leaves themselves. Agricultural land will have different susceptibilities at different times of the year - after the ploughing season the soil will be bare and void from protection (Robinson et al, 2000).

Climate, landuse and soil type are closely interlinked, as it is the combination of various soil types with climate that influence the landuse of an area. Areas with fertile soils and plentiful rain make good agricultural lands, whilst peaty soil and a harsh climate such as the Pennines tend to be used for rough grazing only.

2.7.5 Topography

Elevation is an important factor in the determination of sediment sources. It controls the gradient, slope length and in some areas the amount of precipitation received. Studies have shown that the average annual rainfall increases with elevation (Nelson, 1998). There is a strong positive relationship between rainfall and elevation in the Tees area (see chapter 3).

The steeper the slope the greater the likelihood of erosion (Lal, 1988), owing to greater instability on steep slopes, with slip, creep and slide mechanisms more common on steep than on shallow slopes. Erosion increases with increases in slope steepness and length as a result of the respective increase in velocity and volume of surface runoff (Morgan, 1995). The relation between erosion and slope can be expressed as:

$$E \propto \tan^{m} \theta L^{n}$$

E is the soil loss per unit area,

θ is the gradient

L is the slope length.

Where m is an exponent for slope steepness

Where n is an exponent for slope length

Zingg (1940) returned values of $m = 1.4$ and $n = 0.6$, from five experimental stations in the US. The steepest areas of a catchment are often considered to be the main sediment producing zones. On a flat surface no runoff may take place at all, leading to ponding and deposition of detached particles. Moseley (1973) found that on a 25-degree slope 95% of the eroded particles moved downslope and total transport increased six-fold between 0 and 25 degrees.

The effects of slope length (point of origin to channel or place of deposition) on erosion are related to the velocity of runoff, which can easily be altered by soil and crop management. Kramer & Meyer (1969) showed that long slopes increased the amount of erosion and Lal (1988) concluded that soil erosion increases in proportion to a power of slope length, especially in ploughed fields. The combination of slope length and steepness can increase erosion as Laflen & Savenson (1970) showed that runoff increased linearly with an increase in the ratio of slope steepness: slope length.

A digital elevation map (DEM) provides data which allows the calculation of slope gradient, flow direction, contributing upstream areas (controls potential discharge), stream power index (contributing area/slope gradient) and the delineation of watersheds (deRoo et al, 1989; Burrough, 1986; Moore et al, 1993). A DEM can be used with rainfall data to create a rainfall coverage map of the catchment, as done for this study.

The direction in which the slope faces determines the amount of wind, rain and sunshine it receives. A slope facing the storm front (generally the west in this country) may receive more rainfall and hence be subject to more erosion (Parsons, 1988). The opposite slope is likely to be in a rainshadow (especially if topography is great) and therefore will receive less rain; also storms may have died out before reaching the shadow side.

Prevailing wind is important, as it is a powerful eroding agent and carries most of the rain bearing weather systems. Woodruff & Siddoway (1965) and Hagen (1991) designed wind erosion models, along the same principles as the universal soil loss equation (explained later). A slope constantly buffeted by winds will undergo more erosion that a sheltered slope. The aspect of the slope also affects the amount of sunshine it receives. Slopes facing the sun are likely to be drier resulting in more infiltration and therefore less runoff. Dry slopes could also increase erosion as the dry material can easily be blown away or they may be baked hard by the sun. Wetter slopes can be more vulnerable to slips, creeps and slides than dry ones as the water pressure can cause instability.

2.7.6 Drainage density

The higher the drainage density, defined as km of river per km^2 in a catchment (Dingman, 1993), the faster the rainfall runoff can reach a stream channel. This reduces the time available for infiltration before being intersected by a stream channel and the flow in the stream will increase as a result. At a local scale, drainage density is related to rock and soil type, while at a regional scale it is dependent upon the mean annual precipitation and lithology (Gardiner, 1995). A high drainage density gives a wider river coverage throughout the catchment and will potentially have access to more erosion sites. The peak flow will occur shortly after the peak rainfall and the higher discharges in the river means more energy to erode riverbeds and banks.

2.7.7 Lakes and Reservoirs

Lakes and reservoirs are effectively sediment sinks and at times will retain most of the sediment entering them. As a rule of thumb, a reservoir that can hold 1% of water that flows into it can trap half the sediment input, whilst one that can hold 10% of the water flowing into it can trap 80-90% of the inflowing sediment (Brune, 1953). The trap efficiency of a reservoir is important as it gives an estimate of the amount of sediment entering the reservoir which is retained behind the containing wall. Reservoirs may not be permanent storage sites for sediment as large volumes can be flushed out by large floods, according to Gross et al (1978). The construction of a reservoir on the Aswan Dam on the River Nile reduced the sediment yield at the river outlet from ~100 x 10^6 tyr^{-1} to ~ zero (Walling, 1999)

Work in the southern Pennines by Butcher et al (1993) found the trap efficiency to be higher than average for the UK in peat moorlands. This has to be taken into account when modelling sediment transport, as such impoundments decrease the amount of sediment available for transport downstream, and may cause increased erosion of the downstream channel as a result.

2.8 Methods for the Identification of Sediment Sources

2.8.1 Fieldwork and walkover surveys

Simply walking a catchment and taking notes can identify areas of erosion and deposition in a catchment. Thorne (1998) has compiled a set of field reconnaissance notes for easy and accurate identification of river type and condition. By repeating fieldwork, changes in the river behaviour can be noted including eroded banks, deposition in streams. Photographs and measurement of features will allow easier identification of changes.

2.8.2 Erosion Pins

Cylindrical steel pins inserted into the ground at regular intervals are a volumetric method of measuring erosion and deposition in a small area. The pins are normally placed in a grid format and placed so that they do not interfere with the natural processes acting upon the surface. The pins should be of a diameter and spacing so as not to induce scouring around the base of the pin. The pins are left with a fixed amount exposed, the change in the protruding surface indicates erosion or deposition by the lengthening or shortening of the pins respectively. The new height of exposed pin is the amount of surface lowering or raising. Sirvent et al (1997) successfully used erosion pins in a Spanish catchment to determine the spatial distribution of processes and erosion values.

2.8.3 The use of GIS (Geographical Information Systems) information

It has long been understood that factors such as landuse, topography, soil type, rainfall intensity and duration exert a strong control over soil erosion (Morgan, 1995; Jain & Kothyari, 2000). Work has been done to determine the relationships between these factors and the erosion potential i.e. rainfall (Wischmeier, 1959; Hudson, 1981; Walling, 1988), topography (Zingg, 1940), landuse (Atkinson, 1995; Walling, 1999) and soil type (Browning et al, 1947).

Wischmeier & Smith (1958, 1978) developed an empirical technique to predict sediment loss from field sized areas in the United States of America. The Universal Soil Loss Equation (USLE) was developed from almost 10,000 plot years of data from small plots under the influence of different climatic regimes, agricultural uses, soil types and slopes. Soil conservation planners designed the USLE for field use and to guide the selection of conservation practices for specific sites. The USLE predicts the long-term average annual sheet and rill erosion from field sized areas and is successful in the areas for which it was developed. The soil losses computed are the best available estimate rather than an absolute value (Wischmeier, 1976) and there may also be errors due to unmeasured variables. The soil loss equation is

$$A = K\,R\,L\,S\,C\,P$$

Where:

A = soil loss (tonnes per hectare per year)

R = rainfall erosivity index (a number which indicated the erosivity of the rain based on the EI index)

K = soil erodability factor (a number which reflects the liability of a soil to erosion)

L = length factor (a ratio which compares soil loss with that from a specified length of 22.6m)

S = slope factor (a ratio which compares the soil loss with that from a field of specified slope 9%)

C = crop management factor (a ratio that compares the soil loss with that from a field under standard treatment)

P = conservation practice (a ratio that compares soil loss with that from a field with no conservation practice)

This method has been used within a GIS framework to identify areas of high/low erosion risk (Meijerink et al, 1988; White, 1993; Bradbury et al, 1993)

2.8.4 Aerial photography and remote sensing

Aerial photography has been widely used in identifying sediment sources. Sediment sources and erosive structures can easily be identified by a trained eye from a photograph. The scale of the photographs used depends on the depth of the study involved (Townshend, 1981). For a reconnaissance study or regional scale study 1:2 000 000 is used, for more detailed surveys (to identify landuses, major erosion features) then 1:25 000 or 1:50 000 is used. For more detailed studies i.e. at the field level 1:10 000 or larger is used. Photographs can be used on their own to identify sources of sediment in the river network (Trimble, 1997; Su & Stohr, 2000). Where available, sets of aerial photographs spanning years or decades can be used to estimate the change in the river network (Ham & Church, 2000; Winterbottom & Gilvear, 2000; Widjenes et al, 2000, Besson & Doyle, 1995; Brizga & Finlayson, 1994).

Ries & Marzolff (1997) used large-scale photographs (ranging from a ground surface area of 12 x 18m to 257 x 386m) to identify sediment erosion and processes acting using a specially designed Blimp (air balloon). Salo et al (1986) and Raey et al (1999) used satellite imagery (visual imagery) to detect/ calculate areas of erosion and deposition in river networks. Fadul et al (1999) combined aerial photographs with Landsat images (landcover) to estimate gully erosion in the Atbara River, Sudan. They found that modern agricultural methods accelerated gully erosion and led to a significant loss of arable land. Dwivedi et al (1997) using Landsat MSS (multi spectral scanner) and Landsat TM (thermal mapper) studied the effect of landuse change on soil erosion in India.

Pickup & Marks (2001) used airborne geophysical surveys to identify patterns of erosion and deposition in four small catchments in Australia. Gamma ray emissions from surface and near surface material allowed estimation of K, Th and U content, which are controlled by lithology. Changes due to weathering, erosion and deposition can be detected. Gamma radiometric profiles generally show lower values on hillslopes and higher values on valley floors, which is explained by the weathering of hillslopes and deposition lower down in the valleys. This research showed that the concentration of all radiometrics in the four catchments increased as the potential for deposition increased.

Mezosi & Szatmari (1998) used remote sensing (Landsat and SPOT) to predict areas of wind erosion in Hungary. They calculated the soil wetness index (SWI) in cultivated sandy soils, as drier soils are more likely to be blown away. The results were to be used to implement soil conservation methods. Soil erosion probability maps were produced by Baban & Yusof (1991) using a combination of remote sensing, USLE and GIS, while Reusing et al (2000) integrated remote sensing data, GIS and the USLE to model soil loss rates.

2.8.5 Fingerprinting

Sediment fingerprinting is used to identify deposited or suspended sediment sources by comparison with the characteristics of soils in the catchment. The idea is that sediment derived from different areas of the catchment with different geology, landuse etc will display distinctively different characteristics (Collins et al, 1997a, 1997b, 1997c). When determining sediment source, it is presumed that the parameters measured have been mixed evenly and conservatively, with no additions or removals as no account is taken of alteration and selective transport. The advantage of this technique is that it is less labour intensive than previous methods used, can cover large areas of a catchment and has the ability to determine the sources and the relative mixing of different areas upstream of the sampling point. Earlier work to identify sediment sources of erosion by field studies/USLE was limited as there were many operational problems and it was essentially impossible on anything other than small areas (Oldfield et al, 1979).

To characterise a catchment, it must be broken down into groups, e.g. separated on the basis of landuse, geology etc. Fieldwork is conducted to collect surface (i.e. agriculture, woodland) and subsoil (i.e. channel banks) samples throughout the catchment to give a representative cover of all the group types. The samples are then analysed to identify diagnostic determinants that are able to successfully discriminate between the groups selected. A determinant is a physical or chemical property identified that is present in both the field (source) samples and the deposited or suspended sediment samples. These diagnostic properties identified will be dependent on the catchment and its variables (landuse, geology etc). If potential sediment sources can be characterised they can be compared with suspended sediment samples and allow an approximation of the relative importance of the various sources to be deduced (Walling et al, 1999).

2.8.5.1 Determinants

A variety of diagnostic properties have been used in fingerprinting. These include mineral magnetics (Yu & Oldfield, 1989, 1993; Walden et al, 1997; Walling et al, 1979; Stott, 1986; Caitcheon, 1993; Slatterly et al, 1995; Oldfield et al, 1979), radionuclides (Murray et al 1993; Walling & Woodward 1992), elemental concentrations (Collins et al, 1997, 1998), particle size & morphology (deBoer & Crosby, 1995), radioactivity (Shankar et al, 1994), colour (Grimshaw & Lewin, 1980) and mineralogy (Wood, 1978). Geochemical properties reflect spatially variable factors such as soil and landuse, whilst radionuclide properties are independent of lithology or soil type as they are derived from the air.

The upper horizons of many soil profiles have a higher concentration of magnetic forms of iron than the parent weathered material due to secondary enhancement (Oldfield, 1979). Burning, dehydration of minerals, reduction, oxidation and the substitution of cations in the substrate cause secondary enhancement in soils. The highest magnetic susceptibilities are found in forests where there is less surface erosion and the soils have therefore retained the highest concentration of secondary ferrimagnetic minerals near the surface. Bankside soils generally have susceptibilities similar to unaltered substrate whilst the susceptibility of arable topsoil is between woodland and unweathered material (Mullins, 1977). Gleyed soils generally have low susceptibilities as waterlogging inhibits formation of secondary minerals. Magnetic susceptibility is not always proportional to the quality of a magnetic mineral and the method of measurement affects the values obtained (Mullins, 1977).

Cs^{137} has been used in determining spatially distributed soil erosion for many years (He & Walling, 2003). Cs^{137} can be used irrespective of landuse or soil type as the deposition of Cs^{137} is primarily from the atmosphere in association with precipitation. Cs^{137} is a radioactive product of nuclear fission with a half life of 30.2 years. It was distributed world wide after atmospheric testing of nuclear weapons in the 1950's and 1960's (Sutherland 1991). When using Cs^{137} for determining soil loss, a reference inventory from a stable non-eroding source must be obtained. Soil samples taken from eroding sites can be compared against the inventory; areas with lower Cs^{137} values than the inventory indicates that erosion has taken place – removing the Cs^{137} layer. Where areas contain values higher than the inventory, the site in question is likely to be a sink – the soil is enriched due to deposition.

2.8.5.2 Particle size effects

Selective particle size transport has been well documented (Foster et al, 1998) and contaminants (i.e. heavy metals) are known to be concentrated in finer grained material (Horowitz & Elrick, 1987; Horowitz, 1991). A more direct correlation between source samples and suspended samples can be achieved by conducting analysis on samples below 63μm (Walden et al, 1997; Walling et al, 1993; Yu & Oldfield, 1989). Correction factors to account for particle size differences are used along with <63μm samples by some authors (Collins et al, 1997a, 1997b, 1998; Walling et al, 1999).

2.8.5.3 Need for a composite fingerprint

Due to the spatial variability in a catchment and the need to deal with several sediment sources, a single diagnostic property cannot be used (Peart & Walling, 1988). The complexity of sediment routing and the delivery process mean that a suspended sediment sample can be very similar to a particular sediment source or it could represent mixtures of different sites. To overcome this problem, several properties are used together to build a composite fingerprint for the catchment. Authors that have used combinations of different subsets of determinants include Walling et al (1993) who used a combination of radionuclides and mineral magnetics, and Walling et al (1999) who used radionuclides, mineral magnetics and elemental data. The properties used should be controlled by different environmental factors, as this will allow a greater degree of independence between determinants, thereby providing a higher degree of discrimination between sources and improving the reliability of the composite fingerprint (Walling et al, 1993).

2.8.5.4 Statistical testing of determinants

All the parameters measured undergo vigorous statistical testing in order to define properties capable of discriminating between different groups. The parameters selected should have low variability about the mean to minimise errors when determining sources. The statistical methods commonly used to test if differences between groups are significant are Kruskall-Wallis (Collins et al, 1997b, 1998, Walling et al, 1999), Mann-Whitney (Collins et al, 1997a, 1997b), factor analysis (Walden et al, 1997) and cluster analysis (Yu & Oldfield, 1989; Walling et al, 1993; deBoer & Crosby, 1995).

When the properties that can discriminate between groups have been identified, they are subjected to a further statistical procedure to minimise over-parameterisation, i.e. to identify the fewest number of tracers that when used together, can clearly distinguish between groups. This is achieved using multivariate discriminant function analysis (Walling et al, 1999). Collins et al (1997a, 1997b, 1997c) used the minimisation of Wilks lambda as a stepwise algorithm whilst Rowan et al (2000) used the stepwise Mahalanbois procedure. Stepwise multi-discriminant analysis works through the sediment properties in order of their relative discriminating power until all the variables have either been included in the discriminant function or excluded because they add no further information. The properties selected are deemed to be those that can used to successfully distinguish between groups and therefore represent the composite fingerprint.

2.8.5.5 Mixing model design

A multivariate-mixing model is used to estimate the relative contributions of the potential sediment sources in the samples collected from rivers (to 'unmix' the suspended sediment samples). The source proportions are obtained mathematically by solving linear equations. The model assumes that the properties of the suspended sediment are dependent on the sediment sources defined in the catchment. The parameters used in the model need to be linearly additive, so that when parameter x_1 and x_2 are mixed in proportions p_1 and p_2, the resultant mixture can be defined as $x_m = p_1x_1 + p_2x_2$ (Walden et al, 1997; Stott, 1986). Lees (1997) has raised doubts about the linear additivity of some mineral magnetic properties.

The model assumes that the source materials behave conservatively during mixing and deposition, i.e. they do not degrade, react, weather and mix evenly. No account is taken of any processes acting during erosion, transport or deposition and it is assumed that samples are true indicators of the sources. Since the material has been weathered and eroded before reaching the channel, the significance of diagenesis may be small (Petts & Foster, 1985). All sediment sources in the catchment need to be recognised or the model will fail to reliably identify source types.

The mixing model is represented by a series of simultaneous equations and an iterative search is carried out to find the optimum combination of properties that minimises the differences between the measured properties and the properties of the mathematical mixture of the sources. The model needs to meet two linear constraints - the contributions from all source areas are non-negative and the contributions from all areas sum to unity.

Models developed using constrained linear programming methods are generally over-determined if the number of tracer properties is greater than the number of source groups and therefore require optimisation procedures to determine the relative contributions made by each group. The optimised solution is gauged by the goodness of fit or likelihood function.

Walling et al (1999) and Collins et al (1998) attempted to overcome this uncertainty in the mixing model results by using the least squares method rather than solving the linear equations directly. The proportions were estimated by minimising the sum of the squares of the residual R for the *n* tracer properties and *m* source groups. The assessment of goodness of fit was undertaken by comparing the actual fingerprint property concentrations for a selection of suspended sediment samples with predicted values based on the estimates from the percentage contributions from each of the sources within each source category (Collins et al, 1997a, 1997b). The accuracy of the goodness of fit was found to vary between ±7 and ±14 percent (Walling et al, 2000).

Similarly, Rowan et al (2000) used 'explained variance' to determine the likelihood or efficiency of the solution, as the same goodness of fit can be obtained by a variety of different parameter combinations (Beven, 1996). This means the solution is not unique and only one from a range of statistically possibly outcomes. Rowan et al (2000) used GLUE (Generalised Likelihood Uncertainty Estimation; Beven & Binley, 1992) and updated a programme called SPARSSE (systematic parameter space search engine) to calculate the efficiency of mixing model results. They determined that even when results were updated for likelihood the confidence level intervals remained at ± 25 percent.

Yu and Oldfield (1989) and Walden et al (1997) used SIMPLEX (a solver add-in to Excel) as the model to estimate sediment sources. SIMPLEX allows numerous sources and multiple variables to be used. When using SIMPLEX, initial starting proportions are input, and the computer moves away from these to find the optimum fit. For the model to run, the data used in forming the linear equations, maximum error allowed (typically 10^{-5}) and the number of iterations ($\sim 20 \times n^2$) are needed (Thompson, 1986). The model can show sensitivity to initial starting proportions (Walden et al, 1997), which can be overcome by running the model from a number of different start conditions to ensure that an optimum solution is found.

2.8.6 Previous use of fingerprinting

Early approaches to fingerprinting were non-statistical and based on observations of differences in the catchment mineralogy (Klages & Hsieh, 1975) and sediment colour in combination with the sediment-discharge hydrograph (Grimshaw & Lewin, 1980). Caitcheon (1993) used mineral magnetics to tag tributaries in several river catchments in Australia. The properties of the bedload and suspended sediment in tributaries were determined above stream junctions and the resultant binary mix in the trunk downstream was studied. He was able to identify the dominant source category (banks versus fields) by identifying a sequence of confluence measurements along a drainage network. The relative tributary contributions were calculated using a simple proportion equation, it being assumed that the sediment transport mechanics would have an averaging effect - i.e. the sediments would be well mixed

Mineral magnetics have been used by several authors, particularly Oldfield et al (1979) and (Yu & Oldfield 1989 and 1993) to distinguish between source types (undisturbed, arable and streambank sediments). The mineral magnetic properties commonly used by the authors are shown in Table 2.1. Yu & Oldfield (1989) compared a physical mixing model with a linear regression model and they found that most observations fitted well with the regression models. Unusual observations were found with extreme cases e.g. single source samples.

Table 2.1 Explanation of magnetic properties

Magnetic property	Properties
Susceptibility (χ/χ_{lf})	Roughly proportional to the concentration of ferrimagnetic minerals in a sample
Saturation Isothermal Remanent Magnetism (SIRM)	Relates to mineral type and concentration
Frequency dependant susceptibility (χfd)	Variation of susceptability with frequencies - sensitive to magnetic grain size
Anhysteretic Remanent Magnetism (ARM)	Related to concentration of finer grain sizes of ferrimagnetic samples
Iosthermal Remanent Magnetism	Sensitive to concentration of antiferromagnetic species
ARM/χ	Can indicate concentration of finer grain sizes of ferrimagnetic minerals
SIRM/χ	Diagnostic of mineralogy, or if samples are similar, the dominant magnetic grain size.

Collins et al (1997a) successfully used elemental data to identify sediment and sources in two river catchments in the UK (Dart 46 km^2 and Plynlimon – a small headwater catchment of the River Severn, 8.7 km^2). They used trace metals (Fe, Mn & Al), heavy metals (Cu, Zn, Pb, Cr, Co, Ni), base cations (Na, Mg, Ca & K) and organic & inorganic constituents (C, N and total P) to identify the differences between surface and subsurface soils. They found that five determinants could be used to distinguish sources in the Dart catchment (Ni, Co, K, total P and N), whilst in Plynlimon only three were needed (N, Cu and Cs^{137}). In both catchments 100% of samples could be sourced. They were also able to identify distinct seasonal, inter- and intra-storm variations in the contributions from different source types.

Collins et al (1997b) used the same elemental subsets along with radionuclide properties to fingerprint two larger catchments (Exe, 601km^2, and Severn, 4325 km^2) in the UK. They distinguished between the different tributaries in the catchment and the source types within the subcatchments using a variety of determinants. Each tributary had a separate set of determinants that distinguished it. Collins et al (1998) distinguished between geological groups and seasonal variability in the same two catchments.

Walling et al (1999) used metal concentrations, radionuclide and mineral magnetic subsets in the Ouse catchment in North East England. Ten determinants could determine 94% of the samples when determining between source types (N, total P, Sr, Ni, Zn, Ra^{226}, Cs^{137}, unsupported Pb^{210}, Fe and Al). Identifying sediments from different geological groups was less accurate (80%); Mn, N, Mg, χ_{lf} χ_{fd}, K, Sr and Ni were used. They found the geology, topography and landuse to be inter-related. The geology, landuse and topography are similar to that seen in the Tees catchment. They were able to distinguish between source types, geological groups and estimate the relative proportions of sediment load carried by each tributary.

The samples collected by Walling et al (1999) were weighted according to the instantaneous suspended sediment load at the time of sampling to allow the overall importance of the various source groups to be calculated. The results showed that, for the Ouse, uncultivated land produced 25% of the suspended sediment load whilst cultivated land added 38% and channel bank sources contributed approximately 37%. When the contributing areas in the Ouse were analysed in terms of their geological grouping, the Carboniferous provided 24%, Permian and Triassic 41% and the Jurassic supplied 35%. They also found relationships between rainfall distribution and suspended sediment source. When precipitation was greatest over the Pennine Carboniferous rocks, these were the dominant source. When the precipitation was evenly distributed over the catchment, the suspended sediment was from all areas.

2.8.7 Principal Components Analysis used in identifying sediment sources

Principal Components Analysis (PCA), is a multivariate technique conducted on a correlation matrix, in order to reduce the dimensionality of the dataset and explain the variance between the new factors produced. By using eigenvalues and eigenvectors a component factor plot can be drawn which shows the relationships between the different samples. Qu et al (2001) successfully used PCA to assess the degree of contamination and spatial distribution of heavy metals and nutrients of Taihu Lake, China. They were able to relate the distinct spatial distribution to man's activities around the lake. Qu & Kelderman (2001) analysed canal sediments and compared them with suspended solids in the Rhine River; they were able to explain the behaviour and sources of each metal through PCA. Soares et al (1999) used PCA to classify the heavy metals in the Ave river basin, Portugal. They conducted the analysis on samples sieved through 63μm and found that this fraction was an adequate method for determining metal pollution.

2.9 Earlier Work in the River Tees Catchment

There has been limited research into identifying sediment sources and the measurement of suspended sediment in the Tees catchment. Before the construction of the Tees Barrage, HR Wallingford (1992) produced a report on potential sedimentation of the impoundment. This report predicted the amount of sediment likely to enter the barrage impoundment each year. These results were based on an annual suspended sediment load calculated by sediment-discharge rating curves for the Tees at Low Moor and the River Leven at Leven Bridge. The average annual sediment yields for the rivers Tees and Leven were estimated to be 35,000 and 5,000 tonnes respectively. These figures were calculated based on an annual freshwater input of 618 million cubic metres. In a year with no significant floods the total annual yield is expected to be 10-20,000 tonnes, compared with 60,000 in years with numerous floods.

Recent studies have been conducted to identify the history of sediment flux and storage in the Tees estuary. Plater et al (2000) found that the metal contamination (Zn, Ba, Pb and to a lesser extent Cu, Ni, Co and AS) in the estuarine sediments peaked in the mid-twentieth century, possibly due to a combination of mining activity and sediment reworking. There has been a notable decrease from 1980's onwards in the sedimentary record. Plater et al (1998) found that the heavy metal contamination in a series of boreholes in the estuary and lower parts of the Tees was widespread and very variable. They found that the iron-oxyhydroxides were the dominant metal bearing phase in the downstream parts of the catchment. This agrees with work done by Hudson-Edwards et al (1997). They also found high correlation coefficients between organic matter and metal concentrations, which disagrees with work done by Davies et al (1991). They did however find that a high organic content does not always relate to a high concentration of heavy metals. Hudson-Edwards et al (1997) found that heavy metals adhered to sulphides and carbonates were abundant in the upper catchment, whilst iron-oxyhydroxides dominated downstream

Work undertaken as part of the SIMBA project has found that the sediment transport in the River Tees appears to have changed after an exceptionally wet autumn and winter in 2000/2001. Preceding this event the peak suspended sediment concentration lagged behind the peak discharge at the Low Moor monitoring site (White et al, 2000). Since this wet period, the concentration per unit runoff is much higher and the peak sediment concentration often precedes the peak flow and there is greater non-flow-related variability. This suggest new sources were mobilised; observation of extensive bank failures upstream support this interpretation (White et al, 2001). Estimated annual transport rates for the Tees are $67km^{-2}yr^{-1}$, which is similar to that quoted for other UK rivers (Walling, 1983). The high flow events are responsible for most of the sediment yield. From December 1999 to February 2001, 80% of sediment transported was associated with high flows that occur only 10% of the time - ie in excess of $74m^3/s^{-1}$ (White et al, 2002).

Some relevant work has been undertaken in the upper parts of the catchment. Warburton & Evans (1998) measured downstream bedload movement in a small upland tributary. Warburton et al (1998) used sediment tracers to measure the movement of bedload in a Pennine stream; they used different shaped rocks to measure the effect of shape on transport. They found that there was a clear pattern of shape selected transport, with sphere and rod shaped stones moving furthest, with blade and disc shapes rarely moving. Carling (1986), Crisp et al (1964) and Warburton & Higgitt (1995) have studied landslides in the peaty uplands, whose affects have been seen in the Tees at least as far downstream as Broken Scar. Conway & Millar (1960) studied the effects of ground cover in three small catchments near Moorhouse in the upland Pennines. As expected the site with bare ground (which had been severely burnt) produced a great deal more sediment than the natural vegetated land.

2.10 Methods to be Used in this Research Study

Fingerprinting gives a wider view of sediment source identification and has proved to be successful in numerous catchments around the world, allowing contributing landuse types, geology and tributaries to be identified. It potentially allows the areas contributing most to the sediment load to be pinpointed and the relative importance of different areas in the catchment to be deduced. By fingerprinting the catchment a link between chemistry and landuse/geology/soil type or subcatchment can possibly be identified.

Ideally properties from different environmental subsets should be used when attempting to use the fingerprint technique but the resources available for this study do not permit this. Instead, fingerprinting will be carried out using analysis of the different phases of the major elements (at the different bonding sites) as these are affected by different environmental controls (bound to carbonates, organics etc).

This technique is being used in preference to other methods of source identification since aerial photography and remote sensing only allows identification of sources and not necessarily their relative importance. GIS techniques have been used to identify samples sites so that a representative sample of all categories is achieved. Values and source areas identified using USLE methods cannot be validated due to lack of instrumentation and suspended sediment data for all areas of the catchment. In any case USLE methods predict erosion from sheet and rill, which are not the dominant processes in the Tees. When fingerprinting has identified sediment source areas in the Tees catchment, the use of GIS could allow the factors affecting sediment production to be identified.

Chapter 3 Field Area and Data Collection

This chapter introduces the study area in detail and identifies characteristics that are unique to the area. It also describes the programme of field data collection carried out to provide samples of soil and river sediment for analysis reported in chapter 5.

3.1 Catchment, Topography and Climate

The River Tees rises on the eastern slopes of the Northern Pennines between Cross Fell and Little Dun (890mAOD) and has a catchment area of $2400km^2$ (Environment Agency, 1996). The river flows south eastwards through the Upper Teesdale National Nature Reserve (NNR). After passing through Darlington the river meanders then flows north easterly through Stockton and out to sea north of Middlesborough, see Figure 3.1. The estuary was impounded by a total exclusion barrage in 1995. Upstream of Barnard Castle the landuse is predominantly Pennine upland with rough pasture. Downstream of Barnard Castle the landscape is mainly lowland and agricultural. The average annual rainfall varies considerably across the catchment from 2300 $mmyr^{-1}$ in the Pennines to 610 $mmyr^{-1}$ in the western coastal areas (Environment Agency, 1996). The prevailing wind is from the southwest, but north and northeasterly winds also exert their influence bringing cold continental air to the area. The River Tees has many tributaries, the most important being the Skerne, Leven, Greta, Lune and Balder, all of which join the Tees upstream of the barrage.

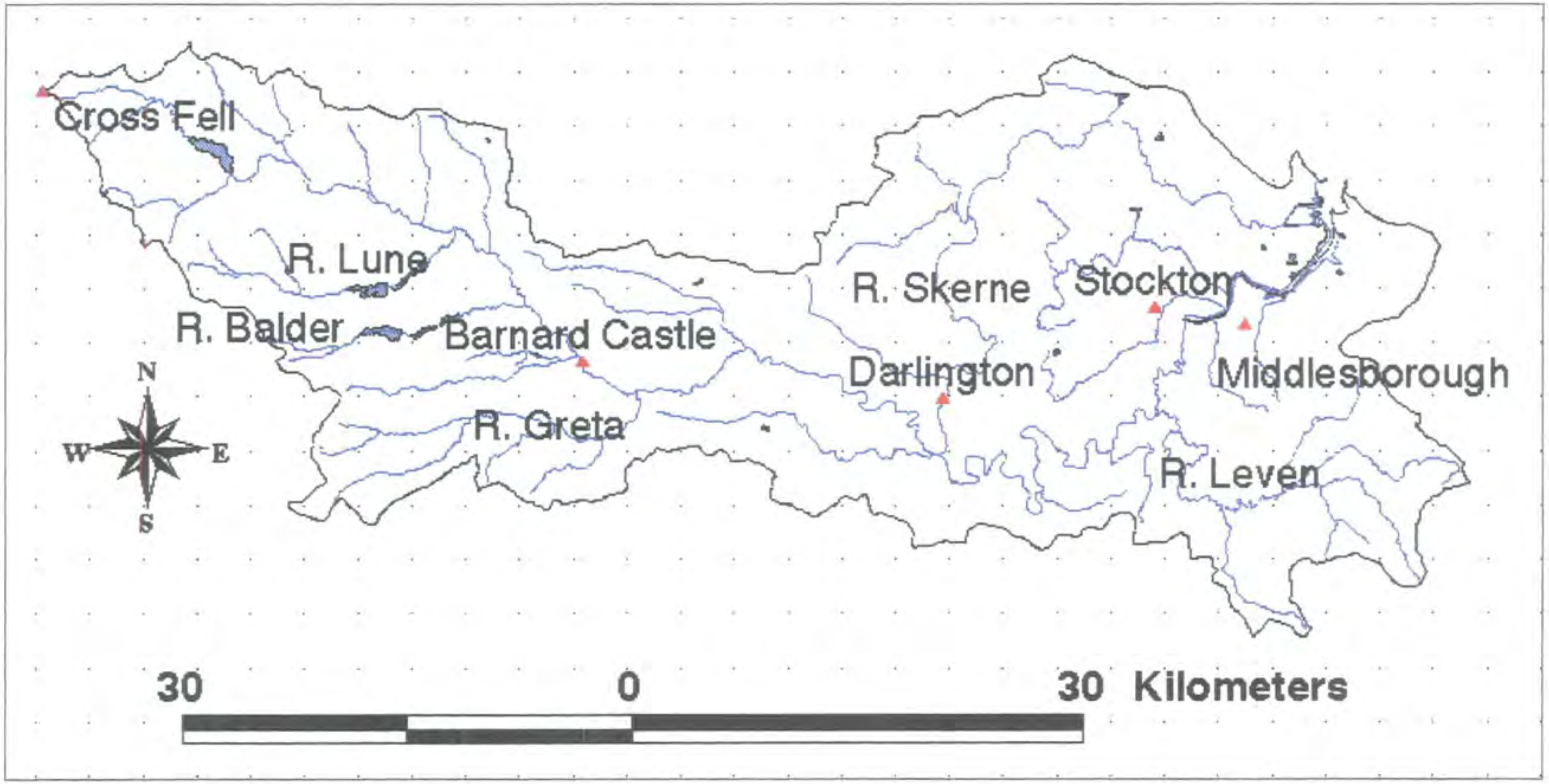


Figure 3.1 Locations in the River Tees Catchment

3.2 Geology

Upper Teesdale lies on the crest of the Teesdale dome, a broad uplift that affects the high ground between Stainmore and the Tyne Valley (Archer 1992). This has created a gentle easterly dip in the Teesdale Valley, with the oldest rocks in the west and the youngest in the east. The Carboniferous dominates the upper and middle parts of the Tees as shown in Figure 3.2. The Lower Carboniferous consists of the Lower Limestone Group with some sandstones, grits and shales with local coal seams. The Upper Carboniferous is composed of the middle limestone group - a rhythmic sequence of limestones, sandstones and shales. The Ordovician Skiddaw Slate Group outcrops in the Tees valley upstream of Middleton.

The eastern half of the catchment consists of Permian, Triassic and Jurassic rocks. The River Skerne catchment is predominantly Permian magnesian limestones and marls (calcareous mudstones). The Sherwood sandstone group of the Permo-Triassic era outcrop to the east of the magnesian limestones and is a major aquifer. From the Skerne confluence to the estuary and in the lower Leven valley the geology consists of Triassic mudstones and sandstones. The Cleveland hills in the upper Leven catchment are composed of Jurassic argillaceous rocks (a succession of siltstones, mudstones/shales and ironstones). Drift geology is found throughout the catchment except for the high moors and consists of boulder clay, sand and gravels, peat and alluvium.

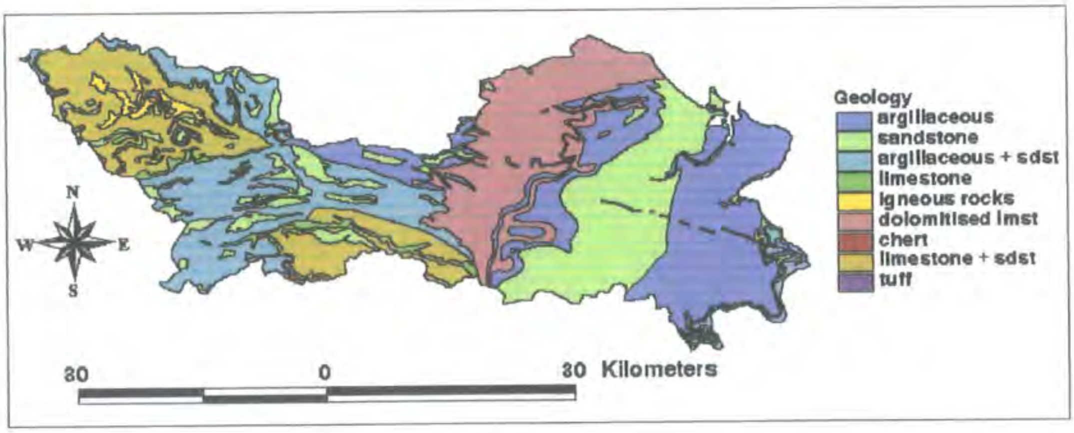


Figure 3.2 The Geology of the River Tees catchment (British Geological Society, 2000)

An important geological feature in Teesdale is the Whin Sill, a quartz dolerite intrusion. The horizontal sheets of dark coloured, finely crystalline igneous rock were emplaced as hot magma into the Carboniferous limestone series about 295 million years ago. The Whin sill is hard and therefore resistant to erosion, and it is responsible for the waterfalls at High Force and Low Force, and the ravine at Cauldron Snout.

The general eastwards dip is disrupted by faults, which are often persistent over wide areas. Many of these fault lines were channels for movement of late and post-Carboniferous mineralising fluids, which formed mineral veins in fractures. The minerals, lead, zinc, flurospar and barytes, have been worked in Upper Teesdale since mediaeval times (Dunham 1988). In the Northern Pennine Orefield approximately 3.9 x 10^5 tonnes of lead (Pb) concentrates with 60-75% Pb have been removed, whilst 750 tonnes of zinc (Zn) with concentrates of 56-60% Zn have been removed from Roman times to present day. Lead mining peaked in 1815-1880, whilst the zinc mining peaked later from 1880-1920, the last mine (Coldberry in the Hudeshope area) closing in 1955 (Hudson-Edwards et al 1997).

The Jurassic rocks of the Cleveland Hills have also been mined in past times. The Cleveland Ironstone Formation (CIF) of the Middle Lias has also been mined since mediaeval times (Hemingway 1974). Production peaked between 1870-1920 and finally ceased in 1964. The CIF is a succession of marine shales, ironstones with siltstones, conglomerates and shelly beds. The low-grade iron-ore was mined from four main seams which contained approximately one-third siderite, one-third chamosite and one-third ancillary constituents (including collophanite 4% (phosphate mineral), calcite, pyrite and clay minerals). By 1870 over 4 millions tonnes of ore was removed annually from Cleveland, this reached 6 million by 1875. A small part of these works were within the Tees catchment. The approximate composition of the Cleveland Ironstones is 13% SiO_2, 10% Al_2O_3, 3% Fe_2O_3, 32% FeO, 5% CaO and 19% CO_2 (Hallimond, 1925).

Copper and Lead were also mined south of Barnard Castle, at sites now used as landfill sites. Limestone extraction takes place at Barton, Aycliffe and Thrislington quarry. Basalt is removed at Force Garth near High Force and barytes at Close House (Lunedale) (Environment Agency, 1996).

The geological data used in this study originated from the BGS 1:250 000 published solid geology maps and was supplied in 100km by 100km tiles. The data was in vector format (easily converted to GRID) and contained the lithostratigraphy (formation names) and lithology (rock type). The rock type was used in this research to determine different geological areas along with the simplified geological map in the Tees Leap Report (Environment Agency, 1996).

For the purposes of this research the main rock types in the catchment area are summarised as:

- Limestone (lmst)
- Dolomitised limestone (dldo)
- Argillaceous and sandstone (arsd)
- Argillaceous (arg)
- Igneous rocks - located mostly in the upper catchment (mgac)

3.3 Soils

The underlying geology and surface drift control the production, chemistry, texture and depth of the soil stratum. The chemistry and texture greatly affect the soil erodibility, types of vegetation, landuse and the chemical composition of the soil. The river water is frequently coloured by runoff from the peat highlands.

Surface water gleys dominate to the east of and within Darlington. These are non-alluvial, seasonally waterlogged slowly permeable soils formed at elevations of 3mAOD and above. These soils are common in over 50% of the River Tees catchment.

West of Darlington and mainly confined to valley bottoms are the brown soils. Generally these are non-alluvial loamy soils with a non-calcareous subsoil without significant clay enrichment (Environment Agency, 1996). They are free draining permeable soils making up almost 10% of the catchment. They are developed mainly on permeable materials at elevations below ~ 300mAOD and most are in agricultural use.

On the high moors in the western area of the catchment moor Peat Soils are dominant. These are predominantly organic soils derived from partially decomposed plant remains that accumulated under waterlogged conditions. Nearly 30% of the catchment consists of these permanently wet upland peats.

The Soil Survey & Land Research Centre (SSLRC) at Cranfield University kindly provided one kilometre resolution gridded soil data. The data consisted of 2 Excel files containing various soil properties (see appendix for full details) which were converted to a spatial format using GRID. The soil properties are the amalgamation of all samples taken nationally for a particular soil series/type, and provide average characteristics for the different soil series. The eastings and northings of each sample was given at 1km resolution, the number of samples per 1km^2 varied over the catchment but was generally about 20 samples.

The dataset contained a large number of variables of which only HOST (Hydrology of Soil Types), total sand %, total silt % and total clay % were used in this research. These variables were chosen as they were the best indicators of the erodibility of the soils. The

HOST data (Boorman et al 1995, Lilly et al 1998) was developed for hydrological applications and gives an indication of runoff after a rainfall event. The HOST dataset replaces WRAP (Winter Rainfall Acceptance Potential) and was developed in the 1980's by the SSLRC and the Macaulay Land Use Research Institute (MLURI). It uses data from the Surface Water Archive (SWA) and the Flood Event Archive (both from the Centre for Ecology and Hydrology, Wallingford).

The HOST information was constructed using links between the soil type and hydrological response using fieldwork samples and hydrological databases (Boorman et al 1995). The properties of the soil govern the processes of storage, infiltration and overland movement of water. Flood Event data was used for each soil type to describe runoff under standardised rainfall events and antecedent moisture contents. The classification schemes used in HOST were derived from conceptual models of catchment response and the feedback from applying them. The result is 29 HOST classes - see Table 3.1 for a brief description of each. Only twenty HOST classes are shown in Figure 3.3, as the remaining nine classes were not found in the Tees catchment area.

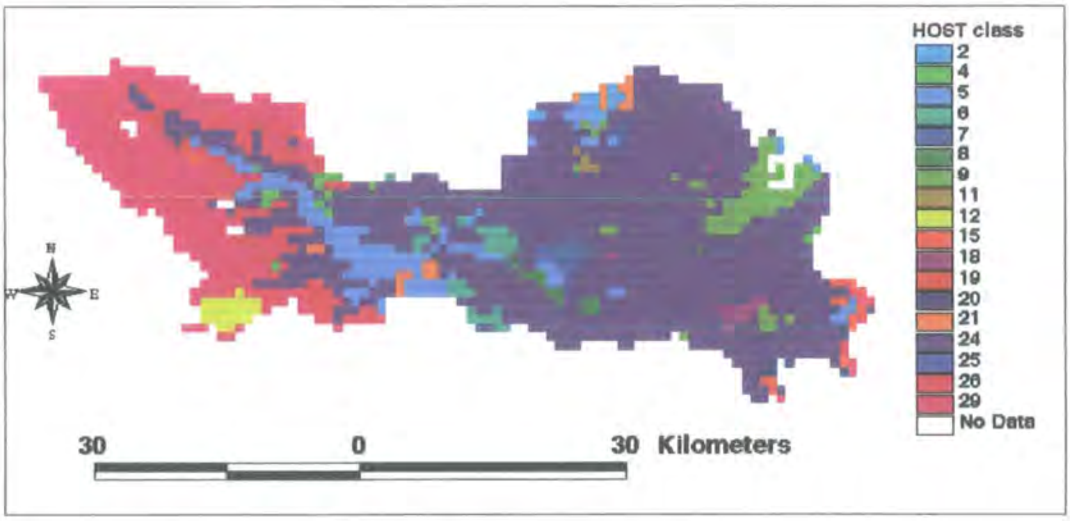


Figure 3.3 HOST class distribution over the River Tees Catchment

Table 3.1 HOST descriptions of soil types

HOST	DESCRIPTION
2	Free draining permeable soils on 'brashy' or dolomitic limestone substrates with high permeability and moderate storage capacity
4	Free draining permeable soils on hard but fissured rocks with high permeability but low to moderate storage capacity
5	Free draining permeable soils in unconsolidated sands or gravels with relatively high permeability and high storage capacity
6	Free draining permeable soils in unconsolidated loams or clays with low permeability and storage capacity
7	Free draining permeable soils in unconsolidated sands or gravels with groundwater at less than 2m from the surface
8	Free draining permeable soils in unconsolidated loams or clays with groundwater at less than 2m from the surface
9	Soils seasonally waterlogged by fluctuating groundwater and with relatively slow lateral saturated conductivity
10	Soils seasonally waterlogged by fluctuating groundwater and with relatively rigid lateral saturated conductivity
11	Drained lowland peaty soils with groundwater controlled by pumping
12	Undrained lowland peaty soils waterlogged by groundwater
15	Permanently wet, peaty topped upland soils over relatively free draining permeable rocks
17	Relatively free draining soils with a large storage capacity over hard impermeable rocks with no storage capacity
18	Slowly permeable soils with slight seasonal waterlogging and moderate storage capacity over slowly permeable substrates with negligible storage
19	Relatively free draining soils with a moderate storage capacity over hard impermeable rocks with no storage capacity
20	Slowly permeable soils with slight seasonal waterlogging and moderate storage capacity over impermeable clay substrates with no storage capacity
21	Slowly permeable soils with slight seasonal waterlogging and low storage capacity over slowly permeable substrates with negligible storage capacity
24	Slowly permeable, seasonally waterlogged soils over slowly permeable

	substrates with negligible storage capacity
25	Slowly permeable, seasonally waterlogged soils over impermeable clay substrates with no storage capacity
26	Permanently wet, peaty topped soils over slowly permeable substrates with negligible storage capacity
29	Permanently wet upland blanket peat

3.4 Vegetation Cover and Landuse

The breakdown of different landuse categories in the Tees catchment is shown in Table 3.2 and Figure 3.4. In the Western uplands the harsh climate and poor soils restrict the land to livestock farming, with only sheep rearing on the hill farms (Environment Agency, 1996). In the middle Tees catchment arable agricultural use dominates, the main crops being cereals (mostly wheat) and oil seed rape. The lower Tees is dominated by urban areas such as Stockton and Middlesborough. The Tees estuary is dominated by industrial use, with large areas of land being reclaimed from salt marsh.

Table 3.2 Landuse cover in the Tees Catchment

Landuse type	% cover in Tees catchment
No data	0.6
Water	0.5
Semi-natural grass	23.3
Natural	27.7
Woodland	2.8
Tilled land	33.6
Urbanised areas	11.5

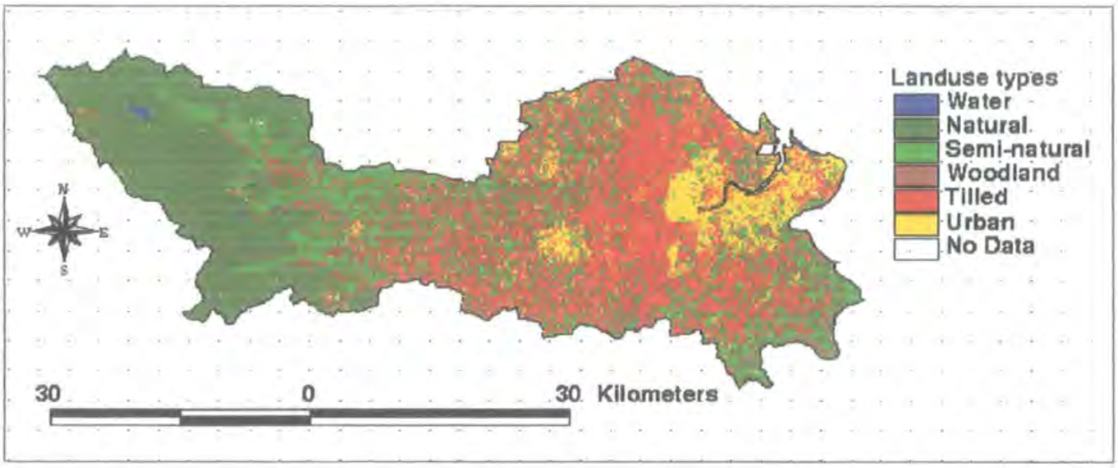


Figure 3.4 Landuse types in the River Tees Catchment

The landuse data used in this study originated from the Land Cover Map of Great Britain, which identified 25 'target' cover-types as shown in Table 3.3. The data used in this work came in a 25-metre grid format. The data was re-classed into six categories to suit the needs of this investigation before being converted to 50m grids in line with other digital data used in this research. The first category contains the water-based covers. Although saltmarsh is very different from inland water and beach they did not need to be separated - all the saltmarsh, beach, etc is downstream of the barrage. Upstream of the barrage only reservoirs are likely to be in this category. The second category contains natural vegetation little affected by man. Category 3 is the semi natural - i.e. meadows/ verges, controlled by man but not used for agricultural purposes. Category 4 is an aggregation of deciduous and coniferous woodland in the catchment. Tilled and bare lands were amalgamated to form category 5. The final category is a combination of suburban and urban land types. Figure 3.4 shows the variation of landuse throughout the Tees catchment, whilst Table 3.3 shows the re-classed landuse categories.

Table 3.3 Reclassification of Landuse Categories

Target classes (25 class system)		Landuse type (6 class system)	
1	Sea/ Estuary	1	Water/ Beach
2	Inland Water	1	Water/ Beach
3	Beach and Coastal Bare	1	Water/ Beach
4	Saltmarsh	1	Water/ Beach
5	Grass Heath	2	Natural
9	Moorland Heath		
6	Mown/ Grazed Turf	3	Semi-natural
7	Meadow/ Verge/ Semi-natural		
19	Ruderal Weed	2	Natural
23	Felled Forest		
8	Rough/ Marsh Grass		
25	Open Shrub Heath	2	Natural
10	Open Shrub Moor		
13	Dense Shrub Heath		
11	Dense Shrub Moor		
12	Bracken		
14	Shrub/ Orchard	4	Woodland
15	Deciduous Woodland		
16	Coniferous Woodland		
24	Lowland Bog	2	Natural
17	Upland Bog		
18	Tilled Land	5	Tilled
20	Suburban/ Rural	6	Urban
21	Urban Development		
22	Inland Bare Ground	5	Tilled

3.5 River Regime

The headwaters of the Tees respond rapidly to rainfall events owing to their steepness and high drainage density. The floodwave slows and flattens out as it reaches the lower catchment owing to a variety of factors including shallower gradients, floodplains and large meanders. This is seen in the flood peak travel times witnessed on the Tees (Environment Agency flow data and personal communication, John Dixon - barrage control) in Table 3.4 and the sites are shown in Figure 3.5.

Table 3.4 Flood wave times

Distance	Journey times	Average
Middleton to Barnard Castle	3 -5 hours	4 hours
Barnard Castle to Low Moor	5 - 10 hours	8 hours
Low Moor to Stockton		12 hours

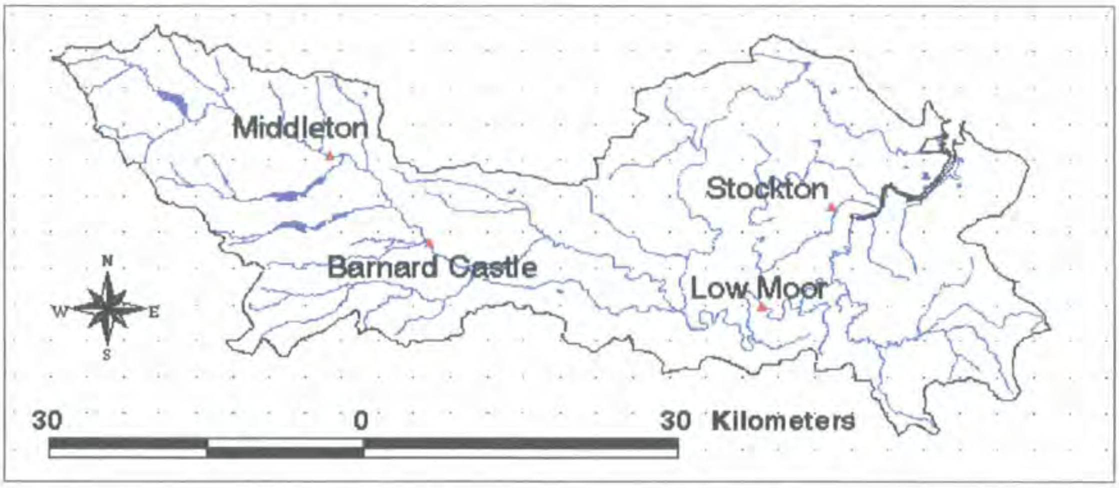


Figure 3.5 Location of sites in Table 3.4

The river and its tributaries are continually monitored at 13 sites throughout the catchment. The river flow between these stations varies considerably as shown in Table 3.5.

Table 3.5 Environment Agency flow monitoring station details

River	**Station**	**Grid Ref.**	**Max flow**	**Mean flow**	**Catchment area**	**Start date**
Trout Beck	Moorhouse	NY759336	11.63	0.54	11.4	18/06/91
Tees	Cow Green	NY813288	23.56	2.74	58.2	01/09/71
Harwood Beck	Harwood	NY849309	28.83	0.97	25.1	01/09/69
Tees	Middleton	NY950250	206.74	8.8	242.1	01/07/71
Tees	Barnard Castle	NZ047166	318.9	13.46	509.2	01/01/90
Greta	Rutherford Bridge	NZ034122	120.17	11.37	86.1	01/12/99
Tees	Broken Scar	NZ259137	663.84	16.58	818	01/01/82
Skerne	Bradbury	NZ318285	16.29	0.37	70.1	01/06/73
Skerne	Preston le Skerne	NZ292238	23.31	0.83	147.0	01/12/72
Skerne	South Park	NZ284129	42.76	1.56	250.1	01/11/56
Tees	Low Moor	NZ364105	538.87	18.33	1264.0	01/09/69
Leven	Easby	NZ585087	7.83	0.068	14.8	29/11/96
Leven	Leven Bridge	NZ445122	124.74	8.44	196.3	01/01/99

Flow is measured in m^3/s^{-1} and catchment area in km^2

3.6 Water Quality and Anthropogenic Factors

The River Tees and its tributaries generally exhibit good water quality. There are some localised discharges of contaminated water from abandoned mines in Upper Teesdale, which are quickly diluted (Novis, 1999). Acid runoff from the peat moorland affects parts of the Tees down to Barnard Castle (Environment Agency, 1996).

There are 41 sewage treatment works in the Tees catchment (Environment Agency, 1996). Fifteen are in the Tees upstream of the Skerne confluence. Eight are in the Skerne catchment and seven are in the Leven.

The River Skerne receives significant discharges from the Northumbrian Water Ltd (NWL) Newton Aycliffe sewage treatment plant and the Darlington sewage treatment works; these inputs downgrade the water quality of the Skerne and 6km of the Tees downstream from the confluence. Northumbrian Water also discharge from sewage treatment works at Stokesley, Great Ayton and Rudby, which downgrade the water quality in the Leven for 7 km downstream of Stokesley.

3.7 Dams and Reservoirs

The headwaters of the Tees and two of its tributaries have been dammed to create reservoirs as shown in Figure 3.6. Cow Green reservoir was completed in 1970 and is the only reservoir on the main River Tees. The River Lune is impounded at two points, the first forming the Selset reservoir which then drains into Grassholme reservoir. The River Balder has three dams, the largest being the Balderhead reservoir. The overflow from Balderhead is directed into Blackton reservoir then into Hury reservoir before reaching the River Tees.

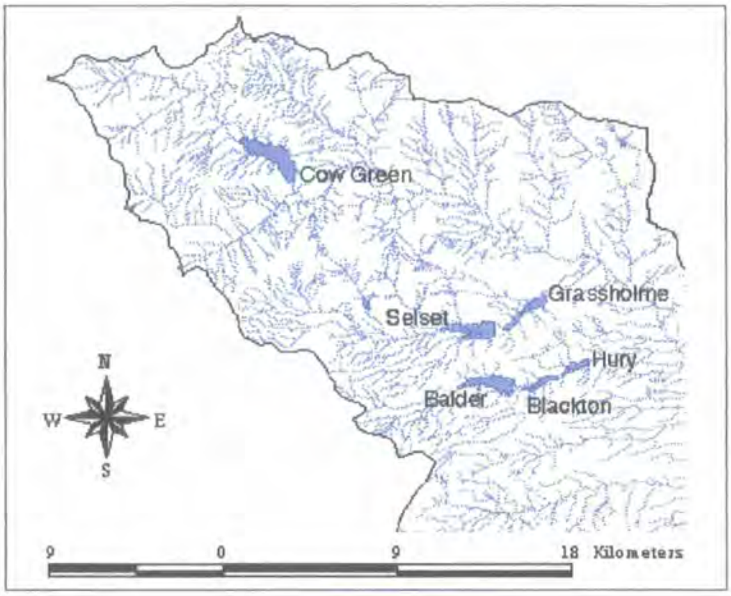


Figure 3.6 Reservoirs in the Upper River Tees Catchment

The reservoirs are operated by Northumbrian Water Limited and have three main purposes:

Drinking water for Darlington and Teeside
River regulation and augmentation to support extraction
Compensation releases

The Lune and Balder reservoirs maintain direct water supply to Lartington treatment works to supply Darlington. Cow Green is the main source of water for regulation. There are three major water extraction sites from the Tees - Broken Scar, Blackwell and Low Worsall, these are shown in Figure 3.7. During periods of drought water supplies from Kielder reservoir are directed into the Tees (via the Tyne and Wear) at Egglestone to ensure a statutory maintained flow in the Tees.

The capacity available at Cow Green is approximately equal to the sum of the other five reservoirs, as shown below in Table 3.6. (Kennard, 1975)

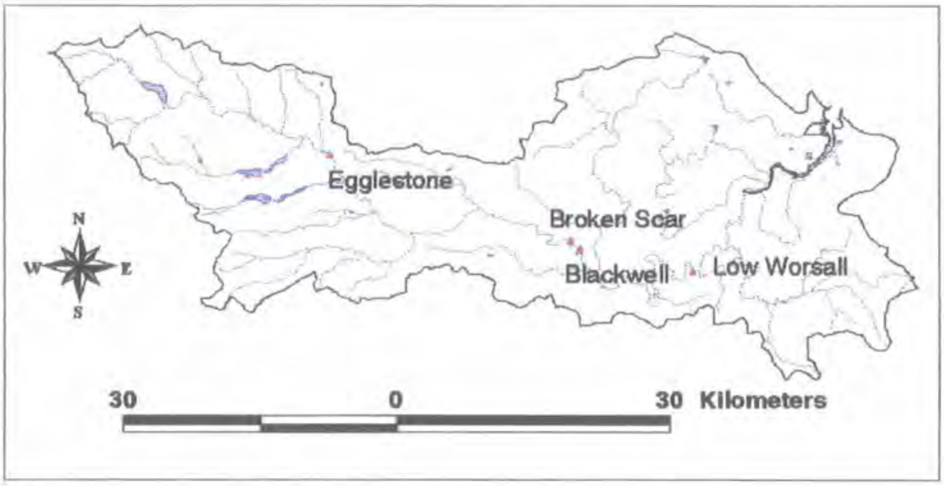


Figure 3.7 Water Extraction Points on the River Tees

Table 3.6 Upper Tees Reservoir Capacities

Reservoir	River	Capacity $m^3 x10^6$
Hury	Balder	3.9
Blackton	Balder	2.1
Grassholme	Lune	6.1
Selset	Lune	14.6
Balderhead	Balder	19.7
Cow Green	Tees	40.8

3.8 The History of the River Tees

The industrialisation of Teeside commenced with the opening of the Stockton – Darlington railway in 1825. In 1926 the Imperial Chemical Industries (ICI) was formed and produced large-scale investment in the chemical complex at Billingham. ICI produce fertilisers, heavy organic chemicals and chlorine. These chemicals are derived from crude oil, with plants converting ethylene, propylene, etc into glycol, polythene and Terylene. The Tees estuary has around 10% of total UK oil refining capacity.

Discharges from the chemical, iron and steel industries are the primary sources of industrial pollution in the Tees estuary, although the additional discharges from a few light engineering works and the electricity supply industry add to the problem. There was also a substantial increase in the discharge of domestic sewage in the 1960's, which became a significant source of pollution in the Tees and is now diverted downstream of the barrage. Northumbrian Water authority has recently built a new sewage treatment works at Bran Sands, where the waste is biologically treated before being discharged at the seaward side of the estuary (Environment Agency 1996)

3.8.1 Pollution History

The River Tees, before the industrialisation of Teeside, had supported a flourishing fishing industry and was noted for its catches of salmon, sea trout, flounders and eels – all of which thrived in the clean water. As a result of industrialisation, a variety of toxic substances - heavy metals, phenols, ammonia and cyanide - were discharged at sufficient quantities to make the water acutely toxic to migratory fish. By 1937 salmon had been virtually eliminated in the Tees. In 1970 the River Tees was considered to be one of the most heavily polluted estuaries in the UK. The daily Biological Oxygen Demand (BOD) load, of more than 500 tonnes, from chemical, petrochemical and steel making industries and untreated domestic sewage left the estuary devoid of oxygen. In dry summer months sections of the Tees estuary would be completely or almost completely deoxygenated as far upstream as Stockton (Rawley et al, 1978). Some organic matter and heavy metals are deposited in the river mud by sedimentation, providing an offensive appearance at low tide.

Common Law control mechanisms had failed to prevent gross pollution of the river Tees. In 1972 Stockton Borough Council drew up a proposal to decrease pollution by domestic sewage. Large interceptor sewers were built to channel discharges from Stockton, Norton and Billingham in the north and from Acklan, Linthorpe and Thornaby in the south, to a newly constructed treatment works at Portrack. A second major pollution initiative in 1980 reduced the BOD discharge load to a quarter of the 1970's load. This caused the re-establishment of a small run of migratory salmonids.

3.8.2 Teeside Development Corporation (TDC)

The Teeside Development Corporation proposed the Tees Barrage in 1987 to promote economic and physical development of Teeside. The then Northumbrian Water

Authority (NWA) carried out the initial feasibility studies. The scheme was then managed by Northern Rivers Association from Autumn 1989, as NWA had to pull out owing to concerns about the potential environmental impact of the barrage – water quality, land drainage, flooding and passage of migratory fish. Royal Assent was given on 26 July 1990, construction commenced in October 1992, and operational impoundments started in January 1995 (Hall, 1996).

The barrage has improved the upstream environment as it prevents the polluted estuary water moving upstream on the tide and also covers the unsightly mudflats. As a result the Tees above the barrage now supports a healthy and diverse fish population, with fish distribution by species following typical zonation by gradient. Brown trout, salmon and grayling are dominant in the upper reaches with roach, dace and chubb abundant in the lower reaches. Improvements in the water quality in the estuary have allowed the return of increasing numbers of salmonids. This is reflected in the declared rod catches of salmon. In 1993 14 were caught, with 38 in 1994 and 100 in 1995. There are still problems with water quality in some parts of the estuary especially in the summer (Walsch, 2001a)

3.8.3 The Tees Barrage

The main barrage is 70 metres long, made of reinforced concrete with a pavilion building at each end and a road running across the top. There are four fish belly flap gates, which are hinged at the bottom. Piers adjacent to the gates incorporate low-level sluices designed to discharge any accumulated low level pollution or saline intrusion. On the left side of the barrage a canoe slalom makes use of the head of water created and is accompanied by a fish pass. On the right bank a navigation channel and lock are installed. The four barrage gates span 13.5 metres and are 8.1 metres deep. The barrage creates an impoundment of 2.65 metres above ordnance datum, which is approximately the height of the mean high water spring tides. A freshwater impoundment of 22 kilometres is created from the formerly tidal river. Figure 3.8 is taken from upstream of the barrage.

Figure 3.8 The Tees Barrage

The water and sediments of the Tees estuary were polluted from decades of high discharges from chemical, industrial and domestic waste. The majority of the pollution entered the estuary downstream of the barrage, so the barrage was built to protect against the polluted water rather than the tides.

3.8.4 Monitored impacts of the barrage

- Water levels/flooding

  The water levels in the barrage are maintained at 2.65mAOD ± 0.05m by the lowering or raising of the barrage gates. This is achieved automatically by a computerised system using pressure transducers to determine water level on the barrage itself (John Dixon, Barrage Control, personal communication). Flooding is minimised in the barrage area and upstream by monitoring upstream river levels at Broken Scar (Darlington) and Low Moor. When the rate of increase of water flow at the stations reaches a critical level, the barrage is contacted and the gates are automatically lowered. The rate of lowering of the gates is controlled by the water level increments upstream. This system ensures that the flood wave is reduced and the water level in the barrage remains constant.

- Discharge rates

  Discharge rates are monitored and controlled in the barrage area. The daily discharge is distributed between the canoe slalom, fish pass, lock and barrage overtopping to ensure that each receives an adequate supply. To achieve this the barrage gates may be increased to prevent overtopping in order for the fish pass and slalom to operate (John Dixon, Barrage Control, personal communication)

- Water quality

  The water quality is monitored by the Environment Agency by regular field monitoring. This involves regulation of sewage and industrial discharges into the river.

- Siltation

  Surveys were conducted by Babtie consultants before construction and at regular intervals afterwards. Initial results indicate there has been no siltation but the surveys were not very detailed

- Flora and Fauna

  Again recorded by the Environment Agency, the improved water quality allowed approximately 7000 salmon and 13,000+ seatrout to enter the Tees during 2000. Seals and birds are also returning to Seal sands at the Tees outlet, as a result of reduced industrial inputs into the river (Walsh, 2001b)

- Groundwater levels – associated with slope stability

  Study undertaken before construction – to be compared with values after completion and at regular intervals.

- Suitability for recreational use

  Ensure cleanliness and that water quality reaches the required quality standards. New Sports Development just completed and opened – The River Tees Watersports Centre

- Aesthetics

  The presence of litter on banks or in the river. This mostly consists of sewage-derived waste, colour and smell of water, presence of oil, scum, foam and dog fouling. The Environment Agency monitor and control these aspects.

3.9 Data Collection

A large amount of data was needed from a number of sources. Digital data were obtained in 2 main formats. Firstly there were the river flow measurements for all stations on the Tees and its tributaries collected by the Environment Agency, along with rainfall data. Also needed were several spatial datasets for map-analysis that included topography, landuse, geology and soils.

As part of the associated SIMBA project a continuous sediment sampler and turbidity sensor was installed at the Environment Agency's Low Moor station on the River Tees. Water turbidity is an expression of the optical properties of water which cause light to be scattered and absorbed, rather than being transmitted in a straight line. It is therefore commonly regarded as the opposite of clarity (Lawler, 1995). Turbidity is a good predictor of suspended sediment concentration as it is mainly caused by the presence of suspended matter and can therefore by used to calculate suspended sediment concentration (Ives et al, 1968). Insitu turbidity is a point measurement and therefore does not represent a whole river section with total certainty (Wass & Leeks, 1999). Turbidity can also be measured at remote sites (Lewis 1996). When used along with frequent suspended sediment samples a calibration relationship can be established to estimate sediment load more efficiently. The Low Moor station was chosen as it was the furthest downstream and is part of the long term monitoring network of the SIMBA project. The sampler was installed at an Environment Agency station to enable the data collected to be used along with continuous flow measurements.

A large amount of fieldwork was undertaken to collect sediment samples throughout the catchment along with suspended sediments during flood events.

3.9.1 River Flow data

The Environment Agency kindly provided flow gauging data for all 13 stations on the River Tees and its tributaries - see Figure 3.9 for locations. The data comprised daily data for all years of monitoring and 15min data for events during the time of the project. The majority of stations have been monitored since the 1970s, giving over 20 years of continuous records. During the period of monitoring there have been numerous large flood events, the largest being on 3rd January 1982 where the average daily flow was $398m^3/s$ at Low Moor. There have been 3 major flood events during the timescale of this research - June 2000, November 2000 and March 2001.

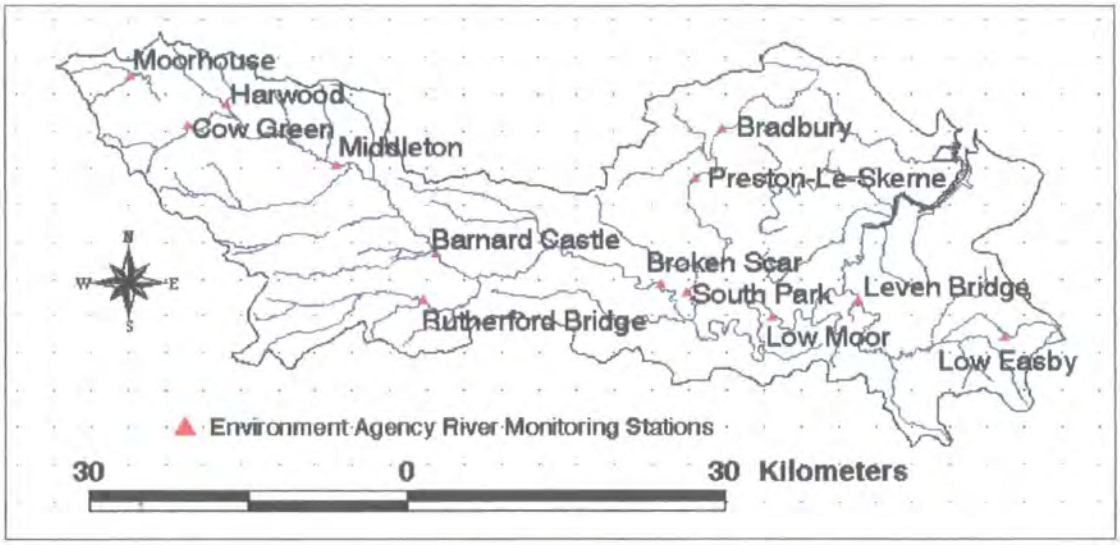


Figure 3.9 Environment Agency flow monitoring stations in the River Tees Catchment area

3.9.2 Rainfall data

Rainfall data within the Tees catchment was obtained for 14 sites, which are shown in Figure 3.10. The timescale of collection at each site varied from daily to monthly. A summary of site data is given in Table 3.7.

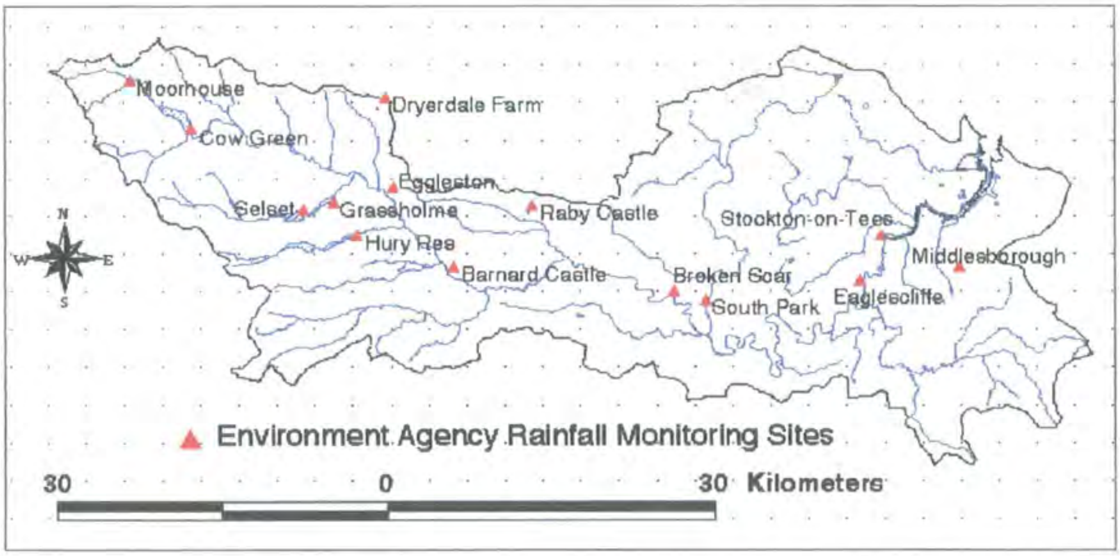


Figure 3.10 Rainfall monitoring sites in the River Tees Catchment

Table 3.7 Summary of rainfall site information

Station	Datum (mAOD)	Annual rainfall (mmyr)	Years of data	Frequency of readings
Moorhouse	533	1873.8	45	Weekly
Cow Green	494	1495.4	30	Daily
Selset	329	997.3	24	Monthly
Grassholme	285	1022.6	96	Irregular
Hury Res	261	927.6	70	Irregular
Eggleston	260	830.7	8	Daily
Barnard Castle	171	776.6	72	Daily
Broken Scar	48	628.7	71	Daily
South Park	30	653	76	Daily
Eaglescliffe	18	618.8	25	Daily
Stockton-on-Tees	13	495.6	17	Daily
Middlesbrough	37	610.2	11	Daily
Dryerdale Farm	197.0	801.1	22	Monthly
Raby Castle	140.0	699.5	29	Daily

3.9.3 Catchment data

Information for the catchment was obtained for landuse, geology, soils, topography, river and catchment outlines. The data was kindly provided by the following organisations:

- Landuse - Institute of Terrestrial Ecology, now Centre for Ecology and Hydrology (CEH) at Merlewood)
- Geology - British Geological Survey
- Soils - Cranfield University
- Topographic and river network – Institute of Hydraulics (now CEH, Wallingford)
- Catchment outlines - Environment Agency

3.9.4 Topography

The topographic data consisted of a series of files, which were imported into Arc View. The data was in 50m grid squares, each square containing the average value of height within the square. The river data originated from a series of co-ordinates from which a river line was generated using ArcINFO. The topographic grid data had to be cleaned i.e. blanks in the data had to be estimated from surrounding cells and sinks had to be infilled (grids with abnormally low values in between normal high values). Figure 3.11 shows the variation of topography throughout the Tees catchment.

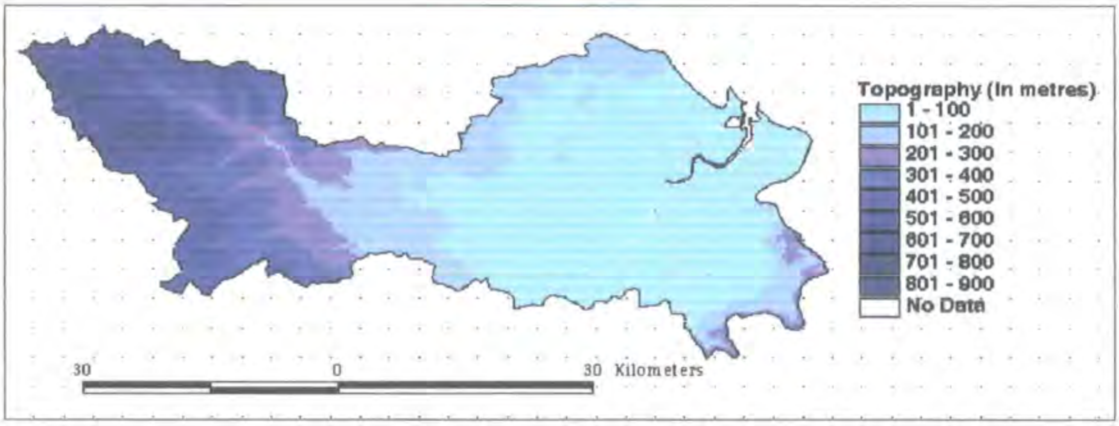


Figure 3.11 Topography of the River Tees Catchment

3.9.5 Monitoring station at Low Moor

A turbidity sensor and sediment sampler were installed at Low Moor, in collaboration with other workers as part of the SIMBA project (Anderton et al 2000). The operation of the sampler was controlled as a function of river discharge by means of a logger/control box and a pressure transducer. The turbidity and water level were measured every 15 minutes and the data relayed to a logger. A stage-discharge relationship identified by the EA was used to convert the water level into river flow in m^3/s. The logger was programmable, which allowed the manual pumping of suspended sediment to be timed according to flow conditions. A sample was taken after a defined flow had passed the station. After an initial period of regular collection the sampler was set to take samples at higher flows only.

3.10 Field Sediment Collection and Analysis

During the summers of 1999 and 2000 a catchment wide survey to collect a large amount of soil and water data for chemical analysis was conducted. There are five components to the fieldwork which include soil samples (fields, beds and bank material), suspended sediment, river water, overbank sediment (after flood events) and finally sediment cores. In 1999 riverbanks and beds were sampled with the aim of covering the majority of rivers, streams and becks to characterise the channel bank materials. In 2000 the survey concentrated on loose surface material in fields and overbank sediments. The idea was to cover a wide spatial area to include all major landuses, geologies and soil types. The breakdown of samples according to groups are shown in Table 3.8. All sampling and analysis was conducted by the author, unless otherwise stated.

Table 3.8 Breakdown of sample groups

Geology		**Landuse**		**Subcatchment**	
Argillaceous rocks	42	Natural land	22	Upper Tees	54
Dolomitised limestone	21	Semi natural land	30	Lower Tees	22
Limestone	21	Tilled land	48	Skerne	19
Igneous rocks	7	Urbanised areas	7	Leven	18
Sandstone	22	woodland	6		
Total	113		113		113

Total of 113 field samples, 14 bed samples and 9 bank samples (bed & bank not included in table)

All samples were later analysed by appropriate methods to determine their chemical breakdown. This was to allow identification of source, trends and anomalies within the catchment area.

These components form the basis for identifying which areas of the catchment provide the most sediment to the barrage. The solid samples will allow identification of distinct chemistries in particular catchment areas, whilst the water samples will allow the determination of different river systems and any contaminants they carry. A comparison of water chemistry and suspended sediment loads may allow the cross referencing of rivers with high flow and high sediment loads. It will also allow the effects of high flow on water chemistry to be determined. Trace metal concentrations in water can be a indicator of metal pollution upstream (Soares et al, 1999). The suspended sediment samples will be used to calculate the concentration of suspended sediment, whilst also allowing the analysis of the sediment particles. The aim is to identify different chemical signatures of suspended sediment in upper catchment areas and the degree of mixing in the lower catchment. Overbank sediments are used to determine which elements are deposited first by the floodwater, whilst sediment cores will show the chemical configuration of earlier deposits and any patterns in the sedimentation record.

3.10.1 Field sample collection and methods

Soil samples were collected from visibly eroding areas in fields, near tributaries and riverbeds/banks, the locations of which are shown in Figure 3.12 and listed in Appendix A. The sites were chosen to give a general coverage of the whole of the Tees catchment above the barrage impoundment. Deciding the actual location of each sample site was determined by many factors. The sites had to include a representative number of samples from each geological group, landuse, subcatchment and soil type. The actual location of each sample was determined by accessibility, which was identified using an OS map, the site had be in easy/suitable walking distance of a road or path When a suitable site was found, the exact landuse, geology and soil type was determined using a GIS map. If the site location could not be sampled during the sampling procedure, a nearby location was sampled and its location marked on the map. The landuse etc were then determined later.

Samples were taken from all major tributaries that were thought to contribute to the sediment load being transported to the barrage. No samples were taken from the Balder and Lune as these rivers are dammed and are operated to control the flood wave, hence it was assumed they would not contribute greatly to the sediment load during flood events. Wass and Leeks (1999) found that reservoirs acted as sediment traps in the Wharfe and Nidd catchments, which had half the suspended sediment concentration of geologically similar catchments without reservoirs.

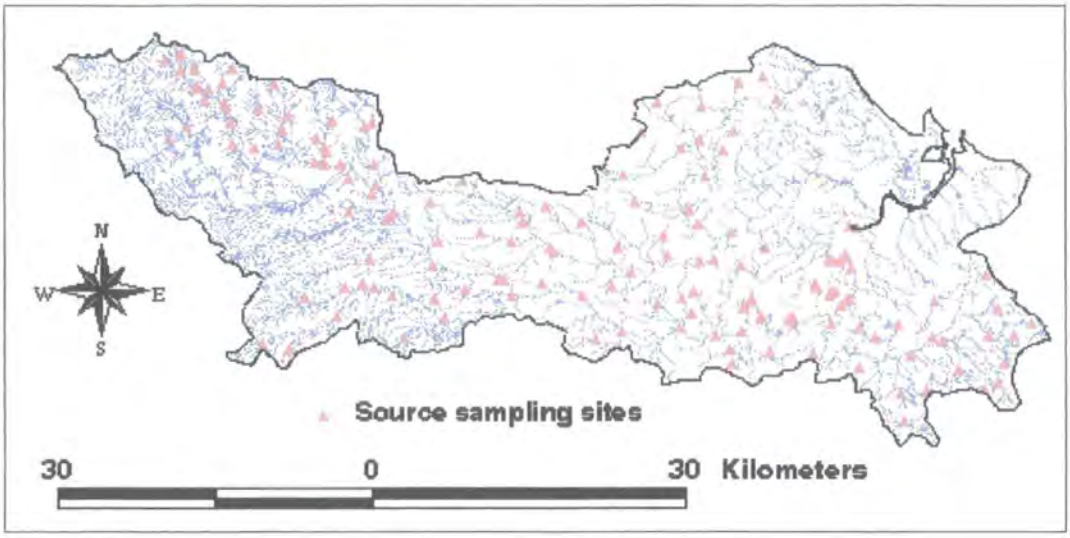


Figure 3.12 Sediment source sampling sites

The samples were collected from the top 0 - 5 cm of the soil surface using a stainless steel trowel. The samples were taken from an area that was composed of loose surface material – as this layer is likely to be transported by overland flow. The samples were placed into a clean plastic bag with site, date and code labels. The samples were labelled according to the subcatchment that they were taken from. An explanation of the codes and numbers taken are shown in Table 3.9.

Table 3.9 Field samples collected

Subcatchment	**Code**	**Samples taken**
Harwood	H	7
Middleton	M	13
Greta	G	8
Skerne	S	19
Low Moor	L	40
Leven	V	19
Low Moor to Barrage	LBG	7
Bed	D	14
Bank	B	9
Suspended	S	38
Overbank	O	15
Water	T	

The collected samples were transported to the laboratory in a cool box to the laboratory and frozen until needed. The samples were kept cooled or frozen to prevent/slow down breakdown of the sample by biological matter. Any breakdown in the material can result in a change in chemical configuration of the sample. After thawing overnight in the refrigerator the samples were wet sieved. Wet sieving has been proved to be more effective in sorting out the finer particles (BS 1377, 1990) and therefore the recovery of more material for analysis. Each sample was passed through a 2mm sieve, and then a 63μm sieve, that portion above 2mm being discarded. The samples retained on each sieve were collected and saved separately. The samples were then oven dried at 105°C overnight. The samples were then stored in an airtight bag until analysis. The drying of the sample and storage conditions should prevent/limit the amount of alteration of the soil sample.

The sediment samples collected were sieved and analysis was undertaken on the below 63μm section to provide a better comparison with suspended sediment. Heavy metals are mainly linked to silt and clay sections, which are present in the <63μm (Soares et al, 1999). Metal concentrations are known to increase with decreasing grain sizes, due to the increased surface area relative to charge. Wet sieving has been found to yield higher metal concentrations in the below 63μm fraction when compared with the corresponding dry sieved fraction (Soares et al, 1999).

3.10.2 Suspended sediment

Suspended sediment samples were collected to allow comparison between source materials in the subcatchment and mixing further downstream. Full details of samples taken, including date, location, flow etc are shown in Appendix A. The sites were chosen to identify suspended sediment signatures in different parts of the catchment. Six sites were decided on, based on the mainstream and tributaries of the River Tees as shown in Figure 3.13.

1. The River Tees at Middleton, to give signature of upper catchment
2. The River Tees at Blackwell Bridge, to give the Tees signature before the Skerne confluence

3. The River Skerne approximately 50m upstream of its confluence with the River Tees, carries high sediment loads and has significantly different landuse and geology to other areas of the catchment.
4. The River Tees at Low Dinsdale, to identify a mixture of the Tees and Skerne signatures.
5. The River Leven at Leven Bridge or Middleton Bridge, has a steep catchment with different geology to the rest of the catchment and also carries high sediment loads
6. The River Tees at Stockton, to identify the suspended sediment that reaches the impounded area - should contain signatures from the Tees, Skerne and Leven.

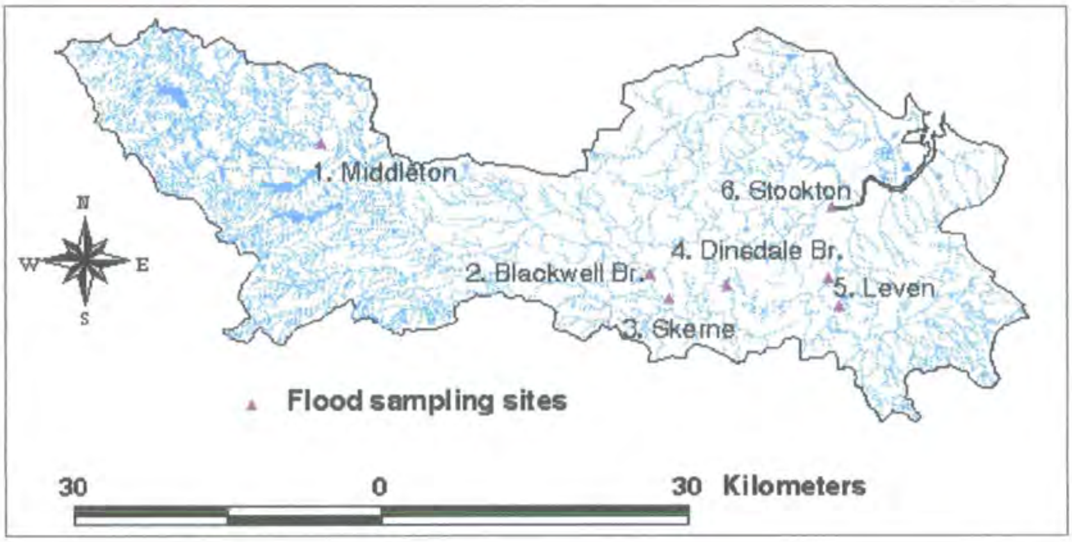


Figure 3.13 Flood sampling sites

The suspended sediment samples were collected from bridges during flood events and were taken from the middle of the river via a bucket on a rope. The suspended sediment loads are highest in floods (Anderton et al 2000) and are thought to be evenly distributed throughout the cross section of the river. Hence a sample taken from the water surface should be a representative sample, whereas a sample taken from a river bank may incorporate some near bottom bed load. The sample was collected in a 5 litre container and stored in a refrigerator until needed. The 5 litre sample bottle was weighed before the contents were tipped into a stainless steel tray and placed in an oven at 100°C to evaporate the water. The empty bottle was then re-weighed to determine volume of water collected. The sediment was removed from the stainless steel tray using a clean soft wire brush, before being placed in a pre-weighed labelled bag. The sediment weight and therefore concentration were calculated.

3.10.3 Water samples

Water samples were collected along with the suspended sediment samples so that the water signature itself could be identified. This allowed a mixing model to be constructed for water to determine whether the tributaries producing the most sediment also contributed the highest flows. Analysis of water samples also allows the differentiation between suspended and dissolved signals. Water samples are collected at the same sites as the suspended sediment. Details of water samples are given in Appendix A.

The water samples were taken from the same bucket as the suspended sediment and the water was swirled around to ensure that the sediment concentration was equal in both samples. The water samples were stored in 750ml bottles. The sample was then stored in a refrigerator until ready for filtering. The samples were filtered through a Whatman 1.2μm sieve, a portion of the water was then retained and 0.1ml of 95% hydrochloric acid was added to prevent any breakdowns/ reactions with the sterilised container. These samples were then stored in a refrigerator until required for analysis.

3.10.4 Overbank sediments

The suspended sediment samples collected were generally quite small i.e. 0.5 - 6 grams, which limited the amount of analysis that could be done. After large flooding events overbank samples were collected to allow large samples of previously suspended sediment to be collected and analysed. Locations are shown in Figure 3.14. The first set of samples was taken at intervals between Low Moor and the barrage after a large flood event in November 1999. The accessibility determined the exact location of these samples, as they were taken from a boat. The collection of overbank samples allows identification of differences in the overbank load along the length of the river. These overbank deposits then become sediment sources for the next flood. A second set of overbank samples were taken in the upper and middle catchment after the high flow event in February 7th 2001. This was in order to identify the overbank sediments in different areas of the catchment, to determine if they reflected the local/upstream field chemistry or bed/bank material.

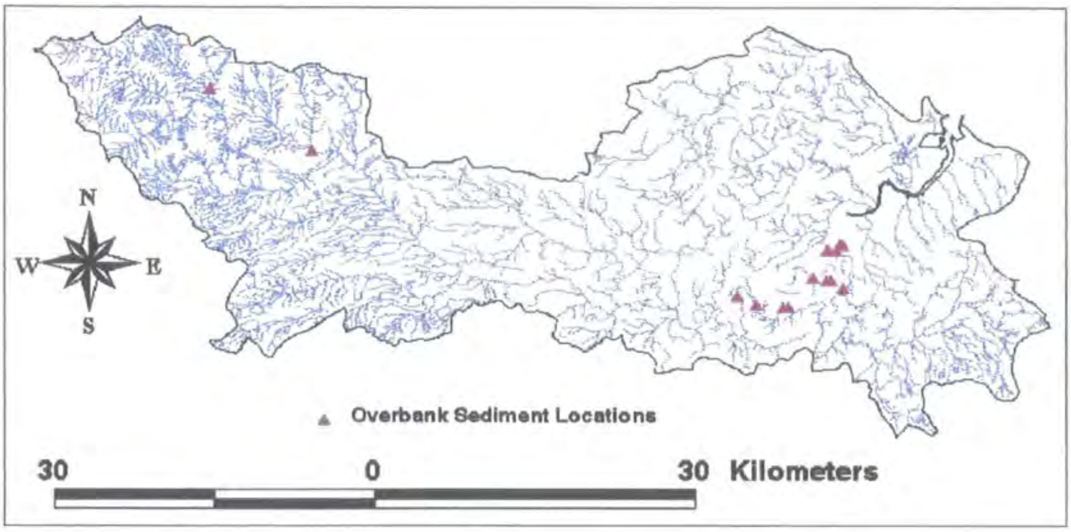


Figure 3.14 Flood overbank sampling sites

The overbank samples were collected using a clean stainless steel trowel. The first eight samples were collected by University technicians from a boat and were obtained from 0.5 - 1.0m above the water level. The second set of samples were collected from riverbanks and beds after the flood. They were stored and processed in the same manner as the field sediments.

3.10.5 Impoundment samples

Sediment was collected from the impounded area immediately upstream of the barrage. These samples were analysed by the same procedure as the field samples. Analysis of bed material in the impoundment gives some insight into previously transported/deposited material and an idea of the potential risk from contaminant bearing sediments.

The samples collected from the barrage area were collected with a grab sampler from a boat in the middle of the river. They were stored and treated in the same manner as field and overbank samples.

Chapter 4 Analytical Techniques

Sediment and water samples were analysed by the procedures outlined in this chapter to provide the data to fingerprint different regions of the catchment chemically. The analysis and techniques used need to be consistent and accurate in providing data, so that the differences between the samples can identified.

4.1 Procedure

The samples were prepared based on a sequential extraction method developed by Tessier et al (1979). Variations of this extraction technique have been used in a wide range of hydrological and sedimentological studies (Harrison, 1987; Foster et al, 1991; Horowitz et al, 1993; Foster & Charlesworth, 1996; Yu et al, 2001; Xiangdong & Thornton, 2001). Sequential extraction is a lengthy procedure and done properly gives very good results. Using only total extraction implies that all forms of a given metal behave in the same way. Sequential extraction gives information about the origin, mode of occurrence, mobilisation and transport of trace metals. When building a fingerprint for an area the different environmental controls on the determinants allow a degree of independence and a higher degree of discrimination. A composite fingerprint is determined instead of a single determinant, which increases signature reliability and allows controls on the metals to be identified.

4.2 The extraction procedure

The samples underwent a four-step extraction procedure. Each of the four steps targeted a particular bonding site. The first step contained the weakest leaching solution, the solutions increased in extraction power with the fourth step being the strongest solution. Each sample was leached for approximately 20-24 hours. By extracting elements in this order allowed the weakest bonds in the samples to be broken first, which are those in the exchangeable state. This was done by using a weak acid, sodium acetate, to leach the ions bound by these weak bonds. These ions are readily available and are likely to be low in concentration (Tessier et al, 1980).

The second step in the procedure uses a stronger acid, the sodium acetate used in step 1 is adjusted to a pH of 5 using acetic acid. This acidic solution is used to attack the bonds that bind the ions with the carbonate material. This step can be expected to yield higher concentration of ions than step 1 (Tessier et al, 1980). The third step in the procedure uses sodium dithionite to extract the ions bound to Fe-Mn oxyhydroxides. These oxides [MO_x OH_y] of a metal M, are thought to be the result of adsorption and co-precipitation and are generally high in concentration (Tessier et al, 1980).

The final step in the procedure uses a strong solution of nitric acid and hydrogen peroxide. The metals in this step are present in a complexed form (Tessier et al, 1980). The relative concentration of each metal in this step is dependant upon the free metal ion concentration and equilibrium constant for the metal-organic complexation.

Limitations in this technique centre on the possibility that selective dissolution and complete recovery of trace metals may not be achieved. The interpretation of results is based on solubility and possible chemical associations rather than specific mineralogy (Xiangdong & Thorton, 2001). A fifth step involving a fresh sample was exposed to the leaching agents used in the fourth step. This step is also known as total extraction and gives an overall indication of the ions present. The extraction steps, environmental control and extraction solutions are summarised in Table 4.1.

Table 4.1 Sequential Extraction Stages

Step	Environmental control	Procedure
1	Bound to exchangeable ions	20ml of Sodium acetate
2	Bound to carbonates	20ml of Sodium acetate adjusted to pH5 with acetic acid
3	Bound to iron and manganese oxides	20ml of sodium dithionite
4	Bound to organic matter	10ml of 0.02M nitric acid 10ml of 30% hydrogen peroxide
5	Total extraction	10ml of 0.02M nitric acid 10ml of 30% hydrogen peroxide

4.2.1 Stage 1 Exchangeable Ions

Exchangeable ions are those that are bonded temporarily to clay particles by weak, electrostatic forces (Andrews et al, 1996). These ions include the positive transition metal ions along with group I and II elements in the Periodic Table.

4.2.2 Stage 2 Bound to carbonates

These are cations that bind with CO_3^{2-} and are typically these elements: Ca, Mg, Fe, Cu, Mn and Zn. Many of these elements have similar structures and charge, which allow interchangeability of cations, also known as isomorphous substitution. This stage is most likely to be influential in limestone dominated areas.

4.2.3 Stage 3 Bound to Iron and Manganese oxyhydroxides

Iron-manganese oxyhydroxides have been found to be the dominant contaminant metal bearing phases in the lower Tees catchment (Hudson-Edwards et al, 1997). Oxyhydroxides are said to be the last stage in the chemical weathering sequence - sulphides - carbonates - oxyhydroxides (Garrels & Christ, 1965). Cobalt, Ni, Cu and Sn are often scavenged by Fe/Mn oxides in sediments (Plant & Raisewell, 1983).

4.2.4 Stage 4 Bound to organic matter

Metals along with elements associated with fertilisers are likely to be bound to organic matter. Non metals associated with fertilisers may be found in high concentrations, eg K and P. Small amounts of metals are sometimes found in fertilisers while Cr, V and Zn can be found in concentrations higher than those normally found in soils (Mattigod & Page, 1983).

4.2.4 Stage 5 Total Extraction

This stage intends to determine the elemental content of the sample without limiting the partitioning to certain sites. Total metal content gives limited information on mobility and bioavailability of heavy metals

Owing to the number of samples analysed and time constraints less than 50% of samples were selected for the full sequential extraction procedure, the remainder being subject to total extraction only, see Table 4.2 for full details. In deciding which field samples were to undergo full extraction a representative number from each area of the catchment was included. The majority of bed, bank and overbank samples were sequentially extracted. All suspended sediment samples that contained enough sediment to be sequentially extracted were analysed this way.

Table 4.2 Samples analysed

	Sequential extraction	**Total extraction only**
Suspended sediment	13	25
Bank sediments	8	1
Bed sediments	12	2
Overbank sediments	14	1
Field sediments	48	65

The full datasheet of all ICP results is provided in Excel format on the disc included.

4.3 Preparation of samples

4.3.1 Sequential extraction

For each sample, 2.5g of <63μm (to allow better correlation with suspended sediment) was analysed, with some samples duplicated for test reliability. The samples were leached in a 100ml clean conical flask at room temperature for 24-48 hours. The samples were then washed through a Whatman grade 1 filter paper (11μm). The samples were made up to 50ml with Milli-Q® 18MΩ.cm water; part of this sample was retained in a 30ml sterilin bottle. After preparation the samples were refrigerated until required for Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) analysis. All glassware was washed twice between samples with tap water, then Milli-Q® 18MΩ.cm water. After filtering the filter paper was dried in an oven at 100°C. After drying the sample was removed, with the paper being weighed before and after to determine the amount of sediment available for the next step. A blank control of the leaching solution was produced at each step, composed of 20ml of the solution, which was subjected to the same environmental conditions as the samples and made up to 50ml after filtering.

4.3.2 Total extraction

For total extraction 1g of sediment was used along with the 20ml of leaching solution. The samples were left to extract for 24-48 hours before filtering as before. The filter paper was discarded after use with no weighing required. A control blank was also made up for each total extraction.

4.3.3 Observations during preparation

During preparation, some samples were seen to alter or react with the leaching agent, particularly stages 3, 4 and 5. In stage 3 several samples turned grey ie lost their colour, the most likely reason for this being the removal of iron from the sample. The samples that lost their colour are shown in Table 4.3. After analysis of the samples, a link between iron concentration and these samples was sought. The samples that turned grey did not always contain large amounts of iron. In stage 4 and 5 some samples were seen to react with the hydrogen peroxide, producing bubbles and gas. This was interpreted as the hydrogen peroxide reacting with the organic fraction of the sample. Again when compared with loss on ignition results (explained later in this chapter) no correlation between those reacting and those with high organic carbon contents was found. Many of the samples that reacted in stages 4 & 5 were suspended sediment samples where no organic data was available or bed/bank samples which contained low organic values.

Table 4.3 Samples that reacted in stages 3, 4 and 5

Stage	Samples that reacted
3	G4, LBG4, LBG6, L3, L8, S14, V13, M9, M2, M13, H1, G1, V10, V17, L10, W9
4	S7, S9, H5, G10, L3, L6, L24, L40, OV4, OV6, OV9, W9, W15, W16, W17, W18, D8, D3, D13, D11, D7, B8, D17
5	L24, L40, V7, V6, G2, G5, V5, M10, S2, S8, S11, S17, L10, L11, L14, L23, L30, L33, LBG1,LBG2, LBG7, W2, W4, W13, OV3, D1, W19, W17, W16, W20, W15, W12, W18, W3, D14, D8, D15, D16, D11, D6, D17, W26, W35, W36, W37, W38, OV13, OV10, OV15, B1, B2

4.3.4 Missing Samples

Seven samples were lost during the sequential extraction procedure; this was due to leakage of the sample from the sterilised bottle in which they were contained. All the samples were lost at stage 4, which indicates that it was possibly as a result of hydrogen peroxide in the sample. The hydrogen peroxide was used to react with the organic matter. Where this reaction has not gone to completion or there is little organic matter in the samples, some hydrogen peroxide may be unused. As a result the hydrogen peroxide may continue to oxidise whilst in the sealed bottle, causing it to fail due to the production of gas. The samples lost were G4, G10, L7, LBG6, V14, V18 and W19.

4.4 Analytical method

The samples were analysed by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) also known as ICP-AES (atomic emission spectrometry). A Perkin Elmer Optima 3000 Family Optima 3300RL ICP Emission Spectrometer was used for the ICP analysis. ICP-OES works on the principal that when atoms and ions are excited, light is emitted. The wavelength and intensity of the light reflects the elements present in the sample. The intensity of the light is recorded as counts per second for all wavelengths and then converted to parts per million by the machine. The elements are analysed simultaneously with a high-resolution spectrometer with a wavelength of 170 - 780nm. The samples are prepared in solution and introduced into the plasma by nebulization. The calibration of lines (wavelengths) is linear with a wide response range and 4 to 5 orders of magnitude can be analysed at the same time. This reduces the analysis time, as there is no need to dilute solutions and the major, minor and trace metals can be analysed in one run. The basic arrangement of the machine is shown in Figure 4.1 (taken from Fairchild et al, 1988).

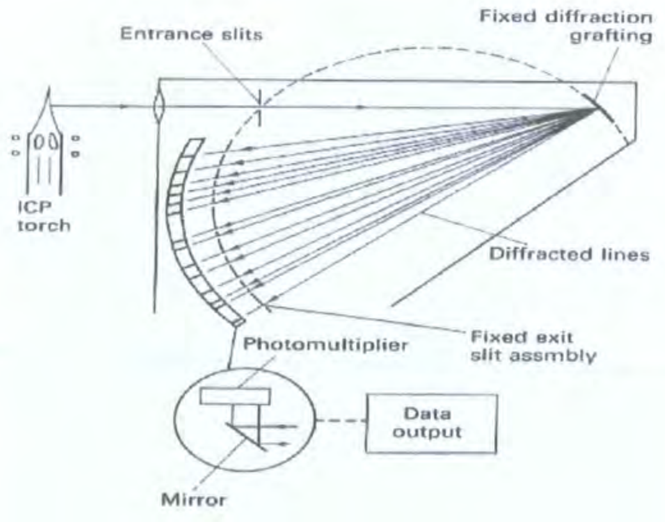


Figure 4.1 Basic layout of ICP-OES machine

Sample solutions are prepared with an internal standard to compensate for instrument sensitivity and electronic drift. An identical concentration of an element that is not normally present in the samples is added to all solutions. The ratio of each measurement to the intensity of the internal standard will permit determination of any error. In this case the spike is yttrium and 0.1ml at 1.0ppm is added to every 10ml sample to be analysed. The yttrium measurement in the results should always equal 1.0. When the yttrium value is above or below this set level, the lines for that sample are multiplied by a factor to return the yttrium level to 1.0.

4.4.1 Calibration

The ICP-OES machine needs to be calibrated before each use. The calibration and reprocessing of signals was performed using the Perkin Elmer Winlab™ Software (Perkin Elmer 1997). This is done by analysing prepared solutions of suitable mixtures for all elements to be analysed. The elements or compound used in calibration must be stoichiometric i.e. fixed and will not vary according to sample preparation and heating history. The element or compound must be of high purity, inert and stable in air, as well as being readily dissolvable in water or dilute acids. These solutions should be resistant to precipitation or decomposition during storage prior to use. Each element is prepared in 2 - 3 concentrations to allow a linear-through-zero graph to be plotted. This graph will plot the relationship between the number of counts per second (CPS) and concentration in parts per million (PPM). The graphs are set to go through zero, so that when very small concentrations (a small number of CPS) of an element are found a negative value is not recorded.

The machine was calibrated using six prepared solutions and a blank. The major metals were calibrated using 'seawater stocks' each of which contained Ca, Fe, K, Mg, Na and S, these stocks were made up to three different concentrations. The minor metals and non-metals were calibrated using separate solutions. The elements and concentrations used in each calibration solution are summarised and shown in Table 4.4. The strength and range of solutions were determined on a pre-run and earlier work done by Wright (personal communication – University of Durham) in 2000 - 2001. Approximately 100 samples were analysed in a run and the machine was calibrated for each run. The correlation coefficients obtained during calibration were always very good with values ranging from 0.9900 to 1.0000 for the wavelengths that were selected (coefficients from one run are shown in Appendix B).

Table 4.4 Sediment Calibration Solutions for ICP-OES

Blank - Milli-Q$^{®}$ 18MΩ.cm		
Minor metals		**Minor non-metals**
	(Al, Co, Cr, Cu, Mn, Ni, Sc, Ti, Sn, V, Zn)	(P, Si)
Low	0.5	5
Mid	1	10
High	2	20

'seawater' stock	Ca	Fe	K	Mg	Na	S
Low	125	125	125	250	2500	2500
Mid	250	250	250	500	5000	5000
High	500	500	500	1000	10000	10000

Note - All concentrations are in parts per million (ppm)

4.4.2 Lines chosen for use in later work

The analysis by ICP-OES resulted in 50 lines (wavelengths, measured in nm) of data. The sodium and sulphur lines were deleted due to their use in the leaching solutions. Yttrium is also deleted as it is used to standardise the solutions. The selection of lines to be used for each element was decided from the correlation coefficients and earlier work done by Geological Sciences Department, Durham University. Some lines always gave bad correlation coefficients and were therefore never used. Where two lines for the same element gave similar coefficients and results, an average was taken for that element.

For example, to determine which lines was used for calcium (Ca), three lines of data were produced - 315, 317 and 422 (see Table 4.5). When the concentration measurement was studied for a particular sample, lines 315 and 317 gave almost identical readings, whilst line 422 would consistently give a lower Ca concentration reading. Therefore, line 422 was not used and an average of lines 315 and 317 were used in the interpretation of the results. The same procedure was used to determine all lines used in Table 4.5. The lines chosen to represent each element were the optimal i.e. the most sensitive for the range of concentrations measured in the data.

The wavelengths shown have been shortened for easier reading and the full wavelengths are reported in Appendix B.

Table 4.5 Selection of wavelengths

Elemental Line	Similarities	Other observations	Lines chosen
Ca 315, 317 & 422	315 + 317 similar 422 lower results	315 + 317 identified by Geology Dept.	Average of 315 + 317
Co 230, 231	Similar		Average
Cr 205, 283	Similar		Average
Cu 221, 324	Similar		Average
Fe 234, 259	Similar		Average
K 404, 766	404 poor correlation coefficient	404 poor stdev in blanks	Line 766
Mg 279, 285, 280	279 + 285 similar 280 = 0.0		Average of 279 + 285
Mn 293, 257	Similar		Average
Na 330.23, 330.29, 589, 588	330.23 + 330.29 similar, 589 higher, 588 = 0.0	Used as a leaching solution, therefore all lines ignored.	Delete all lines
Ni 341, 227	Similar		Average
P 214, 213	Similar		Average
S 189, 180, 181	180 similar to 181, 189 = 0.0	Used in leaching solutions	All lines deleted
Sc 424, 357, 361	424 + 357 similar 361 lower		Average of 424 + 357
Sn 189, 235, 283	189 = 0.0	Line 235 interferes with Fe 234 #	Line 283
Ti 368, 336	Similar		Average
V 270, 310	Similar		Average
Zn 334.50, 334.55, 213	213> 334.50> 334.55	334.55 identified by Geology Dept.	Line 334.55

'seawater' control recorded Sn235 values, Sn235 was not present in this solution - therefore assumed to be interfering with Fe234.

4.5 Preparation of ICP-OES results.

The solution blank produced for each stage of each set was analysed along with the actual samples. The blanks were then subtracted from each sample to remove the effect of reagents used for leaching.

The samples were then corrected for the weight of sample used in each step of the extraction procedure. The results were obtained in parts per million or mgl^{-1}and were converted into mgkg^{-1}, the standard units for this type of work.

The 50ml solutions for stage one were prepared using 2.5g of sediment. Therefore to change to mgkg^{-1} the data was divided by 20 to give mg in 2.5g of sediment and then multiplied by 400. The overall affect of this conversion was to multiply the result by 20. In stage 5 where only 1g of sediment was used, the results were multiplied by 50. During stages one to four the sample weight would reduce, this was overcome by using the new weight and multiplying the data accordingly. The sample would lose approximately 0.1g per extraction, so the starting weight for stage 2 was 2.4g, for stage 3 it was 2.3g etc.

The suspended sediment samples had to be treated separately as the starting weight varied. Sequential extraction was carried out only on samples greater than 2.0g. When only 2.0g were available 1.5g of the sample was used for sequential extraction with the remainder used for total extraction. If less than 2.0g were available total extraction was performed on 2 samples.

4.6 Sources of Error

4.6.1 Steps taken during preparation to reduce contamination risk:

- Samples weighed on individual papers to reduce cross-contamination
- Conical flasks thoroughly washed with tap water then Milli-Q® 18MΩ.cm water before use
- Same conical flask used for each sample through all stages of extraction
- Between stages the sample was weighed on the filter paper to reduce contamination
- Cling film was placed over the conical flasks during stages to keep out dust etc
- Samples measured into same 50ml flask to ensure same volume of liquid
- Analytical grade chemicals used to produce solutions.

4.6.2 Possible areas for introduction of error:

- Pipette may not expel exactly the same volume of reagent each time.
- Slight variations in the materials used to make the reagents. Where possible the same batch was used to make the reagents each time.
- Used several bottles of hydrogen peroxide, but all conformed to the same purity standard.

4.6.3 To determine errors during analysis

During sample runs, three set solutions and a blank were analysed every 20 samples to identify any drift in the ICP-OES analytical technique. Three of the calibration standards were used - seawater, 10ppm major non-metals and 1ppm minor metals. A larger volume (50ml - 80ml) of these solutions was placed in the machine to enable each sample to be analysed a number of times. Ideally when processed the results from these solutions should be the same throughout the analysis period.

The standard deviation of each wavelength measured in the test sample was below 5% for 95% of the tested samples. Table 4.6 below shows the number of lines (out of 50) for each test sample during each run with a standard deviation of more than 5%.

Table 4.6 Test Solution Samples

Date	Seawater mid	10ppm major non-metals	1ppm minor metals	Calibration blank
14/12/00	4	0	0	1
12/01/01	6	1	1	1
19/01/01	6	2	2	6
25/01/01	5	2	2	2
06/03/01	7	2	2	2
07/03/01	4	3	3	3
24/04/01	6	0	0	1
25/04/01	7	0	0	0
26/04/01	6	2	2	2

During every run the four sodium lines, two sulphur lines and potassium 404 (except for 2 cases where the K766 line was just over 5%) were responsible for the large deviations between replicate samples. This can be explained by the saturation of sodium and sulphur in the system from the leaching solutions being carried over to the blanks. In earlier runs samples from stages 4 and 5 were seen to contain high values of sulphur and/or sodium that had been left in the system from the samples from stages 1 - 3 that were analysed earlier. In later analytical runs care was taken to make sure that samples from stages 4 and 5 were placed at the start of the run followed by stage 1, 2 and 3. Potassium 404 was difficult to analyse in all samples and was consequently deleted from all the data.

4.7 Variation within Samples

To take into account the differences which occur within a sample (and partly to determine the reliability of the ICP-OES machine) 60% of the sequentially extracted samples and 40% of the total extraction samples were duplicated. Where a sample was duplicated the average concentration of the two samples was used in the data analysis. The variation within a sample was minimal except for some total extraction samples, where possibly complete extraction had not taken place. Some variation is normal due to the natural variability in samples from the same site.

4.8 Analysis of Water Samples

Water samples were collected at the same time as suspended sediment samples to allow fingerprinting of water. The water samples were acidified with 95% HCL after filtering to preserve the sample. The samples were analysed by the same method as the soil samples. 20ml of the water sample was used, along with 0.1ml of yttrium. The solutions used to calibrate the ICP machine were different from those used for sediment. This is due to the different concentrations of elements that are likely to be found. The solutions were prepared by Wright based on his previous work (2000 – 2001) and are shown in Table 4.7.

Table 4.7 Water Calibration Solutions

Standard:	Analyte:	Concentration:
Minors	Al, Co, Cu, Cr, Mn, Ni, P, S, Sc, Si, Sn, Ti, V and Zn	0.5, 1.0 and 2.0mg/l
Majors	Ca, Fe, K, Mg and Na	5, 10 and 25mg/l

The solutions used to check the accuracy of the machine during analysis were as follows:

Seawater
Major metals - 1ppm
Minor metals - 0.1ppm
Fe - 5ppm
Blank – Milli-Q® 18MΩ.cm water spiked with yttrium

From analysis of these standards the machine showed little variation in the values obtained. Lines K404 and S189 showed small variations between samples, as was seen in the earlier analysis. The seawater standard variations were inaccurate owing to the sample solution running out. Previous data were accurate.

4.9 Sediment Size Analysis

Determination of the particle size of suspended sediment samples was carried out by using a Coulter Granulometer, following the standard procedure of the Department of Geography, Durham University. To prepare the sample approximately 0.5g of sample was placed in a 50ml tube along with 20ml of 20% hydrogen peroxide. The tubes were covered with aluminium foil and placed in a boiling water bath for 2 hours. This stage was to remove the organic material that may be present in the sample. When all the organic material had been dissolved the samples were centrifuged at 4000rpm for 4 minutes and half the supernatant fluid was decanted. This procedure was conducted three times. After the organic material had been removed, 20ml of distilled water was added to the sediment along with 2ml of sodium hexametaphosphate solution. This solution prevents the particles from coagulating so that they remain in suspension. The sample was then analysed by the Coulter Granulometer.

The Coulter Granulometer works by shining a laser through the sample and measuring the angles of diffraction to determine the size of the particles. The output data is easily input to an Excel spreadsheet.

4.10 Loss on Ignition

Loss on ignition (LOI) was conducted to determine the organic carbon content of the samples. The carbon content was determined by heating the samples at 350°C for 2 hours (Leong and Tanner, 1999). At above 400°C there is a considerable loss of hydroxyl ions and bound water, whilst the loss of carbon from carbonates is said to be negligible below 450°C (Davies, 1974). The LOI should relate to the geology and to some extent the landuse of the samples. The loss on ignition may also be conducted at 900°C for 1 hour to determine the inorganic carbon and water.

LOI (%) = 100 (X-Y)/X
Where X = weight (g) before heating
Y = weight (g) after heating

Chapter 5 Analysis of data and mixing model

5.1 Introduction

The basic principle underlying sediment fingerprinting is that different potential sediment sources can be characterised, using a number of diagnostic properties; and comparison of those fingerprints with equivalent information for suspended sediment samples will allow the relative importance of different potential sediment sources to be identified (Walling et al 1999). The diagnostic properties need to be statistically verified to identify the optimum sets of source material, and the sediment properties for use as composite 'fingerprints'.

The aim of this chapter is to use a two step statistical procedure to identify which elements can discriminate correctly between the different source groups selected and hence be used to build a 'composite fingerprint'. The two step statistical procedure will firstly be applied to the field samples as sediment fingerprinting is based on the assumption that sediments derived from areas with contrasting geological/landuse types should exhibit distinctive fingerprints (Collins et al 1998).

The two step procedure will then be applied to water samples to determine if tributaries display distinctive fingerprints as a result of passing over/through soils from different subcatchments. If a composite fingerprint can be identified for significant tributaries or points in the river network, then a 'mixing model' can be designed for river water.

The initial stage of the two-step procedure incorporates all the elemental data into Kruskall-Wallis analysis. The Kruskall-Wallis H-test is used to establish which properties exhibit significant differences between individual source groups within a particular category of sources. Kruskall-Wallis is a non-parametric method of Anova (Analysis of Variance – the variation of data points around the mean value) and can be used to perform analysis on the rank of the data rather than the actual values. This means that extreme high and low values do not distort the end result as is found in Anova, where an outlier can greatly affect the mean value (Mardia et al 1979).

The second step in the two-step statistical procedure involves further testing of the parameters that were judged to be successful in step 1, i.e. those elements selected by Kruskall-Wallis. Multi-discriminant function analysis is used in order to identify the set of properties that afforded optimum discrimination between source groups.

The first step 'filters out' unnecessary data, to reduce the amount of data (and time) used in the stepwise procedure used. The minimisation of Wilks lambda was used as a stepwise selection algorithm to identify the set of parameters, which in combination, were capable of distinguishing correctly 100% of the source materials (Collins et al 1997c). A lambda of 1 indicates that all the group means are equal. Values close to zero occur when variability within a group is small compared to total variability i.e. when most of the total variability is attributable to differences between the group means. Composite signatures capable of discrimination between source groups have lower lambda values.

The elements identified from the two step procedure will form the basis of the composite fingerprint and will be used in a 'mixing model'. The mixing model will allow the determination of the relative proportions of the sediment sources by 'un-mixing' the suspended sediment samples.

5.2 Two-step Statistical Test on Field Samples

5.2.1 First step - Kruskall-Wallis on field samples

Kruskall-Wallis analysis was initially applied to field samples. It was performed for each stage of extraction for the three source groups - geology, landuse and subcatchment. The highlighted results in Table 5.1 indicate the elements in each stage that were proved by Kruskall-Wallis to be able to discriminate between the categories in each source group. Greater inter-group differences provide larger H-values, which is a significance level and is a measure of variance around the mean (Shaw & Wheeler, 1985). When the H-value of a property exceeds the critical H-value, that property is successful in distinguishing between source groups. The critical H-value is significant at 95% where the critical *p* values (probability values) are 0.05. When the probability value is below 0.05 it indicates there is a 95% probability that the differences between the mean values of these fingerprints are not the result of random variables (Collins et al 1997c).

Landuse has the greatest number of highlighted results in Table 5.1, indicating that it is the best discriminator of source group. Extraction stage 2 performed best with only 1 element not selected (this element was not present in this extraction stage). The critical H value for landuse and geology was 11.07 and 7.82 for subcatchments. This H-critical value is calculated from the Minitab© Software Programme that analysed the data. Subcatchment and geology were unable to classify the data as successfully as landuse.

These results show that landuse is the best discriminator of sediment sources, as will seen later in Principle Component Analysis in Chapter 7. Geology had the poorest results, in extraction stages 1 and 4, as no elements were able to distinguish between groups. According to Kruskall-Wallis the effect of the geology appears to be fairly similar throughout the catchment; this may be due to the extensive glacial drift that covers the majority of the Tees Valley.

Table 5.1 Field data Kruskall-Wallis Results

Landuse	***Al***	***Ca***	***Co***	***Cr***	***Cu***	***Fe***	***K***	***Mg***	***Mn***	***Ni***	***P***	***Sc***	***Si***	***Sn***	***Ti***	***V***	***Zn***
Stage1	**13.69**	**13.26**	**13.88**	10.83	10.84	8.81	**15.64**	**15.57**	9.10	7.78	**29.90**	**22.00**	9.87	**22.00**	**13.90**	0.00	**12.13**
	0.02	*0.02*	*0.02*	*0.06*	*0.06*	*0.12*	*0.01*	*0.01*	*0.11*	*0.17*	*0.00*	*0.00*	*0.08*	*0.00*	*0.02*	*1.00*	*0.03*
Stage2	**26.94**	**18.04**	**12.09**	**15.07**	**18.66**	**30.35**	**17.04**	**25.01**	**17.90**	**20.22**	**34.91**	**16.24**	**13.35**	**22.05**	**20.61**	0.00	**13.39**
	0.00	*0.00*	*0.03*	*0.01*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	*0.01*	*0.02*	*0.00*	*0.00*	*1.00*	*0.02*
Stage3	**11.44**	6.67	**17.41**	8.77	10.54	10.61	**13.56**	**12.24**	**12.67**	6.42	**12.02**	2.27	3.84	9.39	**16.47**	**29.07**	10.09
	0.04	*0.25*	*0.00*	*0.12*	*0.06*	*0.06*	*0.02*	*0.03*	*0.03*	*0.27*	*0.04*	*0.81*	*0.57*	*0.09*	*0.01*	*0.00*	*0.07*
Stage4	**13.42**	7.42	6.74	5.55	4.97	7.35	5.59	6.93	6.02	2.16	**24.94**	9.10	**18.24**	5.16	**23.72**	**23.69**	3.32
	0.02	*0.19*	*0.24*	*0.35*	*0.42*	*0.20*	*0.35*	*0.23*	*0.31*	*0.83*	*0.00*	*0.11*	*0.00*	*0.40*	*0.00*	*0.00*	*0.65*
Stage5	**52.44**	**12.34**	10.62	**20.07**	2.82	**47.20**	**23.91**	**26.75**	8.72	**13.84**	**20.18**	**24.07**	**38.79**	3.24	**49.77**	**50.70**	10.59
	0.00	*0.03*	*0.06*	*0.00*	*0.73*	*0.00*	*0.00*	*0.00*	*0.12*	*0.02*	*0.00*	*0.00*	*0.00*	*0.66*	*0.00*	*0.00*	*0.06*
Geology	***Al***	***Ca***	***Co***	***Cr***	***Cu***	***Fe***	***K***	***Mg***	***Mn***	***Ni***	***P***	***Sc***	***Si***	***Sn***	***Ti***	***V***	***Zn***
Stage1	5.88	2.63	6.24	1.12	1.13	6.92	9.11	9.78	6.35	9.40	7.57	3.90	10.16	3.90	8.46	0.00	3.90
	0.32	*0.76*	*0.28*	*0.95*	*0.95*	*0.23*	*0.11*	*0.08*	*0.27*	*0.09*	*0.18*	*0.56*	*0.07*	*0.56*	*0.13*	*1.00*	*0.56*
Stage2	7.68	6.14	**13.30**	3.28	2.21	10.70	10.37	**13.53**	4.61	**12.54**	8.79	6.00	**16.15**	3.46	**12.25**	0.00	2.93
	0.18	*0.29*	*0.02*	*0.66*	*0.82*	*0.06*	*0.07*	*0.02*	*0.47*	*0.03*	*0.12*	*0.31*	*0.01*	*0.63*	*0.03*	*1.00*	*0.71*
Stage3	5.84	9.11	8.02	10.41	6.27	**11.59**	**13.31**	10.00	4.36	5.66	6.23	4.67	**11.42**	10.22	6.18	10.30	5.31
	0.32	*0.11*	*0.16*	*0.06*	*0.28*	*0.04*	*0.02*	*0.08*	*0.50*	*0.34*	*0.29*	*0.46*	*0.04*	*0.07*	*0.29*	*0.07*	*0.38*
Stage4	1.10	2.53	1.16	3.49	3.55	0.46	3.07	4.85	3.42	2.10	10.27	5.37	4.30	7.49	3.46	2.91	6.61
	0.95	*0.77*	*0.95*	*0.63*	*0.62*	*0.99*	*0.69*	*0.43*	*0.64*	*0.84*	*0.07*	*0.37*	*0.51*	*0.19*	*0.63*	*0.71*	*0.25*
Stage5	**19.31**	7.03	4.24	**25.57**	6.73	**15.26**	**16.11**	**25.03**	6.65	2.46	5.08	2.63	9.63	5.55	10.61	**12.12**	4.61
	0.00	*0.22*	*0.52*	*0.00*	*0.24*	*0.01*	*0.01*	*0.00*	*0.25*	*0.78*	*0.41*	*0.76*	*0.09*	*0.35*	*0.06*	*0.03*	*0.47*
Subcat.	***Al***	***Ca***	***Co***	***Cr***	***Cu***	***Fe***	***K***	***Mg***	***Mn***	***Ni***	***P***	***Sc***	***Si***	***Sn***	***Ti***	***V***	***Zn***
Stage1	6.84	**8.38**	3.92	4.98	0.46	2.76	**8.85**	**14.18**	2.93	4.81	2.48	5.13	3.92	5.13	4.82	0.00	0.82
	0.08	*0.04*	*0.27*	*0.17*	*0.93*	*0.43*	*0.03*	*0.00*	*0.40*	*0.19*	*0.48*	*0.16*	*0.27*	*0.16*	*0.19*	*1.00*	*0.85*
Stage2	4.55	4.24	**10.27**	6.25	2.21	**8.31**	**9.55**	**9.09**	5.72	**9.26**	1.21	5.66	**11.36**	4.42	4.14	0.00	0.25
	0.21	*0.24*	*0.02*	*0.10*	*0.53*	*0.04*	*0.02*	*0.03*	*0.13*	*0.03*	*0.75*	*0.13*	*0.01*	*0.22*	*0.25*	*1.00*	*0.97*
Stage3	6.00	4.98	1.01	5.99	1.71	**9.50**	**12.22**	4.46	1.62	1.03	0.78	5.25	3.45	**13.63**	5.13	6.37	0.37
	0.11	*0.17*	*0.80*	*0.11*	*0.64*	*0.02*	*0.01*	*0.22*	*0.65*	*0.79*	*0.86*	*0.15*	*0.33*	*0.00*	*0.16*	*0.10*	*0.95*
Stage4	0.70	3.57	1.54	0.59	4.17	1.52	3.26	0.62	4.74	1.72	**14.24**	3.89	2.07	**10.42**	0.97	3.17	4.05
	0.87	*0.31*	*0.67*	*0.90*	*0.24*	*0.68*	*0.35*	*0.89*	*0.19*	*0.63*	*0.00*	*0.27*	*0.56*	*0.02*	*0.81*	*0.37*	*0.26*
Stage5	7.09	4.83	6.19	**11.54**	2.11	5.78	**14.23**	**10.66**	**9.86**	0.33	4.98	0.10	5.28	2.73	1.34	**12.19**	2.48
	0.07	*0.19*	*0.10*	*0.01*	*0.55*	*0.12*	*0.00*	*0.01*	*0.02*	*0.95*	*0.17*	*0.99*	*0.15*	*0.44*	*0.72*	*0.01*	*0.48*

Values exceeding H are shown in bold, values in italics are p values

5.2.2 Second-step statistical test on field samples

Multi discriminant function analysis was processed using the computer program SPSS. The results were disappointing as can be seen in Table 5.2; the high Lambda values indicate that much of the variability is from within the group. Collins et al (1997c) returned values of 0.22881 – 0.00001 for the River Dart Catchment and 0.07965 – 0.00001 for the River Plynlimon subcatchment. Table 5.2 shows that in this work very few elements were identified as being able to correctly identify which group a sample came from. Therefore, it would seem unfeasible to accurately identify sediment sources from the elements identified by the discriminant function.

Table 5.2 Results of multi-discriminant function analysis

Stage	**Landuse**			**Geology**			**Subcatchment**		
	Element	Cum. %	Wilks Lambda	Element	Cum. %	Wilks Lambda	Element	Cum. %	Wilks Lambda
1	Al	78.3	0.521	none	n/a	n/a	K	100	0.761
	Sc	94.2	0.354						
	Sn	100	0.261						
2	Ni	50.4	0.568	Si	100	0.645	Si	60.4	0.708
	Zn	85.8	0.363				Co	9.37	0.511
	Al	100	0.257				Fe	100	0.389
3	Co	81	0.668	none	n/a	n/a	none	n/a	n/a
	V	98.1	0.442						
	Ti	100	0.332						
4	Ti	100	0.705	none	n/a	n/a	none	n/a	n/a
5	Fe	54.3	0.765	Mg	100	0.796	none	n/a	n/a
	Si	100	0.605						

The poor result in the discriminant function results, shown by the high Wilks lambda values (they should be as close to zero as possible) and the poor selection of elements for classification may be a result of too few samples being analysed. The results returned in this section do not appear to be robust enough to use as a basis for a mixing model.

5.3 Two-step Statistical Test on Suspended Sediment.

The two-stage statistical procedure was also conducted on suspended sediment data. Kruskall-Wallis analysis was performed on all the suspended sediment data from stage 5 (total extraction); stages 1-4 were deemed to have too few samples (13) to allow analysis. When performing analysis on suspended sediment samples, there is no need for particle size correction (Walling et al, 1999). The data was divided into three groups: Upper Tees - all the Tees catchment above the Skerne confluence, the Skerne catchment and the River Leven catchment. If successful, suspended sediment samples at Stockton could be unmixed according to these three sources. The critical H-value is 5.99 and as shown in Table 5.4, only Ca was able to discriminate between the groups.

5.4 Two-step Statistical Test on Water Sample Data

Kruskall-Wallis was also performed on the water data collected alongside suspended sediment. The samples were separated into the same groups (upper River Tees, River Skerne and River Leven) and the H-value was again 5.99. The results are shown in Table 5.5. This time nine elements were selected as being able to classify the samples into the three source groups. These nine elements (Al, Ca, Fe, K, Mg, Mn, P, Si & Ti) were put forward for multidiscriminant function analysis, after which K and P were selected as suitable for classifying the samples into groups, the results of which are shown in Table 5.3.

Table 5.3 Results of multi-discriminant function analysis on water data

Element	**Cumulative percentage (%)**	**Wilk's Lambda**
K	93.4	0.153
P	100.0	0.108

Table 5.4 Suspended sediment Kruskall-Wallis Results

Stage 5 suspended sediment results															
	AL	CA	CO	CR	CU	FE	K	MG	MN	NI	SC	SI	TI	V	ZN
H-value	0.375	**8.004**	0.045	5.067	2.555	5.89	0.621	2.234	0.584	3.956	3.572	3.295	1.06	1.989	1.4
p-value	0.829	0.018	0.978	0.079	0.279	0.053	0.733	0.327	0.747	0.138	0.168	0.193	0.589	0.37	0.497
Note: P and Sn were not present in any stage 5 suspended sediments and were therefore not analysed by Kruskall-Wallis															

Table 5.5 Water samples Kruskall-Wallis Results

Water Sample results											
	AL	CA	CU	FE	K	MG	MN	P	SI	TI	ZN
H-value	**11.08**	**15.29**	2.799	**9.21**	**16.89**	**16.59**	**6.653**	**18.26**	**16.53**	**10.86**	3.56
p-value	0.004	0	0.247	0.01	0	0	0.036	0	0	0.004	0.169
Note: Co, Cr, Ni, Sc, Sn & V were not present in any water samples and were therefore not analysed by Kruskall-Wallis											

5.5 Mixing Model

A mixing model is used to provide quantitative estimates of the relative contributions of the different source areas to the suspended sediment sample procedure (Collins et al, 1997a, Walling et al, 1993). The source proportions are obtained mathematically by solving linear equations and the model assumes that the properties of the suspended sediment are dependent on the composite fingerprint of the sediment sources defined by the two step procedure (Collins et al, 1997b).

The mixing model was conducted using Microsoft Excel Solver (Yu and Oldfield, 1989; Walden et al 1997). The model used in this research was developed at Exeter over several years and was kindly provided by Julie Carter. The model was adjusted in order to take into account the various sources and elements used. Microsoft Excel uses the Generalised Reduced Gradient (GRG2) non-linear optimisation code to find an optimal value for the formula used. Solver works by working on a group of cells that are directly or indirectly related to the formula in the target cell. Solver adjusts these values in the changing cells to produce the results specified in the target cell formula. Constraints are applied to the values in the model and can refer to other cells that affect the target cell formula.

For each tracer property *i* in the composite fingerprint, a linear equation is constructed that relates the concentration of property *i* in the suspended sediment sample to that in the mixture representing the sum of the contributions from the different source groups *j*. The composite fingerprint is therefore represented by a set of linear equations (one for each property *i*). The least squares method is used rather than solving the linear equations directly (Walling et al, 1999). The proportions derived from individual sources are established by minimising the sums of the squares of the residuals for the number of tracer properties involved. The model has to satisfy two linear constraints:

1. The contributions from each source ranges from 0 – 1.
2. The sum of contributions from all sources is 1.

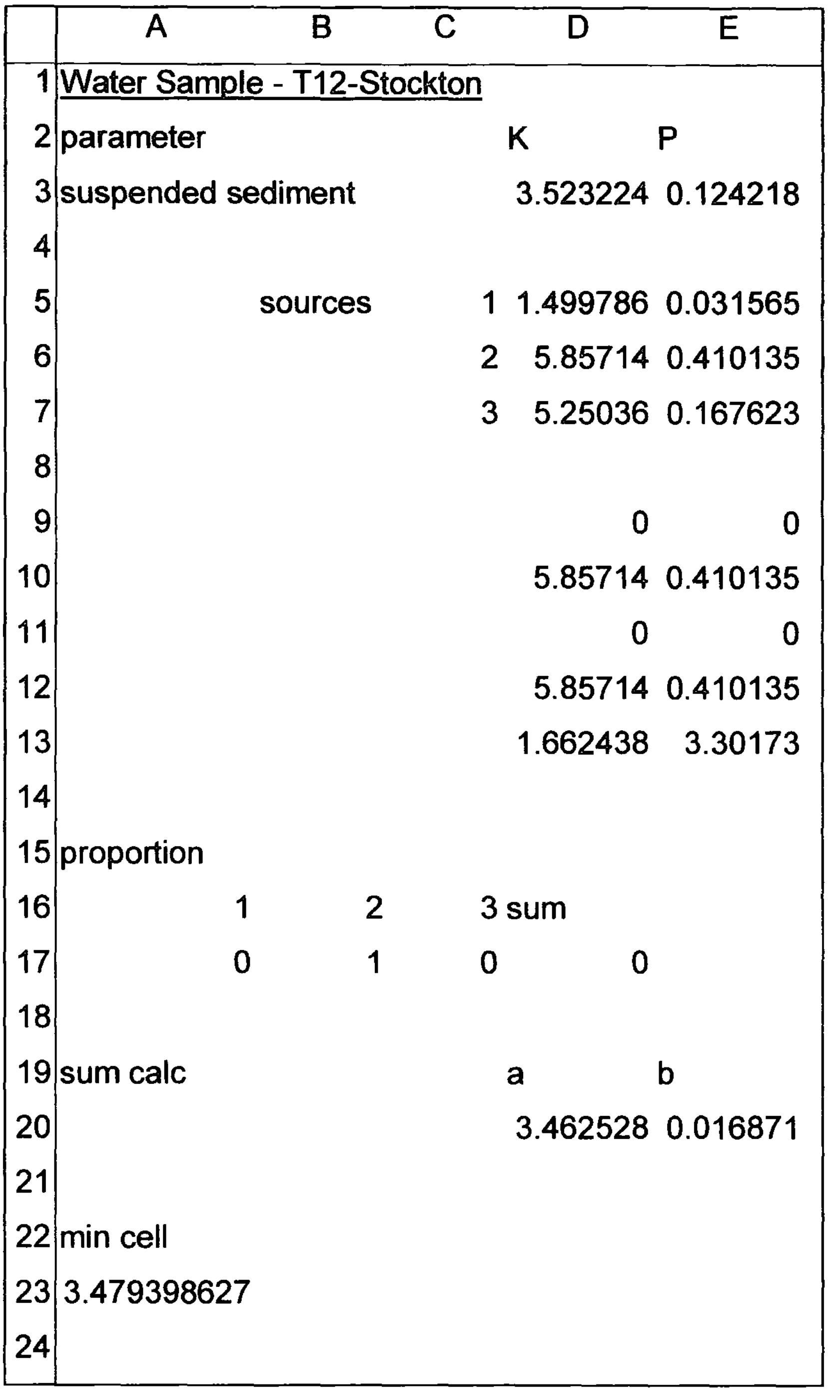
As can be seen from Table 5.6 below, K is significantly higher in the Skerne and Leven catchments, whilst the Skerne is highest in P. As there are clear differences in the K and P content of the Upper Tees, Skerne and Leven and their ranges of values were dissimilar, a mixing model for these sources was developed.

Table 5.6 Data statistics for elments used in mixing model (in mgkg^{-1})

	Upper Tees		Skerne		Leven	
Analyte	K	P	K	P	K	P
Average concentration	1.50	0.03	5.86	0.41	5.25	0.17
Standard deviation	0.96	0.029	0.989	0.277	0.78	0.036
Maximum	3.09	0.09	7.20	0.96	6.28	0.228
Minimum	1.04	0.02	4.89	0.22	4.48	0.137

When using the model to unmix water samples taken at Stockton, all samples returned the source as being 100% Skerne (shown in Figure 5.1), which is clearly not correct - the Skerne has the smallest catchment and lowest flow rate of the 3 source groups identified.

Figure 5.1 Results of Mixing Model, Stockton Sample

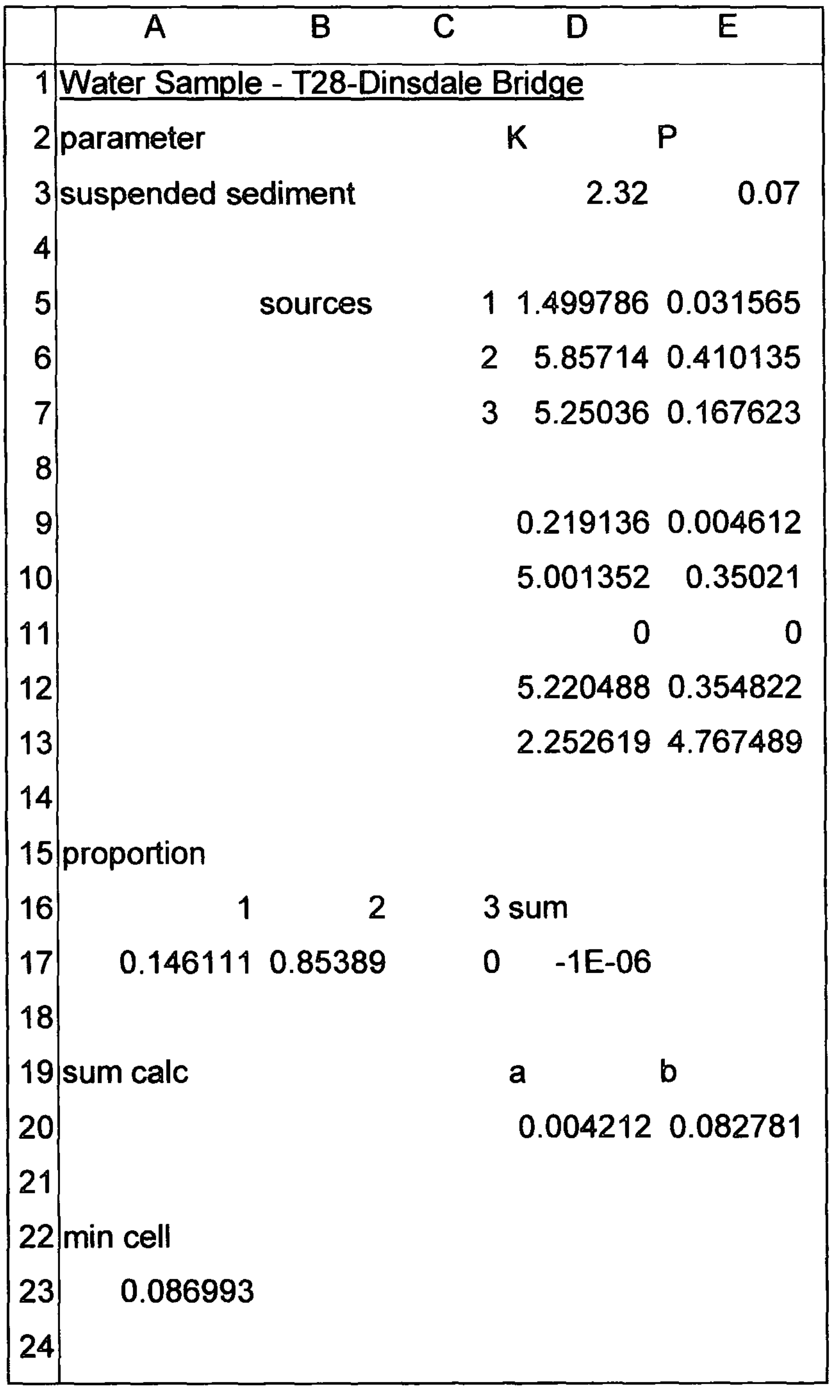


	A	B	C	D	E
1	Water Sample - T12-Stockton				
2	parameter			K	P
3	suspended sediment			3.523224	0.124218
4					
5		sources	1	1.499786	0.031565
6			2	5.85714	0.410135
7			3	5.25036	0.167623
8					
9				0	0
10				5.85714	0.410135
11				0	0
12				5.85714	0.410135
13				1.662438	3.30173
14					
15	proportion				
16	1	2	3	sum	
17	0	1	0	0	
18					
19	sum calc			a	b
20				3.462528	0.016871
21					
22	min cell				
23	3.479398627				
24					

In this model cells D3 and D4 contain the concentration of tracer properties in the suspended sediment sample to be unmixed. Cells D5-7 and E5-7 contain the concentrations of the tracer properties in the different source groups, group 1 is the Upper Tees, group 2 is the River Skerne and group 3 is the River Leven. The values in cells D9 – D11, E9 – E11, D20 and E20 are those used by the model to solve the linear equations by the least squares method. The proportions ascribed to each source after solver has 'unmixed' the samples are shown in cells A17 – C17. The proportions derived from the individual source groups are obtained by minimising the sum of the squares of the residuals for the tracer properties involved. In Solver this is called the target cell and is located at A23.

A sample taken from Dinsdale Bridge gave a reading of 14.6% Upper Tees and 85.4% Skerne as shown in Figure 5.2. This was the only sample where the Skerne did not score 100%.

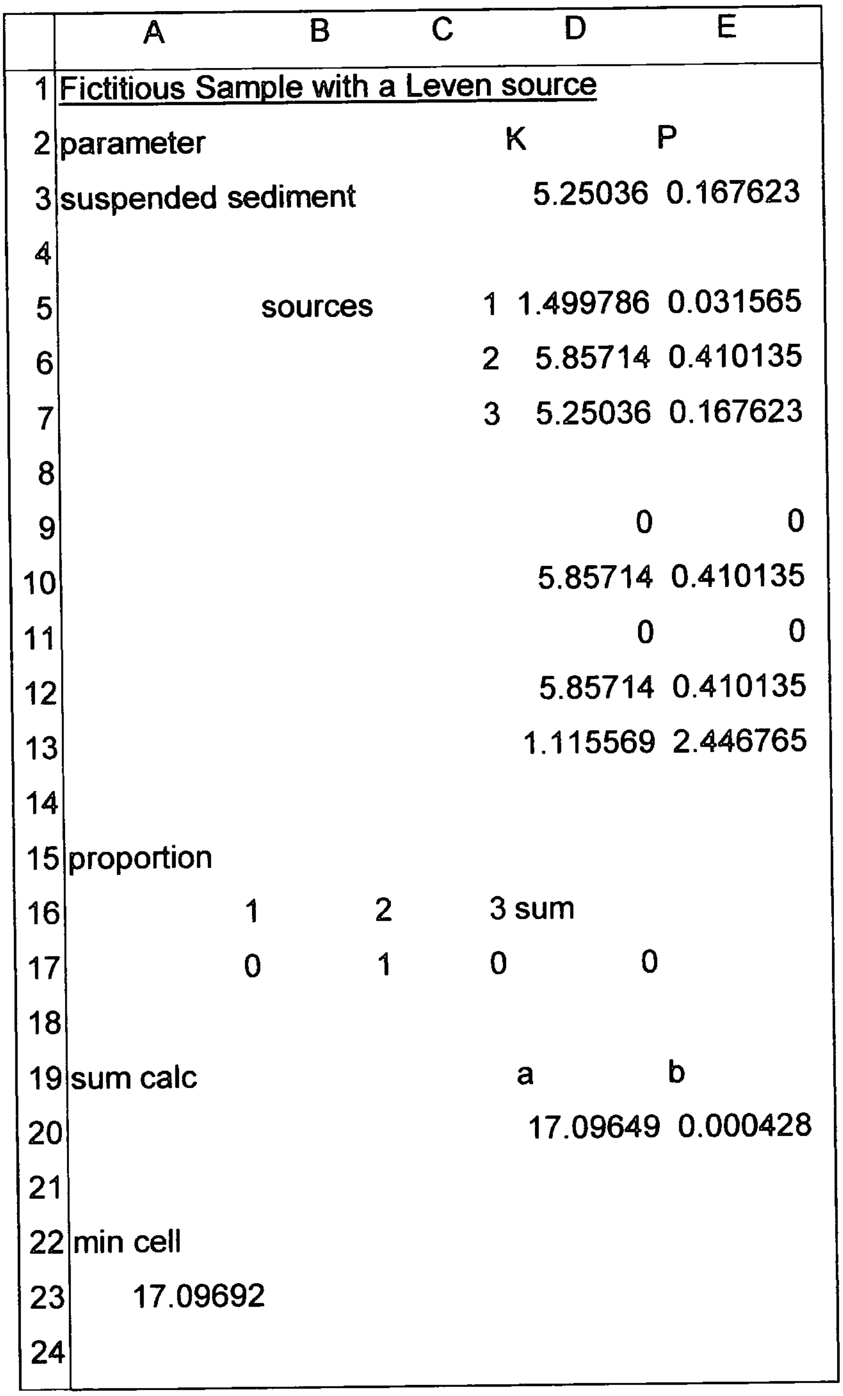
Figure 5.2 Results of Mixing Model, Dinsdale Sample



	A	B	C	D	E
1	Water Sample - T28-Dinsdale Bridge				
2	parameter			K	P
3	suspended sediment			2.32	0.07
4					
5		sources	1	1.499786	0.031565
6			2	5.85714	0.410135
7			3	5.25036	0.167623
8					
9				0.219136	0.004612
10				5.001352	0.35021
11				0	0
12				5.220488	0.354822
13				2.252619	4.767489
14					
15	proportion				
16	1	2	3	sum	
17	0.146111	0.85389	0	-1E-06	
18					
19	sum calc			a	b
20				0.004212	0.082781
21					
22	min cell				
23	0.086993				
24					

As the Skerne and Leven showed similar concentrations for K and P, the model seemed to ignore the Leven catchment, even when the sample being 'unmixed' contained the average Leven values, as shown in Figure 5.3. When experimental values were entered to test the model, K values approaching and exceeding 2.5kgmg^{-1} were entered the Skerne was returned as the dominant contributor. Where theoretical P values of less than 1mgkg^{-1} were entered the upper River Tees catchment was identified as the main source (despite the maximum recorded value being 0.09mgkg^{-1}) even when the P concentration exceeded 0.5mgkg (higher than the average for all catchments). The maximum P content in the river water values was 0.96mgkg^{-1}, which was in the Skerne catchment.

Figure 5.3 Mixing Model with a Leven Source



	A	B	C	D	E
1	Fictitious Sample with a Leven source				
2	parameter			K	P
3	suspended sediment			5.25036	0.167623
4					
5		sources	1	1.499786	0.031565
6			2	5.85714	0.410135
7			3	5.25036	0.167623
8					
9				0	0
10				5.85714	0.410135
11				0	0
12				5.85714	0.410135
13				1.115569	2.446765
14					
15	proportion				
16	1	2	3	sum	
17	0	1	0	0	
18					
19	sum calc			a	b
20				17.09649	0.000428
21					
22	min cell				
23	17.09692				
24					

5.6 Conclusions

Landuse appeared to provide the best correlation between its subset groups, with Kruskall-Wallis selecting all the elements from each extraction stage. However when entered into the second stage of the statistical process (multi discriminant function analysis), only three elements were selected for extraction stages 1, 2 & 3, and only one element in stage 4 and two elements in extraction stage 5. The technique applied is a stepwise method to eliminate variables with little contribution to the classification in order to minimise Wilk's Lambda. As can be seen from Table 5.2 the Wilk's Lambda values obtained ranged from 0.257 to 0.765.

An attempt to determine source areas using suspended sediments as the sources proved unsuccessful, as only one element was capable of discriminating between the three different source areas (upper River Tees catchment, River Skerne and River Leven) according to Kruskall-Wallis.

The river water samples were also ordered into the same three source areas. Nine elements were selected by Kruskall-Wallis but only two of these, K and P, were chosen by the multi discriminant function analysis. When used in the mixing model however, only the Skerne was interpreted as contributing to the water chemistry. The Leven was virtually ignored by the mixing model due to its closeness to the Skerne in terms of its composition in the elements unmixed. The Upper Tees catchment was involved only when the concentrations of K and P in the sample to be unmixed were very low.

Chapter 6 Grouping of Soil Data for Different Landuses and Geology and Subcatchment

6.1 Introduction

The purpose of this chapter is to follow the same trend as chapter 5, a statistical procedure is used to identify those properties that are the best indicators of source groups. The properties identified are then subjected to a multivariate analysis procedure to determine the relationship between different source groups and to identify which source group most resembles the suspended sediment samples.

The initial statistical methods used were to determine the normality of the sample set and therefore the overall distribution of the samples, as this controls which statistical methods can be employed. Analysis of Variance (ANOVA) was then used to identify the properties that are capable of successfully discriminating between the selected groups. These properties were then used in Principal Components Analysis (PCA).

The source samples taken from the River Tees catchment were sorted into various groups. The groups were selected from easily identified parameters, primarily landuse, geology and subcatchment. A subdivision by soil type is not feasible, owing to the large number of soil types present in the Tees catchment. The groups chosen, might be expected to show differences in the chemical composition between groups. For example when using landuse, agricultural areas could expect higher levels of organic material and fertilisers (identified by high phosphorus and potassium values). When looking at geological groups the areas underlain by limestone would be expected to yield higher values of calcium and elements that are preferentially bonded to it. Differences in subcatchments could be the result of different landuses, soil types or geology, particularly drift geology. A large thickness of drift (material laid down by the ice advances during the last glacial period) is known to cover the whole Tees catchment area and consists of boulder clay, sand and gravel, laminated clay, morainic drift and alluvium. The thickness of the superficial cover varies considerably over the catchment, from 20 ft at Piercebridge to 126 ft at Broken Scar, and there are areas of little or no drift in the high Pennine areas (Mill & Hull, 1976). As mentioned earlier some areas of the catchment have been heavily mined, this can be reflected in increased heavy metal concentrations.

6.2 Statistical Analysis

6.2.1 Normality

The data was tested for normality as the distribution of the data influences the statistical procedures that may be performed on it. To test the distribution of the data, the skewness was calculated in Microsoft Excel to characterise the degree of asymmetry about the mean. A sample set with normal distribution will have a bell shaped curve about the mean. The whole dataset was test for skewness and was found to be positively skewed and therefore has a non-normal distribution. It was decided that Anova was robust enough to cope with the slight skewness in the data.

6.2.2 Anova

Statistical methods to determine if there is significant variation between groups include ANOVA (in Excel) for normally distributed data and Kruskall-Wallis for non-normally distributed data. Anova is a simple analysis of variance to test the hypothesis that means from two or more samples are equal (and drawn from populations with the same mean). The significance level is related to the probability of a type one error (rejecting the true hypothesis) and the significance level is set at 0.05 (or 95%).

Both Anova and Kruskall-Wallis tests have been performed on the data but, for the purposes of this chapter, only the Anova results have been used. This is due to Kruskall-Wallis including elements that are rarely present in the dataset as being able to discriminate between source types, when they clearly cannot if they are rarely present. This is due to the method that Kruskall-Wallis employs; it calculates the analysis of variance on the rank of the data rather than the absolute. Anova also returns average values for each groups along with variance in an easy to read format that allows the different relationships between groups to be studied.

The group which showed the greatest potential to distinguish between subset groups was landuse, which had the largest number of elements able to characterise the data. Anova was conducted on two landuse sets; the second set contained bed and bank material as an additional source, whereas the first set contained only field sources. Anova was conducted on each stage for each group; the elements that exceeded the f-critical value are shown in Table 6.1. If the f-value for an element exceeds the f-critical, that element can be deemed to be able to discriminate between groups at the 95% confidence level. Landuse was analysed with and without the bed and bank material

Table 6.1 Anova results

	Landuse (5)	Landuse (6)	Geology	Subcatchment
Stage 1	Al, Ca, Co Cr, Cu, Fe, Mg, Ni, Ti	Al, Cr, Cu, Fe, Ni, P, Ti	None	K, P
Stage 2	Al, Cr, Cu, Fe, Ni, Sc, Si, Sn, Ti	Al, Co, Cr, Cu, Fe, K, Mn, Ni, P, Sc, Si, Sn, Ti, Zn	Mg, Si, Ti	Co, Cr, Fe, K, Mg, Ni, Si
Stage 3	Cr, K, Ni, V	Co, Cu, K, Mn, Ni, Sn, V, Zn	None	Cr, Fe, K, Mg, Sn
Stage 4	None	P, Ti, V	Zn	None
Stage 5	Al, Ca, Fe, Mg, Ni, Si, Ti, V, Zn	Al, Fe, K, Mg, Ni, Sc, Si, Ti, V	Al, Cr, Fe, Mg,	K, V

Landuse (5) includes natural, semi-natural, tilled, urban and woodland.

Landuse (6) includes bed/bank material, natural, semi-natural, tilled, urban and woodland

6.3 Principal Components Analysis

Principal Component Analysis (PCA) is a transformation technique that determines the relationship between the elements in a dataset. PCA is the oldest and best known multivariate technique (Jolliffe, 1986) and was conducted for this study using Minitab. PCA depends upon the fact that at least some of the variables in the dataset are interrelated (Daultrey, 1976) and does not require the data to be normally distributed.

The specific goal of Principal Component Analysis (PCA) is to summarise patterns of correlations amongst observed variables, to reduce a large number of observed variables to a smaller number of factors. Mathematical PCA produces several linear combinations of observed variables, each linear combination a component factor. The components summarise the patterns of correlations in the observed correlation matrix. Steps in PCA involve; extracting a set of components from the correlation matrix, determining the number of components, rotating (probably) the factors to increase interpretability and finally interpreting the results.

The idea of PCA is to extract maximum variance from the data set with each component. The first component is the linear combination of observed variables that maximally separates subjects by maximising the variance of their component scores. The second component is formed from residual correlations; it is the linear combination of observed variables that maximise variability uncorrelated with the first component. Subsequent components also extract maximum variability from residual correlations and are orthogonal to all previously extracted components. The components are ordered, the first component extracts the most variance and the last component the least variance. The solution is mathematically unique and if all components are retained, it reproduces the correlation matrix (Tabachnick & Fidell, 1996)

Interpretation and naming of components depend on the meaning of the particular combination of observed variables that correlate highly with each component. A component is more easily interpreted when several observed variables correlate highly with it and these variables do not correlate with other components. In PCA all variance in the observed variables is analysed.

The idea of multivariate techniques is to reduce the dimensionality of a dataset in which there are a number of inter-related variables. This reduction is achieved by taking variables X_1, X_2, ... X_p and finding combinations of these to produce component factors Z_1, Z_2, ...Z_p that are uncorrelated. The first component Z_1 is obtained by adding the combinations of the variables together, for example; $Z_1 = 0.24X_1 + 0.45X_2 + X_i$..., where X_1, X_2 and X_i represent measurements in the dataset. The component factors are ordered so that Z_1 displays the largest amount of variation. It is hoped that the variance of most of the indices will be so low as to be negligible, so that the variation in the dataset can be described by a few Z variables (Manly, 1986).

To provide a good indication of the relationships between samples and elements, the number of samples used should be 5-6 times greater than the number of variables. To determine which factor components are useful for analysing the data, the eigenvalue for each factor axis is scrutinised. The cut off level for dropping component factor axes is where the eigenvalue is below one or where adding a new component axis does not add any significant further information. These 'components axes' can be interpreted in terms of the original variables which load "most heavily" onto them (Daultrey, 1976), as these components are controlled by a particular element or a group of elements. This will give an indication of the types/availability of the bonding sites in the samples in this study.

6.3.1 Introduction

Principal Components Analysis was performed on various groups of the data in order to find the best method of distinguishing between different sediment source groups. This method of analysis allows relationships between samples and groups to be studied in graph form, so that similarities or differences are clearly visible. The sample combinations were again landuse, geology and subcatchment.

In order to determine which elements are influencing each component factor, the coefficients for each component factor are studied. When choosing coefficients, those that have an absolute value greater than half the maximum coefficient for the relevant component factor are used. As can be seen in Table 6.2, the maximum coefficient for the first component (CF1) is 0.52 and is the element Fe, indicating that iron has the strongest influence on the first component. If the value of this component is halved, the result is 0.26, therefore all elements influencing the first component have coefficients between 0.26 and 0.52. Where the absolute value of the coefficient is between ½ and ¼ of the largest absolute value, i.e. between 0.13 and 0.26 in this example, those elements can be of some interest in the study of the data. The proportion (shown in the second row of Table 6.2) shows how much of the variation in the dataset is explained by that component factor. The cumulative percentage (shown in the third row) is the total variation explained by the total of the factors i.e. the first three components explain 83% of the variation in the dataset.

Table 6.2 Results of Principal Components Analysis – Stage 1 landuse

	CF1	**CF2**	**CF3**	**CF4**
Eigenvalue	2.808	1.818	1.185	0.553
Proportion	0.401	0.260	0.169	0.079
Cumulative %	0.401	0.661	0.830	0.909
Variable	**CF1**	**CF2**	**CF3**	**CF4**
Al	-0.438	0.413	0.252	*0.056*
Cr	-0.404	-0.305	-0.315	-0.351
Cu	*-0.184*	-0.533	0.358	0.612
Fe	-0.520	*0.070*	*-0.099*	-0.324
Ni	-0.424	-0.450	*0.090*	*-0.050*
P	*-0.133*	*0.068*	-0.809	0.536
Ti	-0.379	0.491	*0.191*	0.325

The sign of the data is also important. A positive loading means there is a positive relationship between that variable and the component. When two factors are plotted against one another, a coefficient with a strong positive sign is known to increase in that element in the positive axis direction. When a coefficient has a negative sign, the element in question is said to increase in the direction of the negative axis. The coefficient values for the remainder of the study are shown for each stage in Appendix A, whilst a brief description of the elements governing each component is given in the text. The PCA plots shown in the Chapters 6 and 7 of this report are those believed to show some pattern in the dataset that can be seen and interpreted. Further plots are shown in Appendices E and G.

The elements used in principal components analysis in this section are those that have been identified by Anova as being able to tell apart the different groups. This is to determine if removing elements common to all groups and concentrating on those that are specific to certain groups, will help to improve the identification of sediment sources.

6.3.2 Landuse with elements identified by Anova

Principal component analysis was then undertaken on the six landuse sets (natural, semi-natural, tilled, urban, woodland and bed and bank) as more elements were found to differentiate between subsets. This will also show if bed and bank samples are significantly different from field samples and therefore a separate sediment source.

6.3.2.1 Stage 1 Extraction

The first four principal component factors explained 91% of the variance measured within the data as shown in Table 6.2. The first component was negatively correlated with Al, Cr, Fe, Ni and Ti, whereas the second component was negatively related to Cu and Ni and positively related to (Al, P and Ti). The third component is dominantly controlled by P (negative correlation) and (Al) has a small effect on the positive axis. The fourth component was controlled by Cr, Fe and (Ni) in the negative direction whilst being positively correlated with Al, Cu, P and Ti.

In stage 1 it was difficult to differentiate between any landuse classes and the suspended sediment generally overlapped the field and bed/bank data. Component plots of the first versus the fourth (Figure 6.1) show that suspended sediment samples can be separated according to whether sampling was undertaken on a rising or falling limb. Samples from rising limbs tend to have higher metal concentrations and plot with outlier field samples rather than the general cluster. Suspended sediment samples taken on the falling limbs plot close to the main sediment cluster. Suspended sediment sample V19 (taken from woodland in the River Leven catchment) had to be removed from the graph to allow the study of the data. Sample V19 had a reading of –16 on the first component, which greatly distorted the data. This was due to it having a titanium concentration a factor higher than all other samples (Ti = 1.18 $mgkg^{-1}$) as well as an iron concentration 6 times greater than the rest of the field (Fe = 303$mgkg^{-1}$). This may be due to measurement error but is more likely to be a result of the sample being taken from a hotspot in the Cleveland Hills area. V19 was found to outlie the data in all four extraction stages and in total extraction.

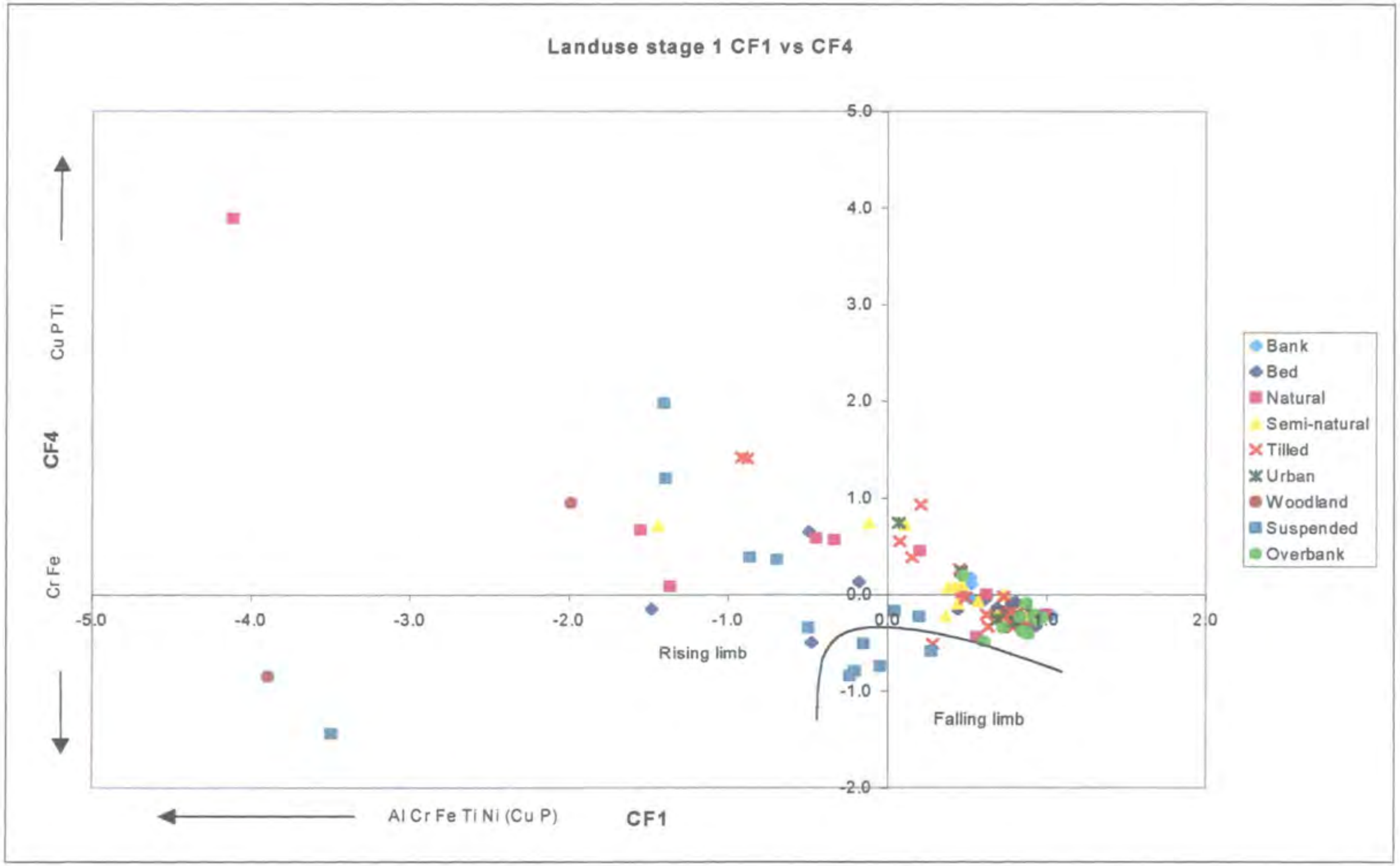


Figure 6.1 Landuse stage 1 CF1 v CF4

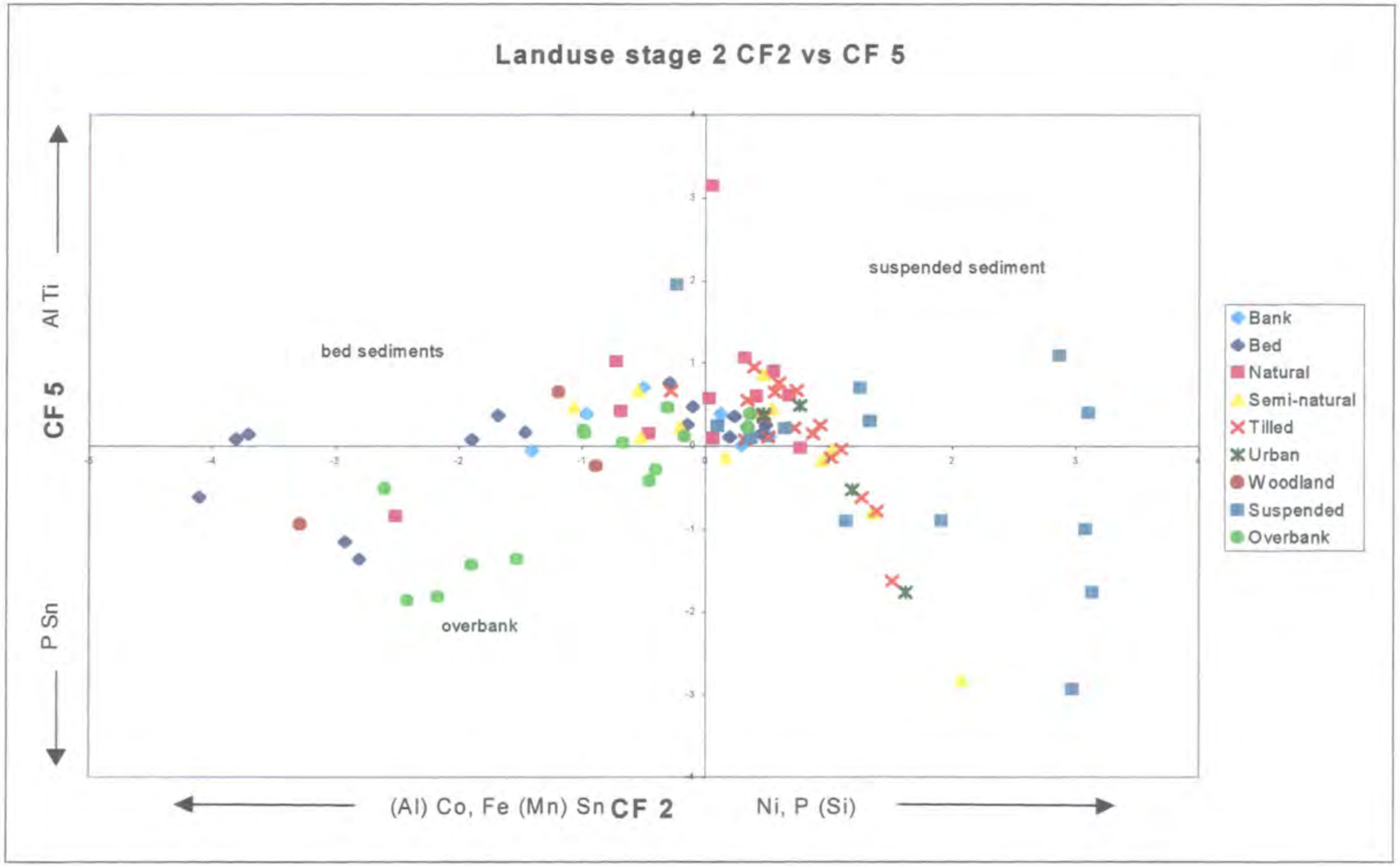


Figure 6.2 Landuse stage 2 CF2 v CF5

6.3.2.2 Stage 2 Extraction

Five components in stage 2 explained 84% of the variance found in the data. The first component was positively correlated with all the elements identified by Anova except for Al, P, Sn and Ti. The second component was negatively related to (Al), Co, Fe, (Mn) and Sn and positively related to (Ni), P and Si. The 3rd, 4th and 5th components were controlled by a number of metals both positively and negatively, as summarised here: The third component - Co & Mn (-ve) Al, Cr, (Fe), (P), (Sn) and Ti (+ve). The fourth component - (Cr, Cu, Sn and Zn) (-ve) and Al, Co, Mn, P and Ti (+ve) and finally the fifth component - P and Sn (-ve) and (Al) and Ti (+ve). Full result tables are shown in Appendix D.

In this stage clear disassociation with the bed and overbank sediments plotting on the opposite side of the field data to the suspended sediment can be identified on several component plots; namely, the component plot second versus the fifth component (shown in Figure 6.2). This indicates that when the erosion takes place, certain fractions are being left behind or deposited in the riverbed and the remainder are held in suspension. In this case it is the heavy metals which are remaining in the riverbed, possibly owing to their high densities.

6.3.2.3 Stage 3 Extraction

The first four components explain 92% of the differences in the data. The first component is negatively related to Cu, (Co), K, Mn, Ni, (V) and Zn, whilst Ti and V control the negative axis on the second component with (Co, Cu, Mn and Zn) controlling the positive axis. The third component is explained by Co, Mn and (Ti) (-ve) and (Cu and K) (+ve), whilst the fourth component is dominated by K on the negative axis. Full result tables are shown in Appendix D.

The first component separates suspended sediment from field and to some extent bed and bank material. When the first component is plotted against the second component, the graph (Figure 6.3) shows that the suspended sediment is closer in chemistry to bed and bank material than the field samples. In Figure 6.4, showing the third component against the fourth, the field and bed and bank samples are clustered together and it is possible to make a distinction between suspended sediment samples from high flow conditions (high in potassium) and samples taken from low flow conditions (high in metals). The high K contents of high flow samples could be due to direct and continued runoff from fields (especially tilled) into watercourses. The high metal concentration at low flow could be due to low input of material from fields, the transport of bed material and the absorption of metals in the riverbed.

6.3.2.4 Stage 4 Extraction

Anova selected only three elements as being able to distinguish between the different landuse classes. Phosphorus (P) was selected despite many of the values being zero. All three elements are correlated with the positive axis, whilst the second component shows P in the positive direction and V in the negative direction. Full result tables are shown in Appendix D.

In stage 4 the field samples are more chemically diverse than the bed and bank, overbank and suspended sediment, all of which show little variation on a plot of the first versus the second component (Figure 6.5). No differentiation of landuse types is possible. Identifying sediment source using stage 4 would be unreliable due to the low concentrations, rarity and variability of these elements.

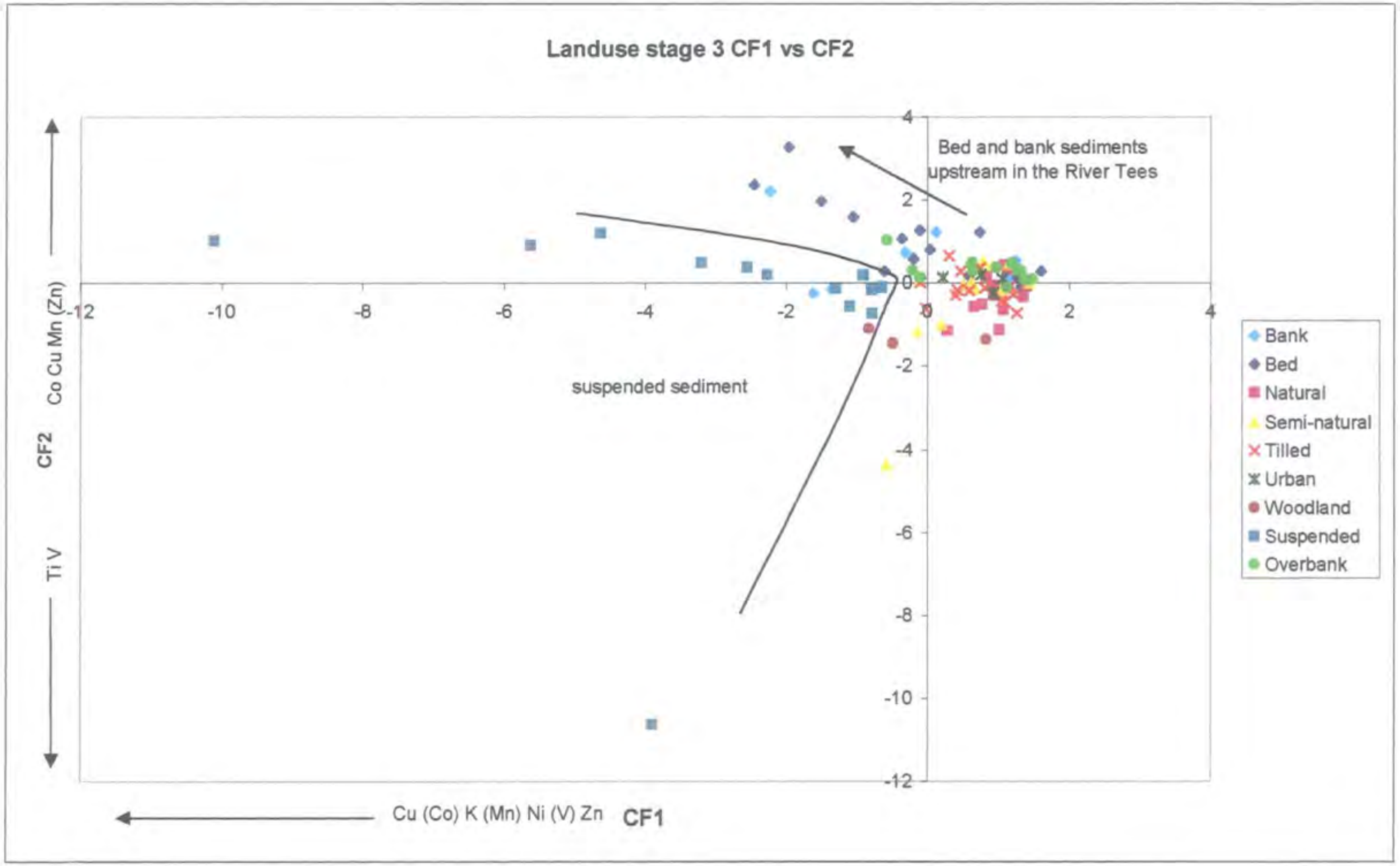


Figure 6.3 Landuse stage 3 CF1 v CF2

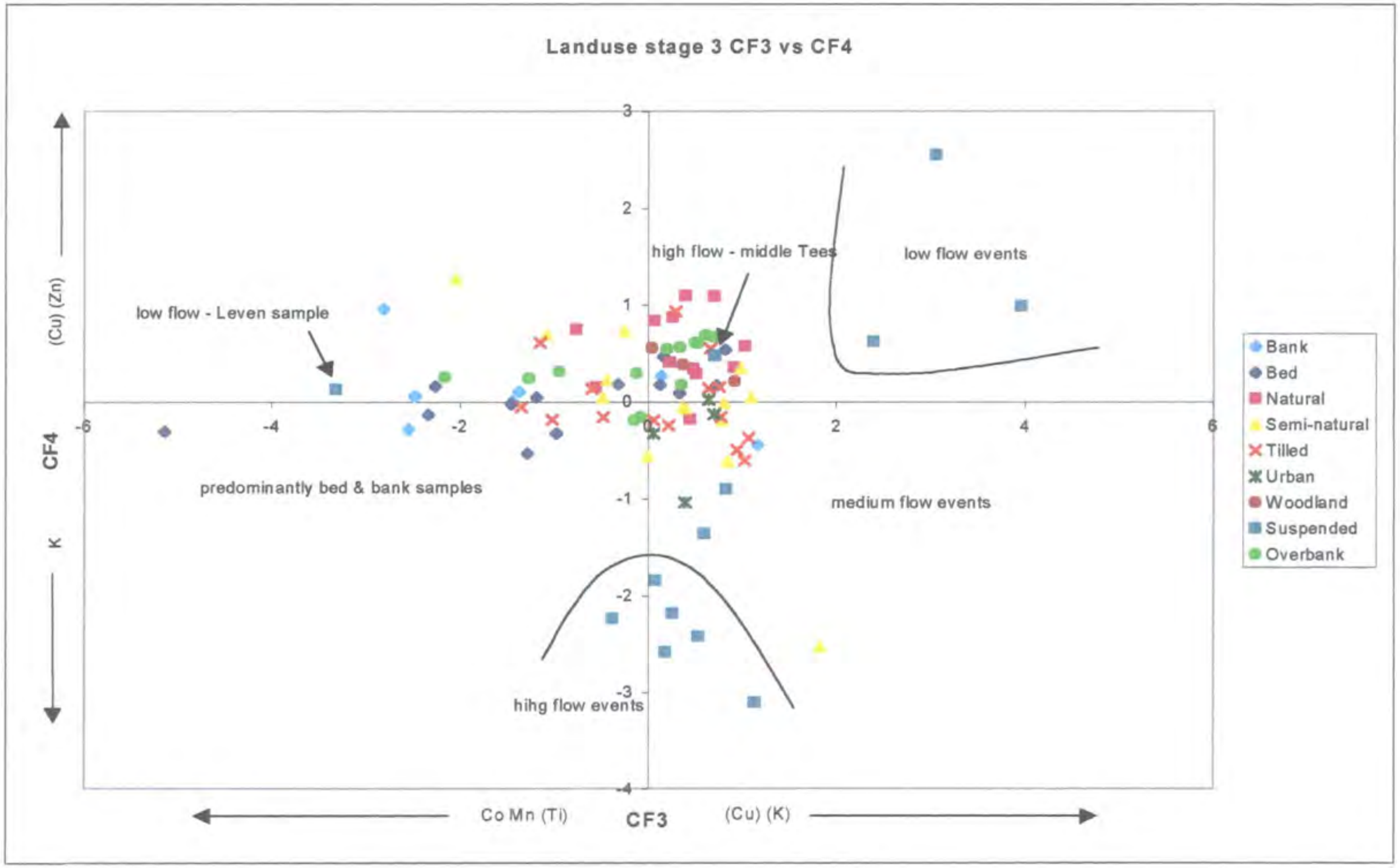


Figure 6.4 Landuse stage 3 CF3 v CF4

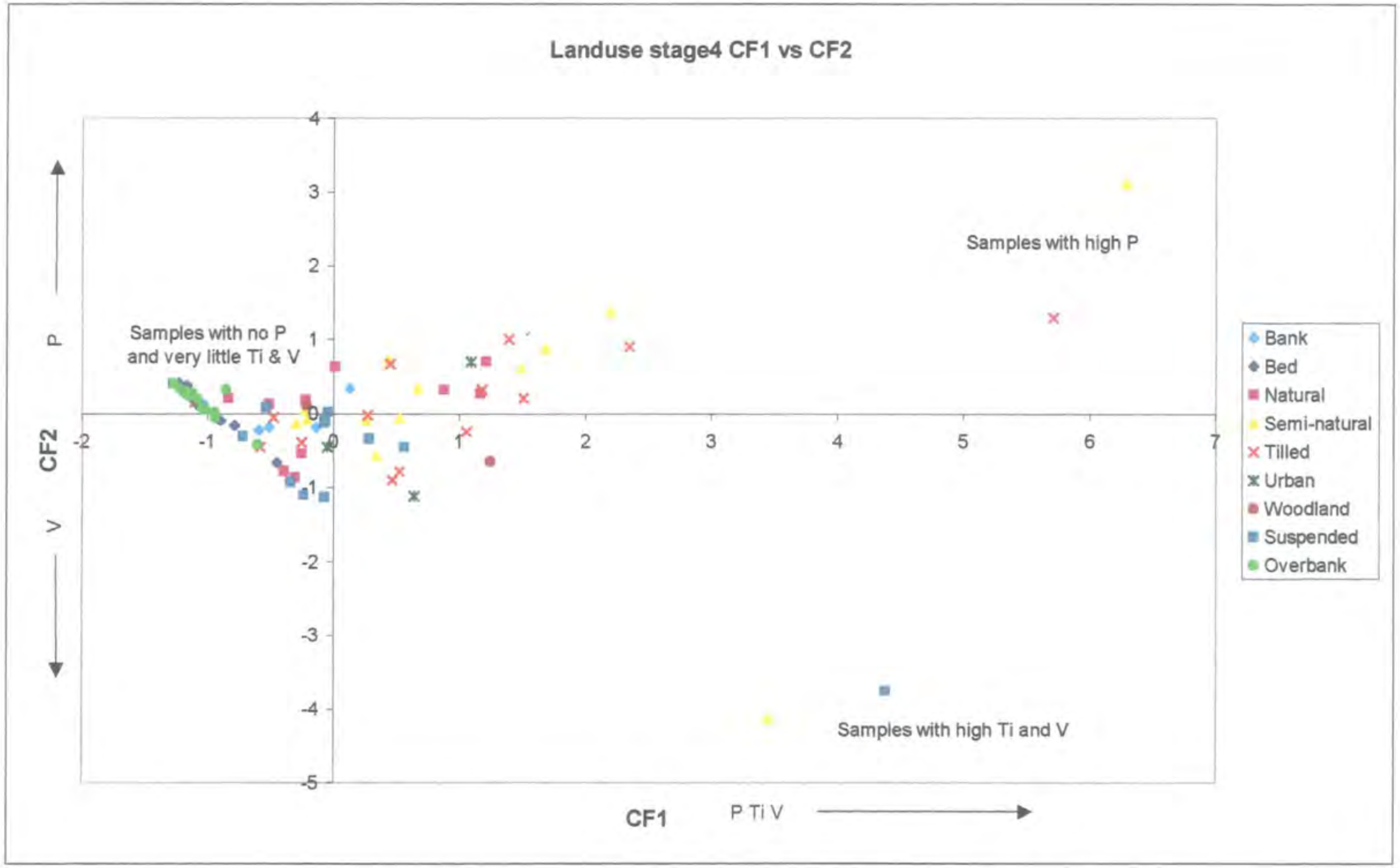


Figure 6.5 Landuse stage 4 CF1 vs CF2

6.3.2.5 Stage 5 Total extraction

Principal components analysis was performed on stage 5 with and without K and Mg - which are strongly controlled by the water chemistry of the suspended sediment and dominate the components, as shown in Figure 6.6. The removal of K and Mg allows a better evaluation of the sediment sources and general overview of the data. Only the component loadings for stage 5 without K and Mg are explained here and between them explain 72% of the variance. The first component is negatively correlated with Al, Fe, Ni, Sc, Ti and (V); with Si and V (-ve) and Sn (+ve) controlling the second component. The third principal component axis is related to (Ni), Sn and (V) only, in the positive direction. Full result tables are shown in Appendix D.

When the samples from stage 5 are plotted as the first component versus the second (Figure 6.7) the suspended sediment plots close to field data, especially tilled and semi natural land, as seen earlier in stage 2. The second component axis shows disassociation of overbank and suspended sediment, with overbank containing more Sn and less Si and V.

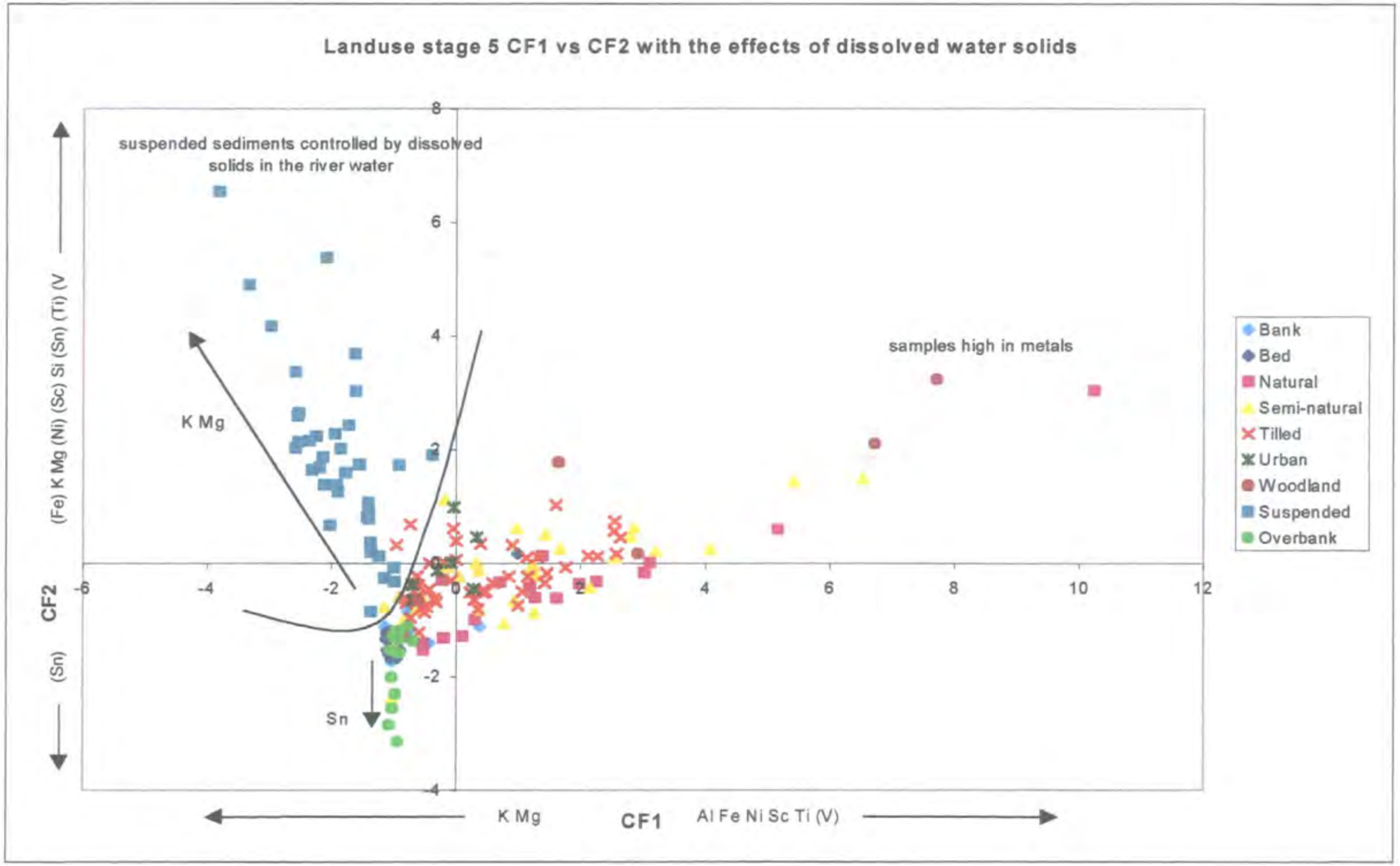


Figure 6.6 Landuse stage 5 CF1 v CF2

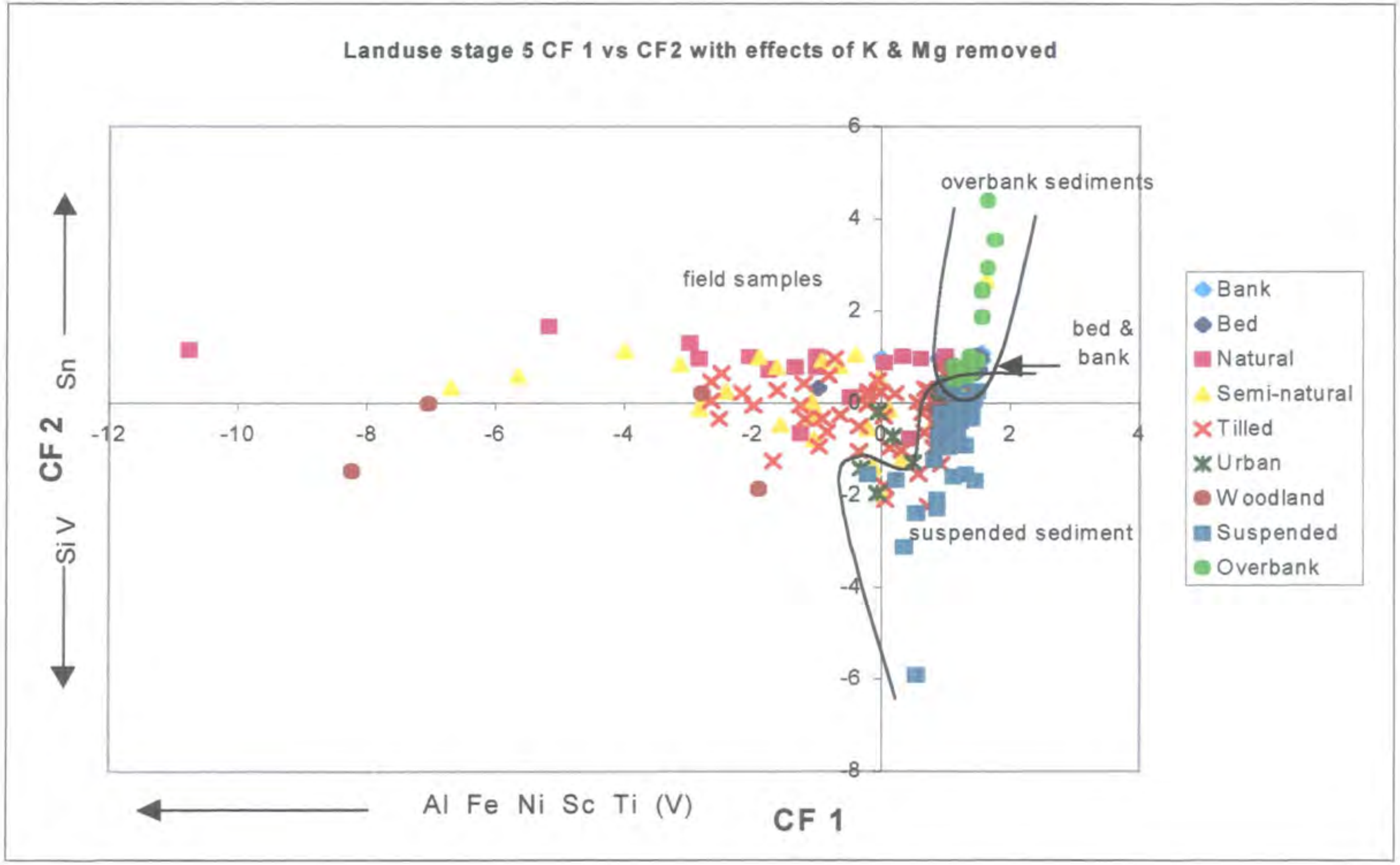


Figure 6.7 Landuse stage 5 CF1 v CF2 (no K & Mg)

6.3.3 Geology using selected elements

Two stages were found to have ample elemental differences between geological types to allow PCA to be undertaken as seen in Table 6.1. The geological groups used below are based on the British Geological Survey's definitions and naming of rock units and are shown in Table 6.3.

Table 6.3 Geological Descriptions

Code Name	**Rock Description**
Arg	Undifferentiated argillaceous rocks (clays and siltstones)
Arsd	Argillaceous rocks interbedded with sandstone
Dldo	Dolomitised limestone and dolomite
Lmst	Limestone often with interbedded argillaceous rocks and sandstone
mgac	Microgabbroic rock (igneous intrusions)
Sdst	Sandstone

6.3.3.1 Stage 2 Extraction

Magnesium (Mg), Si and Ti were selected by Anova as being able to differentiate between source types using extraction stage 2. Magnesium (Mg) and Si were negatively related to the first component whilst Ti alone controlled the second component. There are only seven different Ti values - leading to lines in the plot of component factors. At some stage in data preparation the values have been rounded off to a fixed value. This has not been seen to affect the data in any other stage. These three components explained all the variance in the data. Full result tables are shown in Appendix D.

6.3.3.2 Stage 5 Total Extraction

In stage 5, four elements - Al, Cr, Fe, Mg were deemed able to differentiate between geological groups. Overbank sample, OV4, from Yarm Railway Bridge was removed from the plots shown in Figure 6.8 and Figure 6.9; as its value on the first component of 11.55, causes the rest of the data to be unreadable. The first component is negatively related to Al and Fe, whilst Mg is negatively related. Component two is predominantly controlled by Cr, whilst the third is positively correlated to Cr and negatively to Mg.

These three component factors accounted for 95% of the variance in the data. Full result tables are shown in Appendix D.

A plot of the first component versus the second (Figure 6.8) produces a 'V' shape with the suspended sediment plotting on one side and upper catchment and Leven samples plotting on the opposite side. Most field samples, particularly limestone (lmst), magnesium limestone (dldo), bed, bank and overbank sediments plot in-between. When the first and third components are plotted they show a similar V shape to component plot 1 versus 2.

A component plot of the second versus the third principal axis (Figure 6.9) shows the suspended sediment samples having similar chemistry to some outlying field samples (usually from the undifferentiated (arg) and differentiated (arsd) argillaeous rocks) which are found in the upper catchment. The suspended sediments tend to be high in Mg, whilst arg and arsd rock groups are high in Fe. Overbank sediments however, tend to be high in Cr.

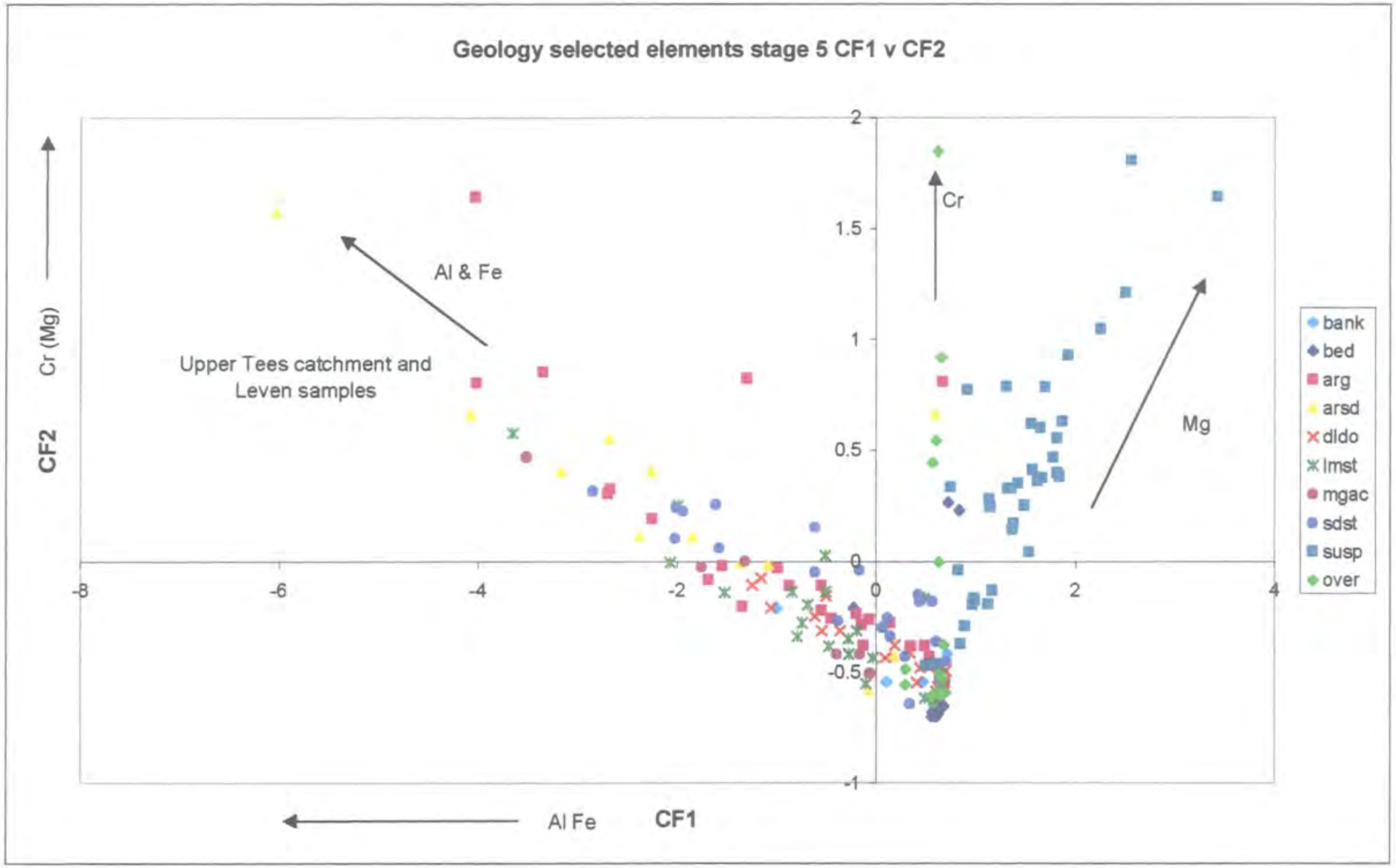


Figure 6.8 Geology stage 5 CF1 v CF2

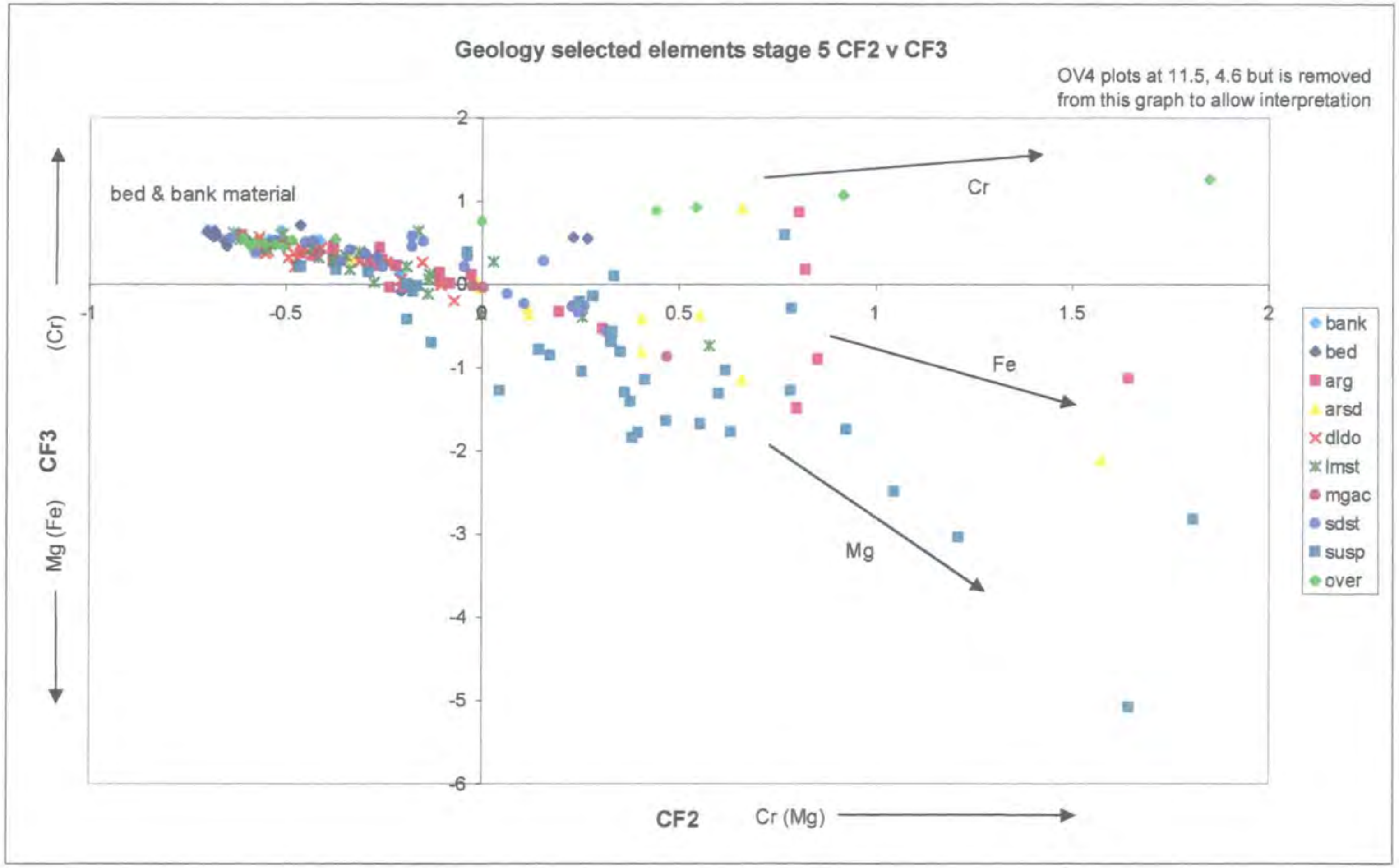


Figure 6.9 Geology stage 5 CF2 v CF3

6.3.4 Subcatchments using selected elements

6.3.4.1 Stage 2 Extraction

The first three component factors explained 91% of the variance in the data in stage 2. The first component included all elements except Fe and they were negatively related to the component factor. The second component differentiates between the samples that are rich in Co and Fe, with concentration increasing along the positive axis. On the third component axis Cr and Fe were negatively correlated whilst Co increased along the positive axis. Full result tables are shown in Appendix D.

In general, in most plots in this report, the suspended sediment samples are different from the field samples and no interpretation can be made with regard to which river was sampled or the timing of the samples relative to the peak. The majority of the field samples plot together with little variation in the Lower Tees and Skerne catchments (Figure 6.10). The bed and overbank materials also plot away from the main cluster owing to their higher Co and Fe contents. The overbank samples in the lower portion of the figure are those taken from downstream of the Leven, several catchment field samples from the Cleveland Hill area plot with these overbank samples.

The plot of the second component axis against the third, which is shown in Figure 6.11, shows the separation of the Upper Tees bed and overbank samples from those taken downstream of the River Leven confluence. The sink samples from the barrage impoundment can quite clearly be seen to plot between these two sediment sources indicating a mixture of the two. Again there is little variation in Skerne and Lower Tees field samples. Trends in the flow can be seen in the suspended sediment in the Leven and Skerne samples. The River Leven samples taken from high flow events plot in the upper part of the figure whilst the low flow samples are in the lower area of the figure. The samples taken from the River Skerne show that as the flow increases the samples plot increasingly to the left as outlined in Figure 6.11.

In Figure 6.11 the suspended sediment samples show some similarities with the field samples taken from throughout the catchment. The high flow Leven suspended samples tended to plot with the middle Leven field data, whilst the lower flow Leven samples plot closer to the Cleveland Hills data. It is possible that during high flows the runoff from fields dominates the suspended sediment chemistry, whilst at low flow material that once originated in the Cleveland Hills and was later deposited in downstream areas is being reactivated. The higher flow Skerne suspended samples plot close to the field samples taken in this catchment, while the lower flow Skerne samples plot closer to bank samples taken from the Skerne catchment. Suspended samples taken from the River Tees tend to plot differently from the Leven and Skerne as they are within the general cluster of field data. Suspended sediment samples W35 (from the River Tees at Blackwell Bridge) and W17 (from the River Tees at Stockton) plot closest to bed samples, whilst W19 (from the River Tees at Dinsdale Bridge) and W37 (Dinsdale Bridge) plot away from bed and are geochemically more similar to Upper Tees source areas.

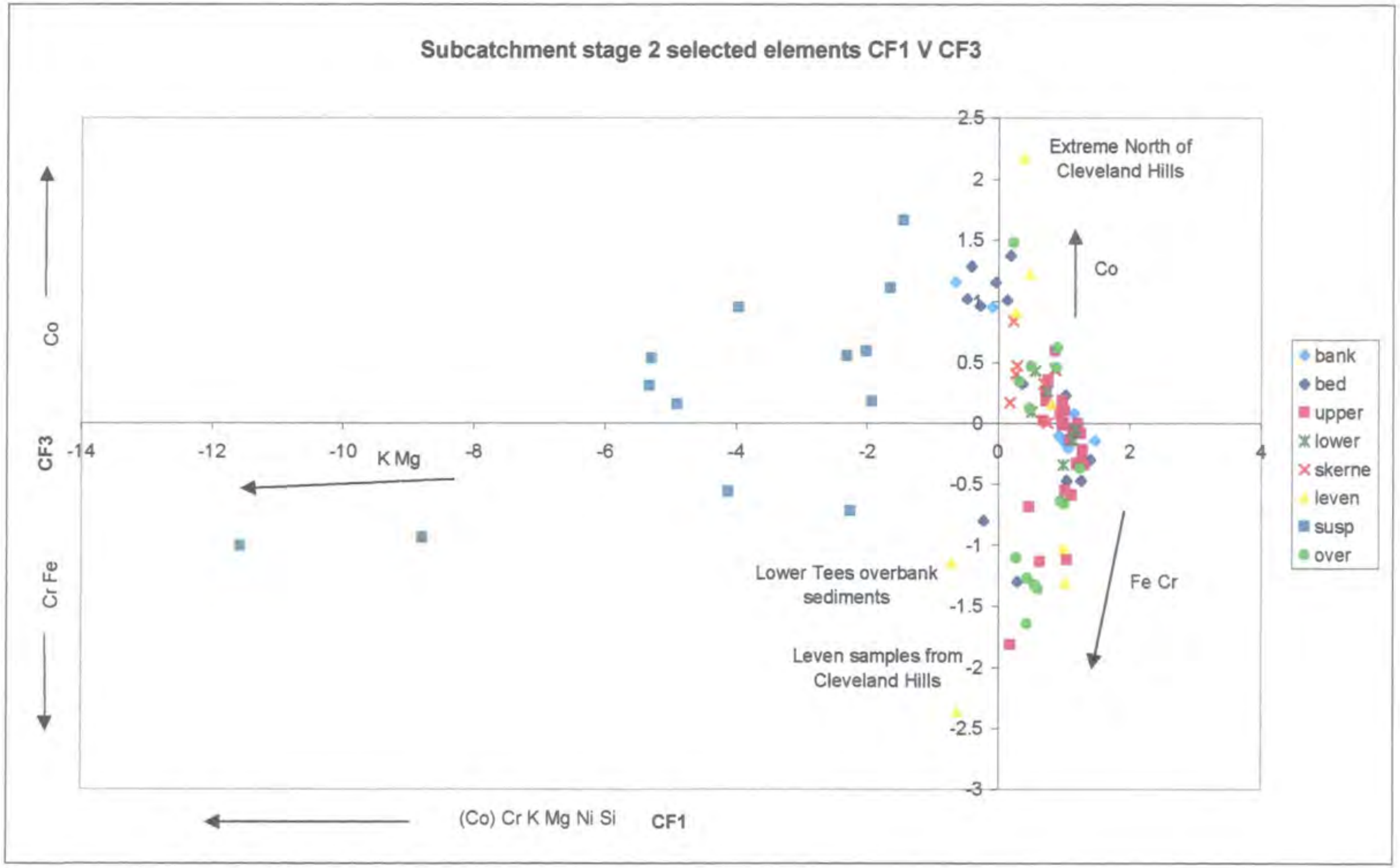


Figure 6.10 Subcatchment stage 2 CF1 v CF3

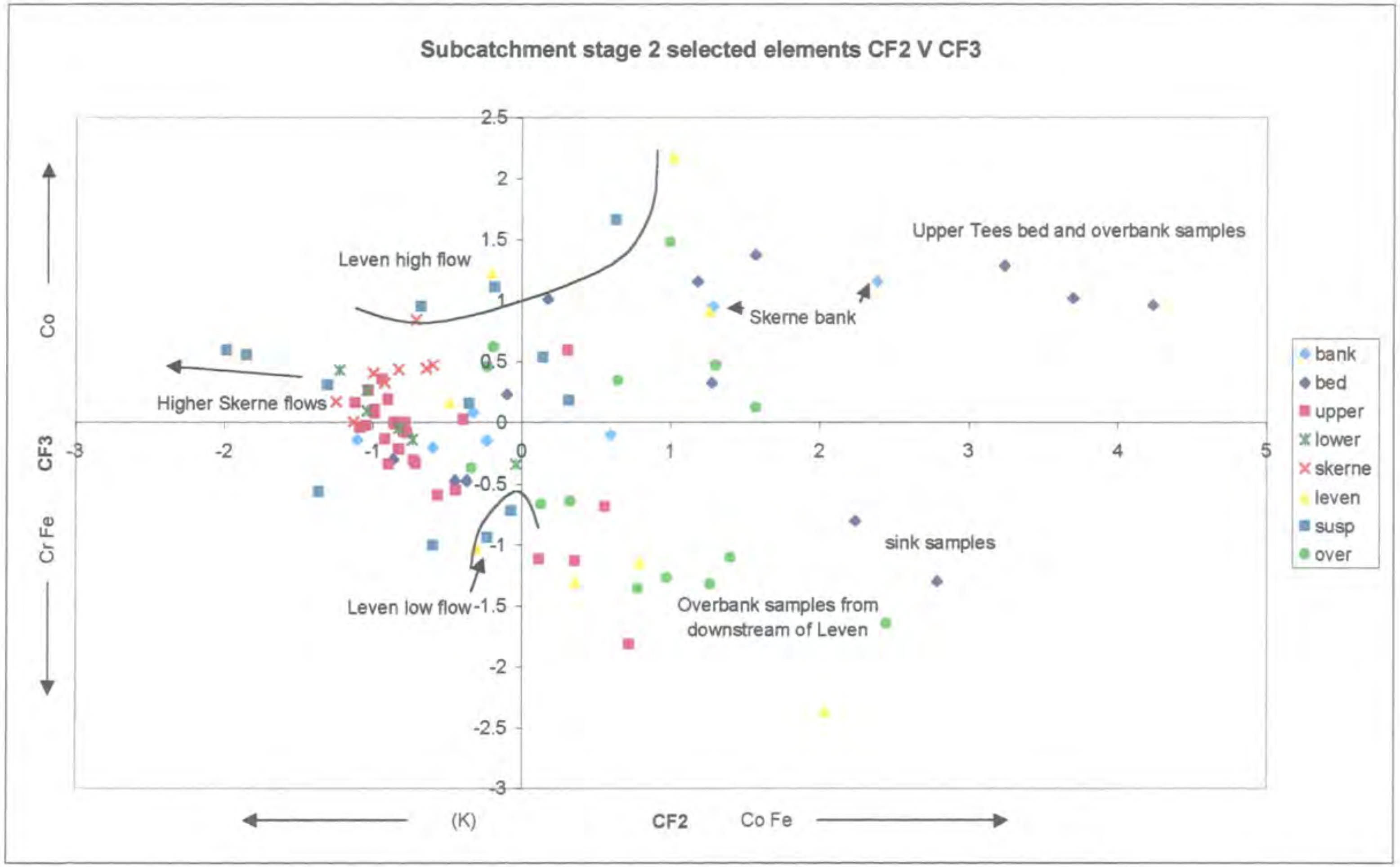


Figure 6.11 Subcatchment stage 2 CF2 v CF3

6.3.4.2 Stage 3 Extraction

The first three principal component axes account for 85 % of the variance in the data. The first component was negatively correlated with all the elements, whilst the second was negatively correlated with K and Mg and positively correlated with Fe and Sn. The third component axis was controlled by (Cr) and Sn (+ve) and Fe and K (-ve). Full result tables are shown in Appendix D.

A plot of the first component axis against the second, shown in Figure 6.12, shows that the suspended samples are separated from the field data, the majority of the field data cluster together, but several outlie the cluster. These are samples from the upper catchment and the Leven.

On a plot of the second component axis against the third, the Leven catchment is the most variable followed by the upper Tees catchment (Figure 6.13). Both are fairly similar chemically with high Fe contents. The sink samples are more similar to these Leven and Upper Tees areas than the main cluster; several overbank samples from downstream of the Leven confluence also plot close to the sink samples. This diagram indicates that most of the suspended sediment is generated from the Skerne and lower Tees catchment sources, as the suspended sediment samples are located on the opposite side of the plot to the upper Tees and Leven samples. Several of the suspended sediment samples taken from the River Leven are more similar to the lower Tees catchment than the Cleveland Hills. Two trends are seen in the overbank sediments - an upper catchment trend and a lower catchment trend. As seen earlier in landuse extraction stage 1, a distinction can be made between suspended sediment samples taken on a rising and falling limb of a flood event.

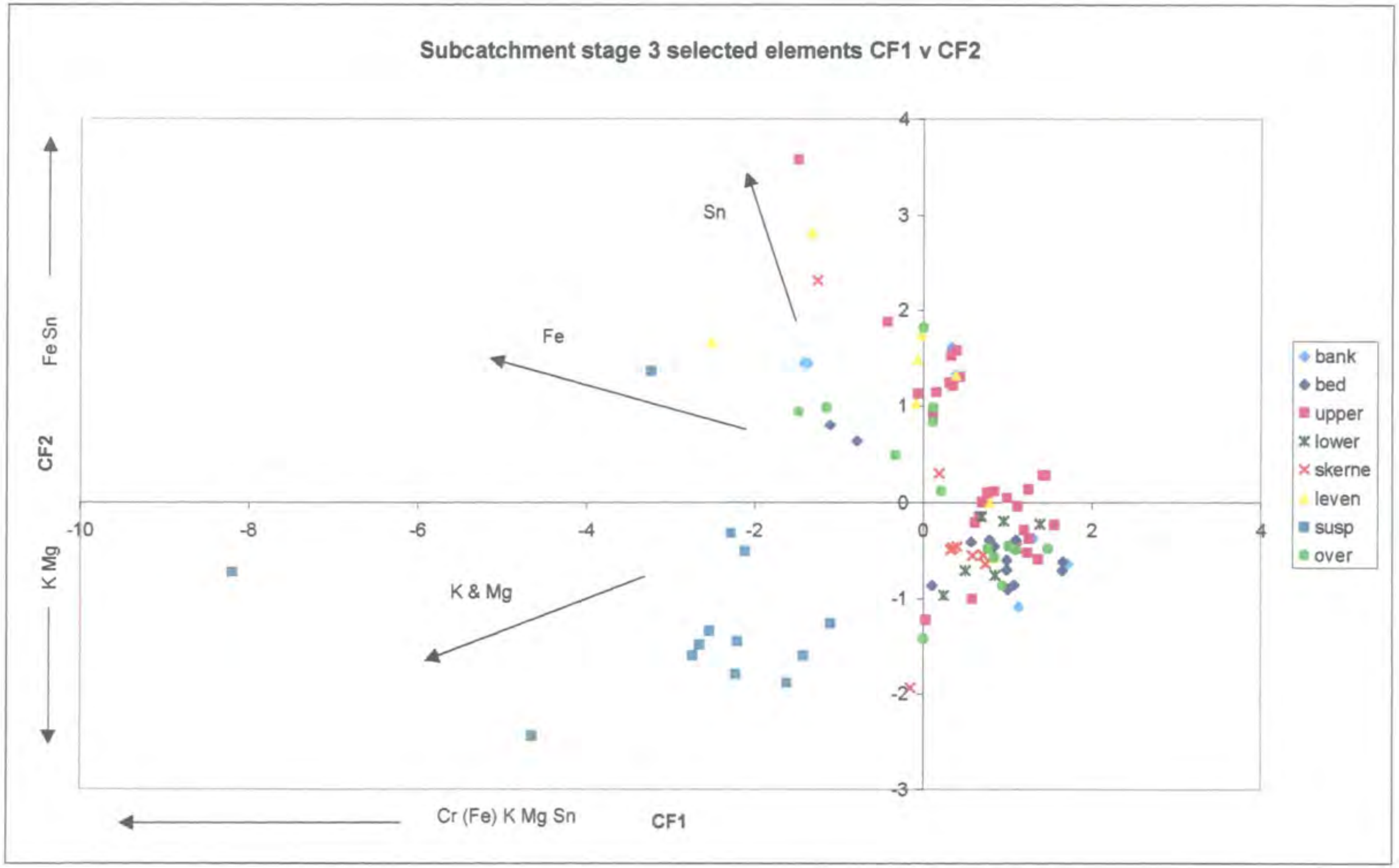


Figure 6.12 Subcatchment stage 3 CF1 v CF2

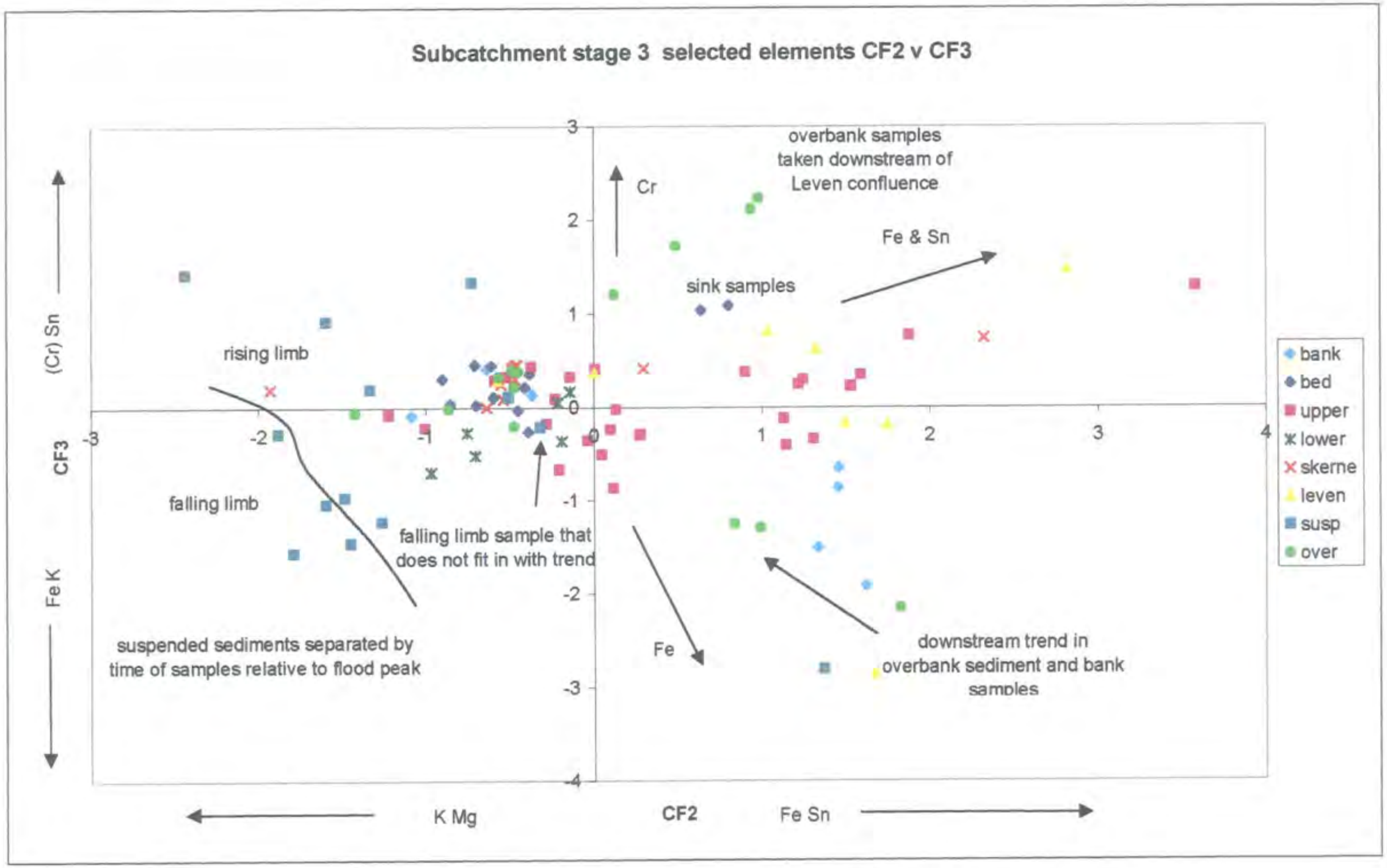


Figure 6.13 Subcatchment stage 3 CF2 v CF3

6.5 Discussion

The general statistics for each group show that there is little variation between the different geologies and subcatchments. There are more differences between landuse groups but this is generally as the result of one group being very different from the rest e.g. woodland is very high in a range of metals, whilst the bed and bank material is high in Co & Mn. The River Skerne catchment has been shown to have higher concentrations of Mg & Si, when plotted as either landuse, geology or as a subcatchment.

Extraction stages 2 and 3 appear to be more likely to be able to distinguish between groups. Stage 3 has also shown to be the phase in which most metals are preferentially bound.

Principal Components Analysis (PCA) was conducted using only those elements that were identified by Anova as being able to differentiate between the different groups being studied. The first component in PCA nearly always separates the suspended sediment from the field data, with the exception being stage 4. A distinction between samples taken on the rising limb of a floodwave and falling limb are seen in landuse stage 1 and subcatchment stage 3, with rising limbs containing a higher concentration of heavy metals. In landuse stage 3 a distinction can be made between samples taken during high and low flows. The high flows are higher in K and the low flow samples are high in Cu and Zn.

Two outlier samples were removed from the graph plots to allow the remaining points to be studied. The samples removed were field samples V19 from the River Leven catchment, in landuse stage 1 (high Ti) and overbank sample OV4 in geology stage 5 (high Cr). Generally a clustering of field samples is seen in all stages and all methods of identifying samples. In landuse extraction stage 2 disassociation is seen, with the bed and overbank sediments plotting on the opposite side of the field samples to suspended sediment. In subcatchment extraction stage 3, three apparent sediment sources are seen – (1) upper River Tees and River Leven catchments, (2) bed and bank material and (3) a main cluster of samples from lower River Tees catchment, River Skerne catchment and middle River Tees catchment samples. In subcatchment extraction stage 3, and as seen earlier in chapter 5, the suspended sediment samples are split between these 3 sources. The upper River Tees and River Leven samples have the most variability, whilst the lower River Tees and River Skerne samples tend to clump together.

Chapter 7 Overall Data Trends for Catchment

7.1 Introduction

The statistical analysis in chapter 6 looked at pre-selected elements. These elements were selected on the basis that they were capable of distinguishing between different source groups. By selecting particular elements the total number of samples in the dataset was reduced therefore allowing quicker processing and analysis time. Under this assumption only the six category landuse group returned properties for each stage. When using only the selected elements; the geology and subcatchment categories and the extraction stage 4 data provided few results. In this chapter all the data was analysed using Principal Component Analysis to determine if using all the elements would produce different results and if any new information could be concluded from them. It would also mean that the stage 4 data would be analysed.

The overall aim of this chapter is look at the chemistry of the full dataset. Firstly the total chemistry of each individual sample will be studied in terms of each phase (which relates to each extraction stage) to determine if a certain phase is more prevalent. This involved adding together the data from each sequential extraction stage (stages 1 – 4) and calculating each stage as a percentage of the total concentration for each element. This allowed the importance of the different bonding sites to be identified, to see if a particular stage always contained the highest percentage of a certain element.

Secondly the samples were again split into subset groups (landuse, geology and subcatchment) and the general variation within each group was explored by the use of boxplots.

Finally all the elements from each stage were analysed using Principal Component Analysis rather than only those identified by their analysis of variance. Each stage was analysed separately using PCA and then all stages together to look at the overall similarity or differences between the different stages.

7.2 Importance of Each Stage in Terms of Overall Metal Concentrations

Extraction stages 1 to 4 were part of a sequential extraction sequence to extract metals from different phases. When these concentrations from each stage are taken and added together they will yield the full metal concentration in a sample. From this, the percentage of the total metal bound to each stage can be calculated. This is useful as it allows the relative importance of different binding sites to be interpreted on a sample or catchment scale, or between different groups i.e. field, bed, bank, overbank and suspended sediments.

Looking at the overall dataset gave an indication as to which bonding sites the elements are preferentially bound to in each sample. The results in Table 7.1, show that the preference of trace metals bound to exchangeable sites was minimal. Only Ca (43%), K (48%) and Mg (35%) were preferentially bound to exchangeable sites. This is due to Ca, K and Mg being large cations which are easily exchangeable in the sample matrix. Calcium (Ca) (39%), Mg (25%), Mn (40%) and Zn (26%) are found bound to carbonates in large amounts. This would be expected as they are all 2^+ cations that would bind easily to CO_3^{2-} and have similar atomic sizes. Carbonates do not appear to be the primary bonding site for any trace elements. Iron was present only in very small amounts attached to carbonates, despite siderite ($FeCO_3$) being a major iron ore in the Tees catchment. All the metal cations were statistically more likely to be bound to Fe-Mn oxyhydroxides in the samples analysed, Hudson-Edwards et al (1997) found the same conclusion for the Tees catchment. Iron (Fe) up to 89%, and Sc (up to 85%) were both generally preferentially bound to oxyhydroxides, i.e. up to 89% of the total iron content is bound to oxyhydroxides in a sample, whilst Al (33%), Cr (40%), Ti (43%) and V (43%) were strongly associated with organic matter. Stage 4 was also important for a wide range of metals - Cu, Fe, Ni, Sc and Zn. The relative importance of each stage is shown in Table 7.1.

Table 7.1 Importance of each stage as a bonding site

Element	Order of Importance
Al	3>>4>>2>1
Ca	1>2>>3>4
Co	3>>2>4>1
Cr	3>4>>2>1
Cu	3>>4>>2>1
Fe	3>>>4>>2>1
K	1>>4>2>3
Mg	1>2 = 4>3
Mn	3>2>>1>4
Ni	3>>4>2>>1
P	3>>>4>2>1
Sc	3>>>4>2>1
Si	4>3>2>1
Sn	3>>2
Ti	3>4>>2 = 1
V	3>4
Zn	3>>2>4

In stage 1 Sn, V and Zn were rare in samples with only 2, 13 and 6 samples respectively containing values above zero. Vanadium was generally absent in stage 2 also, where only 3 samples contained V, which were all suspended sediment samples. It can be concluded that these elements in stage 1 and 2 are of no use in identifying sediment sources in the Tees catchment. Vanadium was present in field, overbank and suspended samples but absent in most bed and bank samples in stage 3. Vanadium is generally not very abundant (Gribble, 1988) and is therefore likely to be found only in negligible amounts. It is often found in fertilisers and may be introduced into the soil this way (Mattigod & Page, 1983).

7.3 General Statistics for each group

After allocation to groups, the overall variability of data within a group and between groups was studied in the form of box plots. This method allows quick visual interpretation of the data, as shown in Appendix H. The boxplots show the average value, maximums, minimums and spread of data along with outliers. The box and whisker plots shown here are a summary plot based on the median, quartiles, and extreme values. The box represents the interquartile range, which contains 50% of the values. The whiskers are lines that extend from the box to the highest and lowest values, excluding outliers. A line across the box indicates the median (Bostock & Chandler, 1994)

Outliers in this dataset are caused by samples having very high heavy metal contents; these can be caused by sampling in, or near an old mine site. The anomalous values could be due to measurement/analytical error. When outliers are removed, the effect on the rest of the data can be analysed. A general indication of the variability between groups can also be assessed, i.e. the spread of values and concentrations from group to group.

7.3.1 Landuse Boxplots

The boxplot graphs are shown in Appendix H, figures H.7 to H.11.

7.3.1.1 Stage 1 Extraction

The values (concentration in mgkg^{-1}) of Al, Co, Fe, Ni & Ti are appreciably higher in woodland than all other landuse groups. This may be a consequence of the majority of the woodland samples coming from the Cleveland Hills, as they contain the Cleveland Ironstone Formation, which has been mined for iron. The remaining landuse classes have little variance, although urban is high in P, Ca and Mg.

7.3.1.2 Stage 2 Extraction

The woodland samples again stand out from the general trend with relatively high values of Cr, Fe, Ni, Sn & Ti and are also consistently relatively lower in Ca, Mg and

Mn. The bed and bank samples are generally relatively higher in Co, Cu, Mn and Zn. This is probably a result of mining in the Pennines as most bed samples are taken in the upper and Middle River Tees. In general natural, semi-natural, tilled and urban have similar ranges of metal concentrations, albeit different averages.

7.3.1.3 Stage 3 Extraction

Woodland again contains significantly higher relative levels of Al, Cr, Ni, Sn, V and Ti than the other landuse groups. Bed and bank materials are once again high in Co, Cu, Mn and Zn as seen in stage 2. The remaining landuse groups have different mean values but similar ranges of values.

7.3.1.4 Stage 4 Extraction

In this stage no groups really stand out as being different. Bed, bank and wood have little or no P and only urban has appreciable amounts of Sn, though other groups have high outlier values. Bed and bank material appears to be relatively lower in Al, Ti and K. Titanium (Ti) shows a wide variation in most groups with wood tending to contain higher concentrations.

7.3.1.5 Stage 5 Extraction

Again woodland can be distinguished by its high values of Al, Cr, Fe, Ni and Ti, whilst high Mn values identify bed and bank materials. The remaining boxplots show variability but are unable to discriminate between groups

7.3.1.6 Stages as a percentage of whole sample

Wooded areas tend to have a greater percentage of total metal ions available in exchangeable form than other landuse types, particularly Co, Cr, Cu, Ni, Sc and Mn. This could possibly be a result of the woodland hampering runoff and therefore allowing metals to build up, or the woodland may have been simply planted on old mine works. Suspended sediment and bank materials have minimal amounts of Mn in extraction stage 1. Overbank sediment has significantly less Mg in the exchangeable state than other landuse types, whereas suspended sediment has ~85% of its total K available in the exchangeable state. Suspended sediment has a large percentage of Ca attached to carbonates, possibly from limestone dominated areas. Cu and Zn also occur frequently in carbonates, especially bed material. Urbanised areas have significantly less of their total Al, Si and Ti bound to the Fe-Mn oxyhydroxides. A large percentage of total metal content is attached to Fe-Mn oxyhydroxides. Natural land has a greater percentage of Ca attached to organics than other landuses - possibly from upland areas, where sites are underlain by limestone and grazed by animals. They also have high Fe and Zn, which are both capable of binding to organic matter and carbonates. Suspended sediment has a very small percentage of K, Mg, Ni and Zn attached to organic matter. Could this be a result of low concentration of organic matter in suspended sediment, or as a result of the metals having preferences for other sites?

7.3.2 Geology Boxplots

The different rock types used are those outlined in section 6.3.3 and will be referred to by their code names, to avoid repetition of long worded rock units. The codes are explained in Table 6.3. The boxplot graphs are shown in Appendix H, figures H.12 to H.16.

7.3.2.1 Stage 1 Extraction

When an element is present the boxplots for each geological group are similar in spread and value, except for Mg, Si and to some extent Mn & P. Dolomitised limestone (dldo) has the smallest range and highest average for Mg, indicating that it is consistently high in all samples taken. The range for lmst and mgac is also small, showing these three groups to be different in their Mg values. However, arg rocks (differentiated and undifferentiated) and sandstone have wide ranges that envelop all categories. Dolomitised limestone (dldo), lmst and mgac have similar patterns with regard to Si content; sdst has the widest spread equalling all other groups. Argillaceous (arg) rocks generally contain more Si than arsd, whereas Fe is rare in all groups. Cobalt (Co) is absent from dldo and lmst, and Cr is only present in arsd and sdst – albeit at low concentrations.

7.3.2.2 Stage 2 Extraction

Dolomitised limestone (dldo) contains the highest concentrations of Ca, K, Mg, Mn and Si (which can all substitute into the Ca-Mg limestone), whilst Fe, Sc and Sn are absent. It is generally difficult to differentiate between groups with any confidence, as sample ranges tend to overlap. Sandstone (sdst) has the greatest range of P values, whilst mgac has highest Zn values. There are many outliers in the data, particularly Ca (5 groups), Co, Cr, Cu, Mn, Sn, Ti and Zn.

7.3.2.3 Stage 3 Extraction

In several elements it is possible to differentiate between three or four of the geological groups from their average concentrations and range of values, but often there are one or two geological types that span the whole data range. Again P has a very wide range of values, most notably in lmst & sdst. Magnesium (Mg) is low in arsd & mgac whilst Zn has the largest range in mgac.

7.3.2.4 Stage 4 Extraction

Igneous material (mgac) has the most variable range of concentration in several metals including Al, Ca, Co, Cu, Fe, Ni, V and Zn. Limestone (lmst) and sdst are the only groups to contain Sn, but only in very small quantities. Other than mgac the concentration ranges are similar in most groups. There is always variability but no ability to differentiate between groups. There are many outlier values that may be disturbing the boxplots including K in arsd, Mn in arsd and arg, Ca in several groups and P in sdst.

7.3.2.5 Stage 5 Extraction

Cobalt (Co), Sc, Sn and V occur only in small concentrations, generally less than 10 mgkg^{-1}. The boxplots show some degree of variability in Al and Mg, although it is impossible to identify any geological types on the basis of the elements shown here with any degree of certainty. There are many outliers in stage 5, especially in Cr, Ni, P, Sn, Ti and Zn.

7.3.2.6 Stages as a percentage of whole sample

There is regularly a similar proportion of each element bound to exchangeable sites in each group. In the carbonate phase the igneous rocks have less of their total amount of Ca and Mg in this phase - these are the only non-sedimentary rocks in the catchment. All the sedimentary formations in the catchment are known to contain some amount of inter-bedded carbonates. The dolomitised limestone contains most of its Mn fraction attached to carbonates rather than to any other geology types; this can be explained by substitution of Mn for Mg in the magnesium limestone. The majority of elements have similar proportions bound to Fe-Mn oxyhydroxides. This phase is the most important for metal ions. Limestone and sandstone have over 70% of available Co bound to Fe-Mn oxyhydroxides. These rock types are generally low in Co (Plant & Raisewell, 1983). Dolomitised limestone has a greater percentage of Cu tied up in Fe-Mn stage than all other geological groups.

7.3.3 Subcatchment Boxplots

The upper catchment referred to in these works consists of all areas above the Skerne confluence. The Skerne and Leven catchments are obviously the full catchment areas for these tributaries. The lower catchment is the River Tees catchment downstream of the Skerne confluence to the barrage, but it does not include the Skerne or Leven catchments. The subcatchment groups do not contain bed and bank material. The boxplots graphs are shown in Appendix H, figures H.17 to H 21.

7.3.3.1 Stage 1

There is little differentiation between most catchments in stage 1. The biggest differences are that the lower catchment is higher in K and P (possibly due to fertiliser use in agricultural areas) and the Leven is high in Ni. There are a number of outliers especially in the Leven – high Al, Cr, Fe and Ti (V19). In the upper catchment some samples contain high amounts of Co, Cu, Mn and Ti.

7.3.3.2 Stage 2

Again Ni is high in the River Leven catchment, which also has wide ranges of concentrations for Al, Cr, Cu, Fe and Ni. The lower catchment again has the greatest spread in K and P, despite the River Skerne catchment having a higher average K value. Magnesium (Mg) is highest and most variable in the River Skerne catchment, where the main rock type is dolomitised limestone. The upper River Tees and River Leven catchments are the only catchment with appreciable amounts of Sc. The River Skerne catchment has the most spread of Zn, but with little Sn, and highest concentrations of Si, Mg and Mn.

7.3.3.3 Stage 3

The lower River Tees catchment contains less Al, Ni and Sn, while Mg, Mn, K, Cu and Ca are highest in the River Skerne catchment. The River Leven catchment has the highest concentrations and most variability in Cr, Fe, Ni and V, but lower Ca, Mg and Mn. In general it is difficult to distinguish between groups. Most outlying values are in the River Leven catchment (K) or upper River Tees catchment (Ca, Cu, Ni, Mg, Ti and V).

7.3.3.4 Stage 4

The lower River Tees catchment has low variability about the mean in virtually all elements, but most variance in Sn. The Rivers Skerne and Leven catchments tend to be the most variable catchments with regard to Al, Cr, Fe and Si. Most outliers are in the upper River Tees catchment in all heavy metals.

7.3.3.5 Stage 5

There is little difference in any element, as the boxplots tend to be the same size and height, and it is impossible to distinguish between any subcatchments using stage 5. All subcatchments contain outlying values.

7.3.3.6 Stage as a percentage of whole sample

There is little or insignificant variation between the percentages bound to each stage in each subcatchment. The River Leven catchment has slightly more Al, Cr, Cu, Fe and

Sc bound in the exchangeable stage. The upper River Tees catchment tends to have more Sn bound to carbonates and Fe-Mn oxyhydroxides. The River Leven catchment has less than 1% of the P content bound to organics, whilst the River Skerne catchment has half the percentage of Cu and Zn bound to organics than do all the other catchments.

7.4 Principal Component Analysis

All Principal Component Analysis was conducted on the full range of elements for each sample. The results are shown using each samples 'landuse type' as the identifier/key as this was the group found to be the best at discriminating between groups. All the PCA eigenvalue results are shown in Appendix F and are explained in the relevant section in the text.

7.4.1 Stage 1 Extraction

The first four components in stage one explain the variance in 84% of the data as shown in Appendix F, Table F.1. The first component includes all the elements except Mn, P & Zn and therefore gives a feel of the general chemistry in the dataset. The second component is controlled by the metals Al, Cr, Fe, Sn and Ti in positive correlation and Ca, Cu, K, Mg, Si and V in the negative direction. The third component is controlled dominantly by Co, Mn and Zn; this is due to a concentration factor present in samples. The fourth component is controlled only by P.

The first principal component factor, (CF1), separates the suspended sediment from field, bank, bed and overbank sediment as the suspended sediment has large concentrations of Ca, K & Mg. Scandium (Sc), Sn, V and Zn are generally rare in all stage 1 samples, whilst Co and Ti appear in less than half the dataset, and then with small values. These elements are likely to be included in CF1 due to their absence in the data as a whole. Overbank sediments tend to plot away from the suspended sediment (Figure 7.1), indicating a depletion of the elements found in suspended sediment.

Component factor 2 and CF3 define outlier samples V19 and D6 respectively. Sample V19 from the Cleveland Hills was found to be an outlier in all stages due to its high metal contents, in this case Al, Co, Cr, Fe, Ni, Sn and Ti. Sample D6 was a bed sample from the middle Tees catchment area and is characterised by high Co, Mn and Zn. The high concentration in this sample is possibly due to upstream mining sources. Phosphorus (P) is the only element defining the fourth component axis, with samples from the lower and middle Tees containing high values. These are areas of the Tees that have a large proportion of agriculture, which could possibly be the cause through fertiliser use. Overbank, bank and bed contain relatively low levels of P, whilst some suspended samples contain high values. This indicates that high P levels in suspended sediment is most likely to have been the result of washing from fields into the river. The graphs produced by plotting the component factors using stage 1 extraction results show a separation of suspended sediment from the rest of the data, along with some outliers as shown in Figure 7.1. The identification of sediment sources is unlikely to be determined using stage 1 extraction.

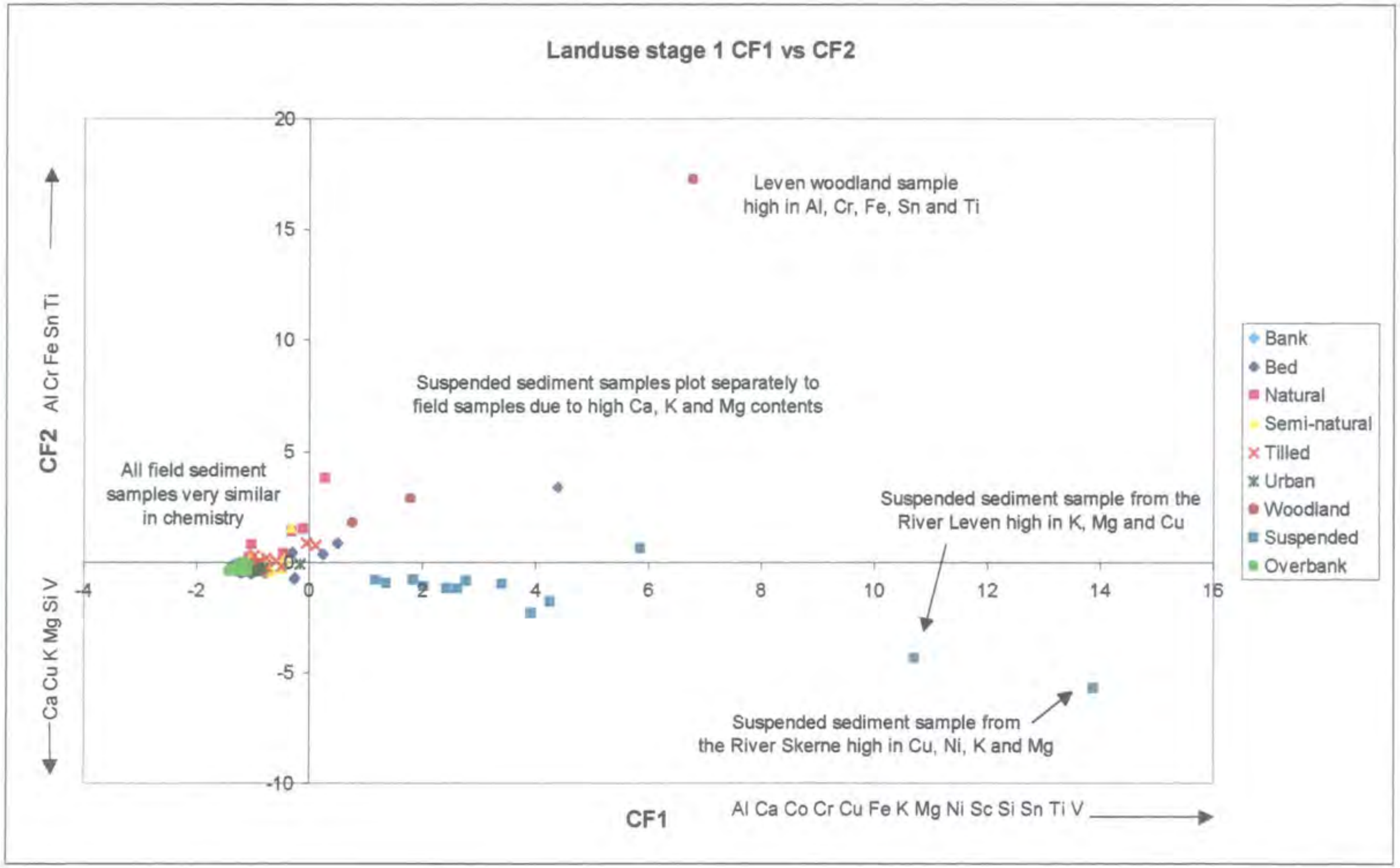


Figure 7.1 Stage 1 CF1 vs CF2

7.4.2 Stage 2 Extraction

The first five component factors in stage 2 explain 82% of the trends in the data, shown in Appendix F, Table F.2. The first component in stage 2 is negatively correlated to all elements analysed except Al, Fe, Mn, P, Sn and Ti. The second component is positively governed by Co, Fe, Mn and Sn and negatively by K and P. The third component is strongly affected by Mn, whilst the negative axis in related to Al, Sc and Ti. The fourth component is controlled by Co, Mn and P, whilst V is negatively correlated. Component 5 is controlled by a mixture of Fe, K, P and Sn in the positive axis and Al and Sc in the negative.

The first principal component again shows general chemistry with most samples containing some Ca, Cr, Cu, K, Mg, Ni, Sc, Si, and Zn, whilst V is generally absent (exception is 3 suspended samples). Scandium (Sc) and Ti are present only in approximately half the samples, with Sc being rare in samples taken from tilled land. Phosphorus (P) is usually absent in bed and bank samples - possibly washed away due to its high mobility. Overall the field samples tend to have lower concentrations of metals than the suspended samples and are separated as such. Bed samples tend to plot in-between suspended and field samples, indicating a half way stage between sediment sources and that carried in river water.

The second component factor separates bed, bank and overbank sediments from the field and suspended sediment samples. The overall K and P concentration of suspended samples resembles that of field samples, whilst the bed, bank and overbank sediments are richer in Co, Fe, Mn and Sn relative to the field samples, as shown in Figure 7.2. The third component axis (CF3) appears to split suspended sediment samples as shown in Figure 7.3. Those samples containing high Al and low Cu plot further away from field data than those with low Al and high Cu. On the fourth component axis (CF4) the samples have a similar spread of values, with the majority of suspended sediment samples plotting close to bed samples and the 3 samples containing V plotting away from the bed sediments. On the fifth component (CF5) all samples are mixed across the axis and no differentiation between land samples can be made. The suspended sediment samples taken from the Skerne plot separately from the remaining sediment as can also be seen on component plots CF2 versus CF4 (Figure 7.4).

7.4.2.1 CF2 v CF3

The field, bed and bank samples form a tertiary plot (a triangular plot with three apparent sources – woodland, tilled/semi-natural and bed material), as seen in Figure 7.3 with the suspended samples plotting within and around the field data. Tilled and urban samples cluster together to produce the main sediment source on the left side of the diagram. The second source is composed of material from the upper catchment – in the upper right quadrant on the graph. The third source is composed of semi-natural, natural and woodland and is situated in the lower right quadrant on the graph. The semi-natural, natural and woodland samples in this cluster were all taken near to old mining areas and were predominantly taken from the Cleveland Hills. These samples could represent the relatively unweathered products of mining in the Cleveland area, whilst the bed/bank samples could represent the weathered end products of mining in the upper catchment. The clustered till and urban samples represent those where no significant mining has taken place. The suspended samples generally plot close to tilled and natural landuse sources, indicating that the suspended sediment is sourced from non-mining areas.

7.4.2.2 CF2 v CF4

This plot shows a tertiary mixing diagram as seen in Figure 7.4 and is similar to that shown on the plot of CF3 v CF4. The majority of field samples plot together whilst an upstream Tees bed and bank source is seen in the upper right quadrant and a predominantly Leven source is seen in the lower right quadrant.

The overbank samples seem to be showing two trends. The sample’s first trend has similar chemistry to the bed and bank samples in the middle catchment. The second trend of note is located downstream of the Leven confluence. These samples plot between V19 (a Leven outlier) and the general cluster of field samples. Samples taken from the Leven bed and bank plot at this end of the cluster, helping to confirm a Leven sediment source.

The two ‘sink’ samples taken from the barrage area, plot between the two sediment sources indicating a mixture of upper Tees and Leven source material. Suspended sediments generally plot away from the two mining source areas and next to field samples, particularly tilled land. A Leven sample from low flow conditions plots near to the suspected Leven source, whilst a high flow sample from Low Moor outlies the whole dataset, owing to its high V content. The suspended sediment samples from the Skerne generally plot in the upper left quadrant, these samples being relatively higher in K and P than other samples. The Skerne is a predominantly tilled catchment, where again high K and P values could be the result of fertiliser use.

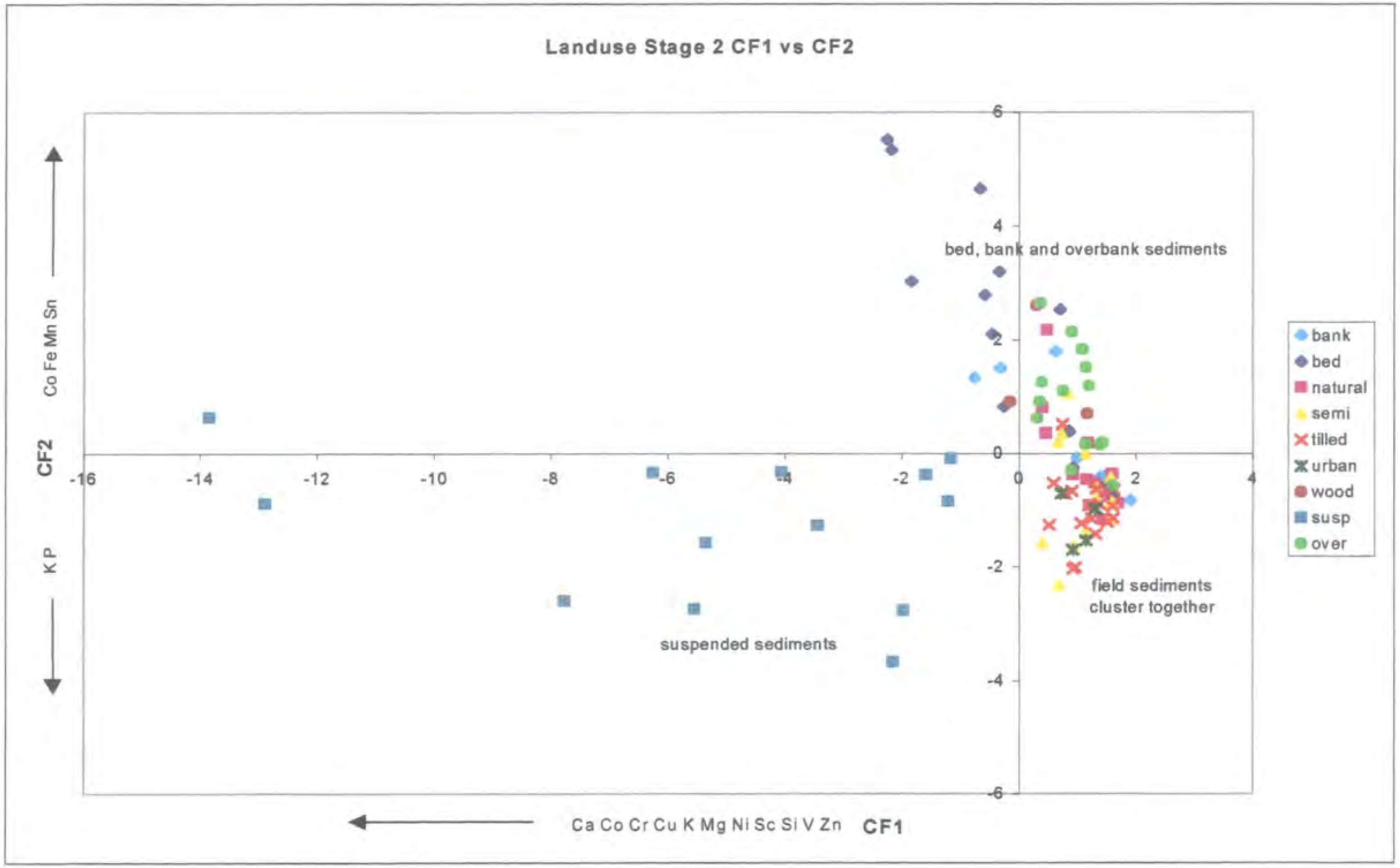


Figure 7.2 Stage 2 CF1 vs CF2

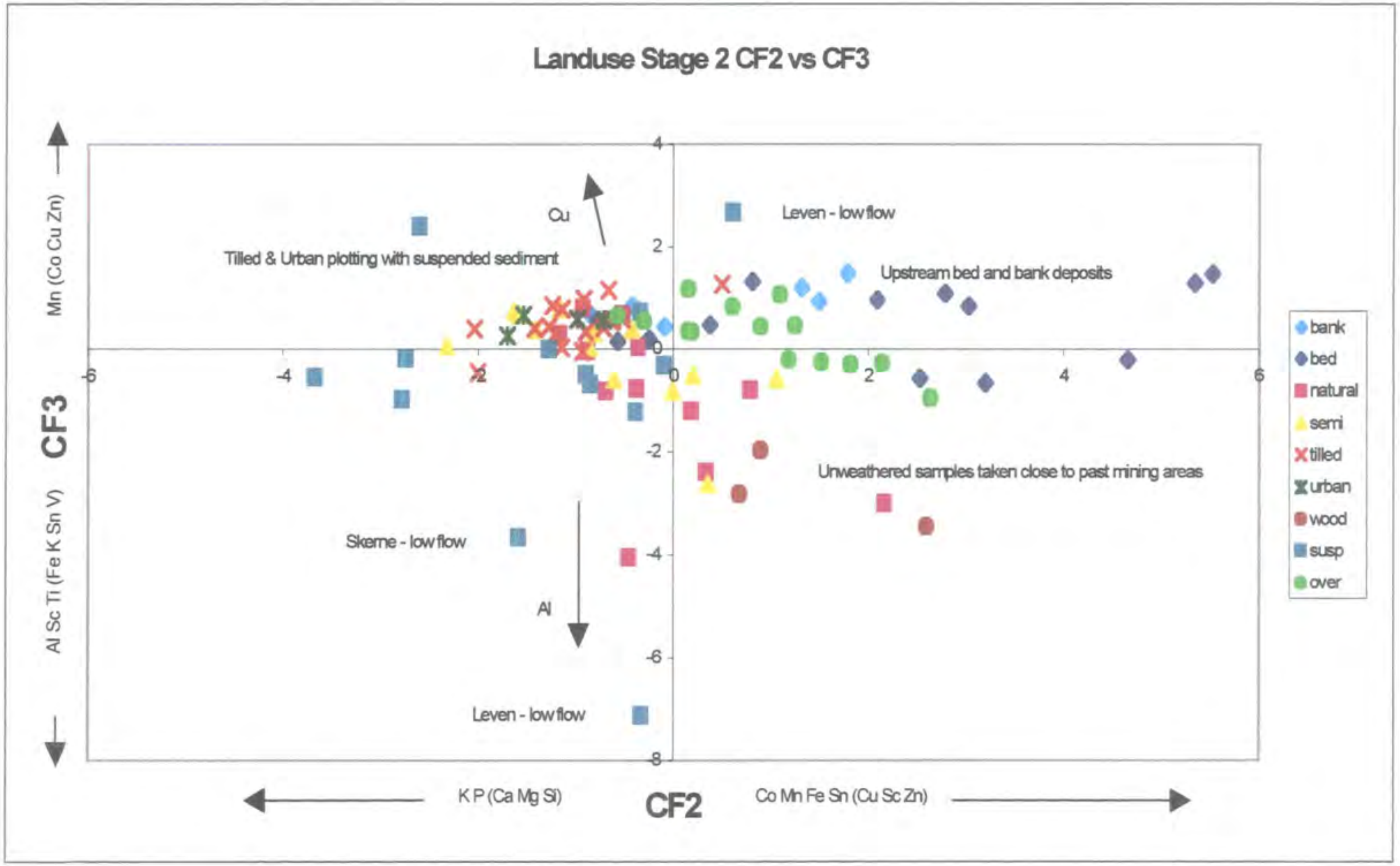


Figure 7.3 Stage 2 CF2 v CF3

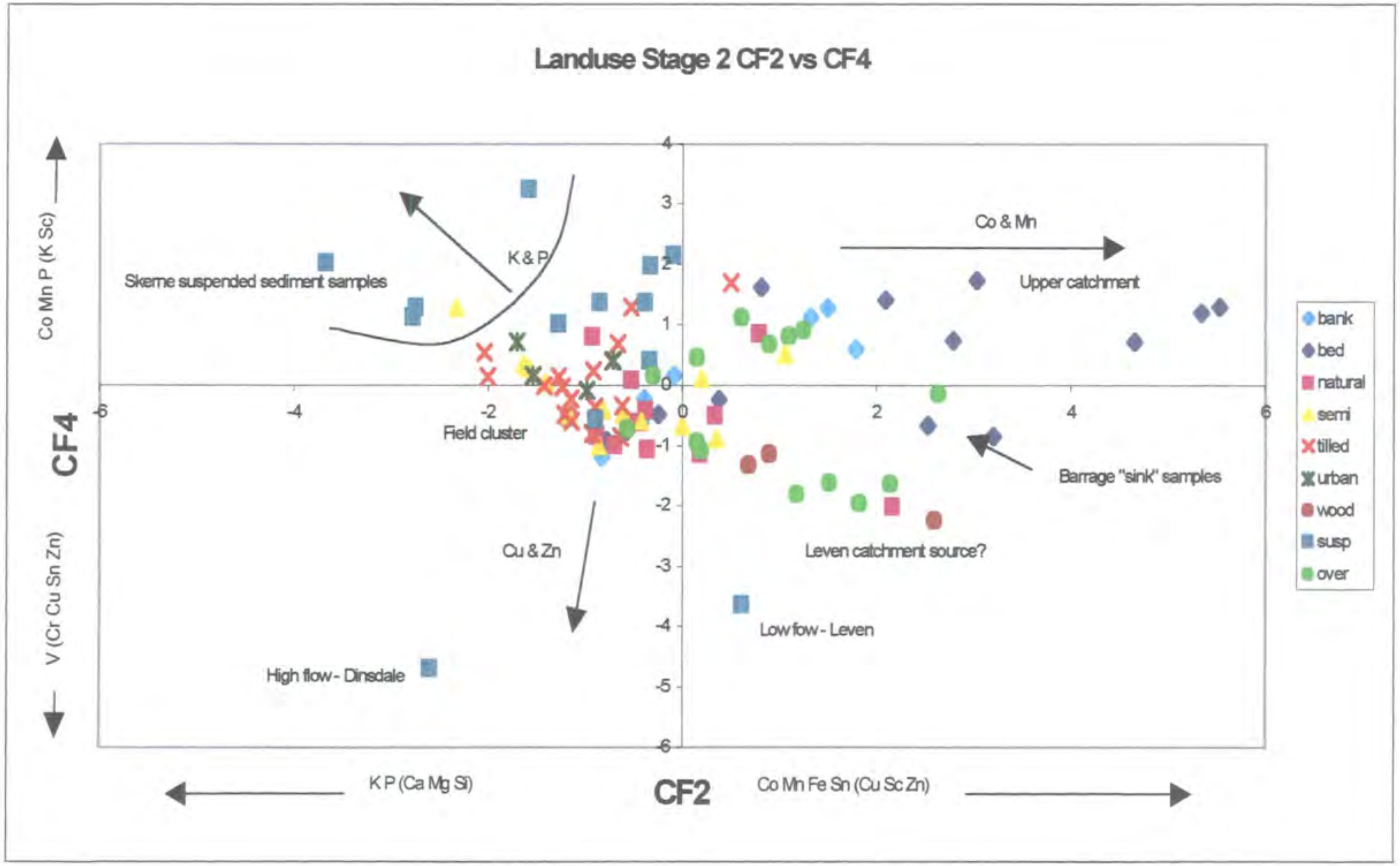


Figure 7.4 Stage 2 CF2 v CF4

7.4.2.3 CF2 v CF5

Again the suspended sediment samples plot with the land samples taken from tilled, urban and semi-natural landuse's as shown in Figure 7.5. The overbank and bed samples plot away from the general cluster. The overbank samples contain high Cr, Fe and Sn, whilst the bed samples contain high Co, Cu, Mn and Zn.

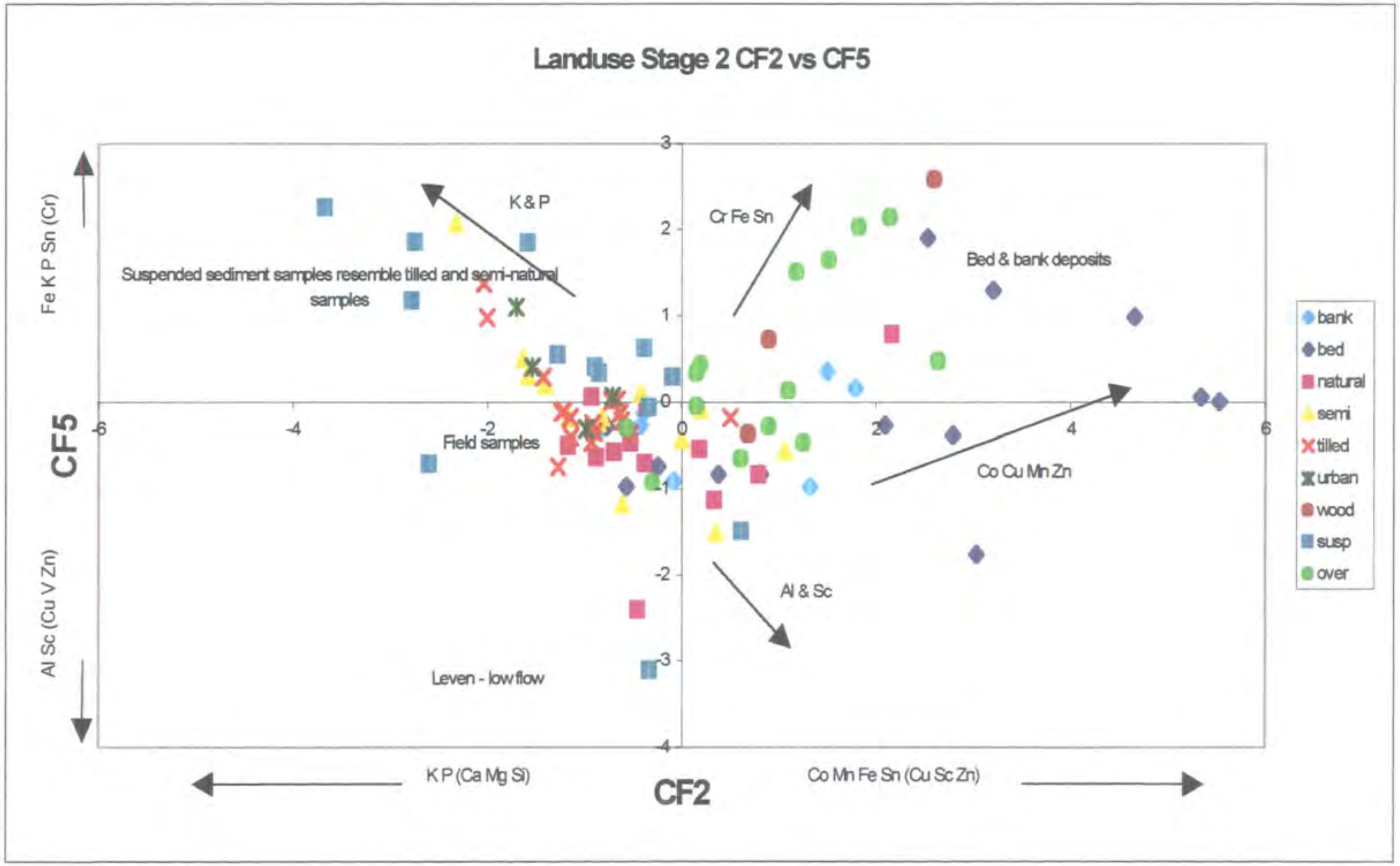


Figure 7.5 Stage 2 CF2 v CF5

7.4.3 Stage 3 Extraction

In stage 3 the first five components explain 84% of the variance in the data, shown in Appendix F, Table F.3. The first principal component is positively related to all elements except Co and Mn, which are positively related to the third component. A good correlation between all samples and the metal concentrations show that there is possibly a common source for all samples (Qu and Kelderman, 2001). The second component axis represents Ca, Cu and Zn on the positive axis and Al, Fe, P, Ti and V on the negative axis. The fourth component is controlled mostly by K and Sc (positive axis) and Sn (negative axis), whilst the fifth component axis is related to K and P (positive axis) and Ti and V (negative axis).

The first component separates the suspended sediment from the rest of the data, with generally higher values of all elements particularly Ca, K, Mg, Ni, Sc, Si, V and Zn. On the second component (CF2) all the non-water samples show little variation and show outliers in the suspended sediment. Suspended sediment sample W5 (from the River Leven) outlies on the negative axis due to its high Al content, which is 5 times greater than the next largest sample, whilst on the positive axis those which are very high in Cu, Mn and Zn (those sampled in the Rivers Skerne & Leven) dominate. The third component (CF3) picks out samples that are higher in Co and Mn than the general trend, which are predominantly bed and bank samples along with an overbank sample from Langdon Beck (in the upper Tees catchment). CF4 shows little differentiation between groups, though some suspended sediment samples plot higher than the rest of the dataset. All samples have similar ranges of values on CF5.

7.4.3.1 CF3 v CF4

Figure 7.6 shows similar results to those seen in stage 2 extraction. All field data are quite variable but cluster loosely together. The bed and bank data plot separately from the field data due to their higher Co & Mn values. The overbank samples plot in two lines as seen in stage 2 extraction. The first runs through the field data (affected by sample V19 and other Leven samples as shown in stage 2) and a smaller pattern following the bed & bank data, indicating more weathered upstream samples. The suspended sediment tends to plot above but close to field samples in CF4 space. There are three suspended samples which plot below/within field data - W9, W11 and W37 (same low/high flow samples seen in stage 2). W35 (upstream of the Skerne) plots within the bed/bank data and is obviously affected by an upstream source.

7.4.3.2 CF3 v CF5

Figure 7.7 is similar to CF3 v CF4 except that the main cluster of suspended samples now plot with the tilled and semi-natural landuses, whilst suspended sediment samples W5, W9 and W37 are below the field data. Suspended sediment sample W35 again is positioned within the bed and bank material.

7.4.3.3 CF4 v CF5

Figure 7.8 shows that the bed samples cluster together - the two outlying samples are from the barrage impoundment (sink samples). On this graph the two sink samples are controlled by field rather than bed/bank samples as seen earlier. The samples from a semi-natural landuse vary when plotted on the fourth component axis, but this cannot be explained in terms of their landuse or location. They have high values of Fe, Sn, Zn and Cr. The high and medium flow suspended samples plot together in a cluster. Suspended sediment sample W35 is again controlled by bed/bank material. Low flow suspended samples W5, W9 and W11 are closer to bed, bank and overbank material than field samples.

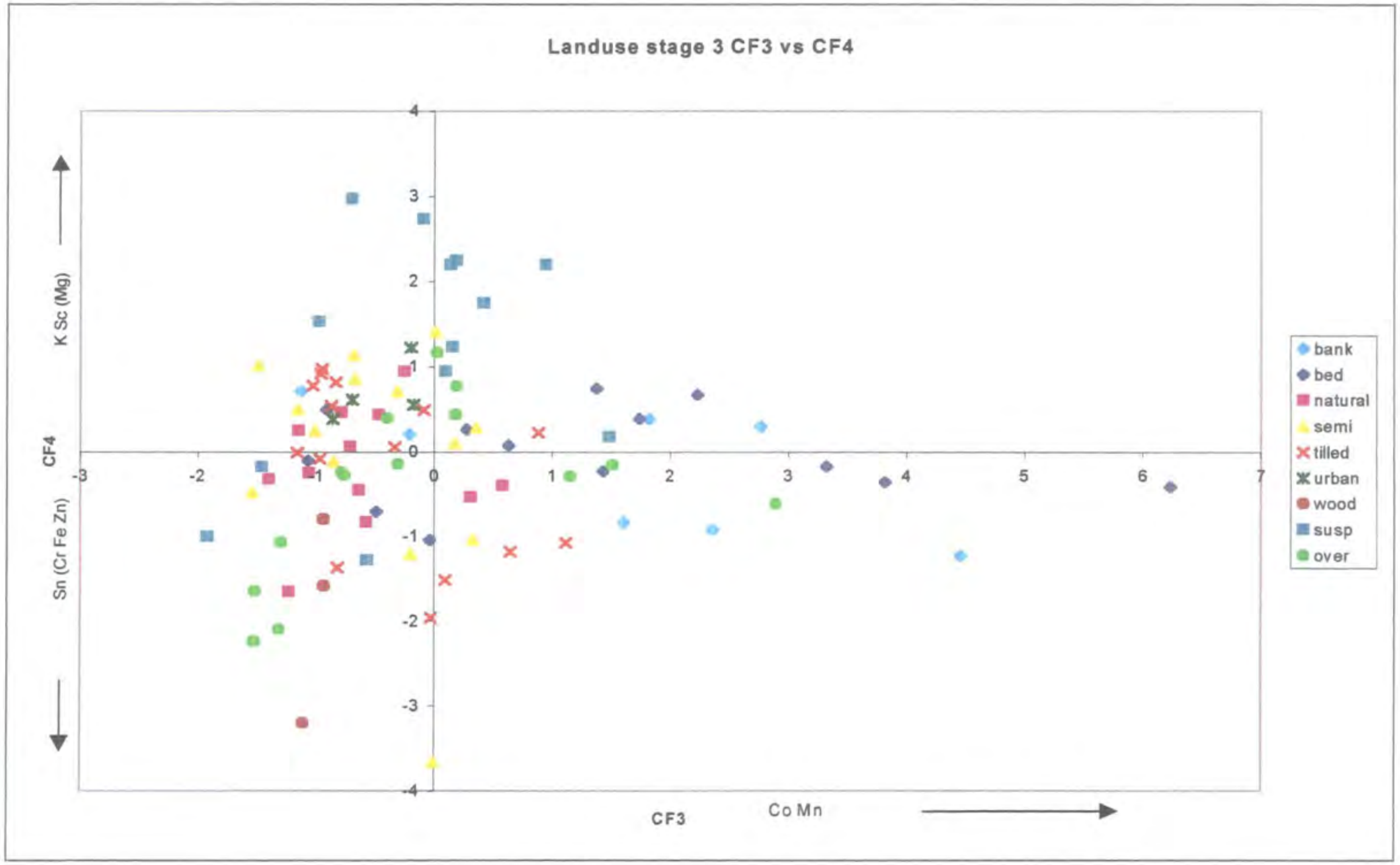


Figure 7.6 Stage 3 CF3 vs CF4

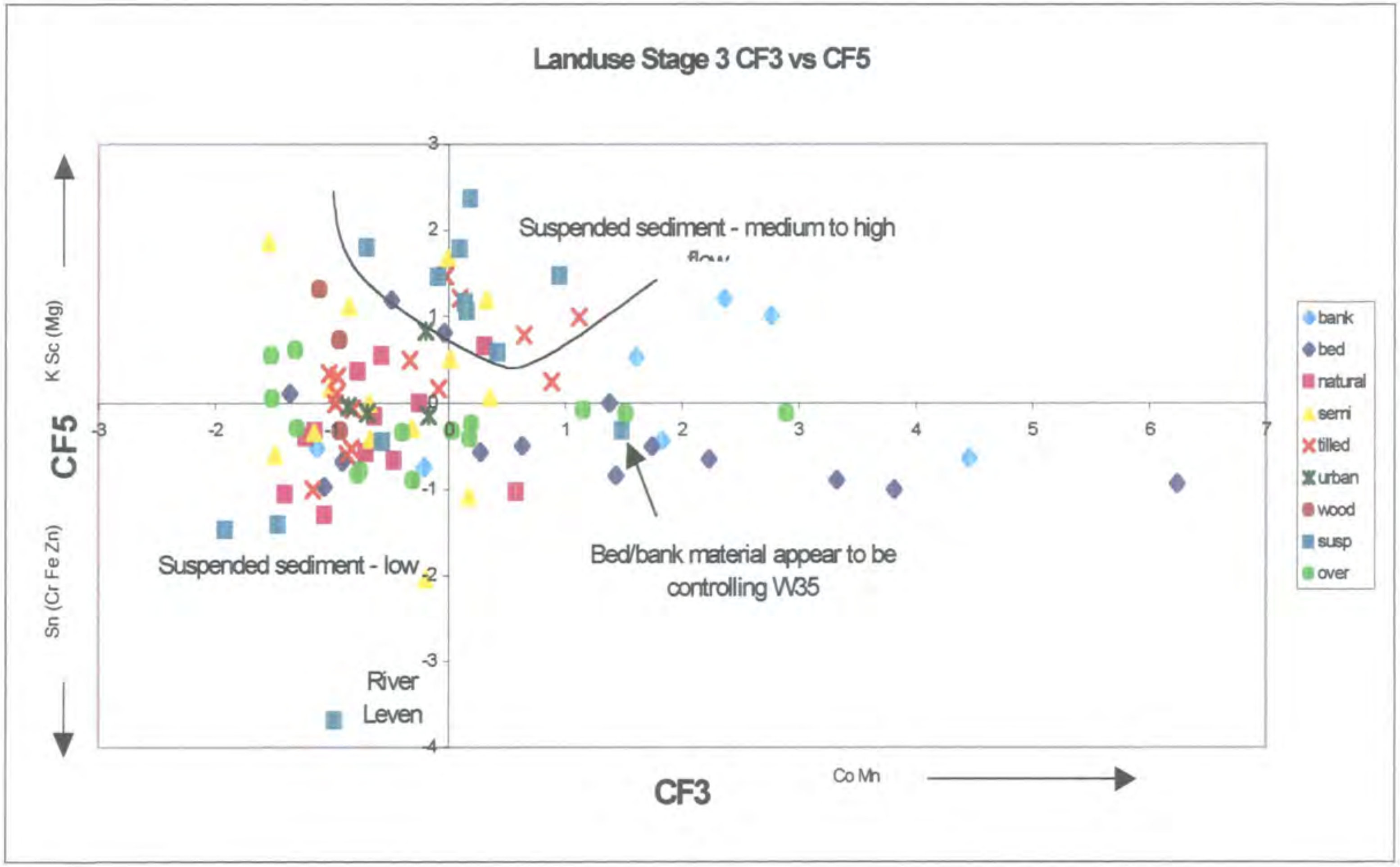


Figure 7.7 Stage 3 CF3 v CF5

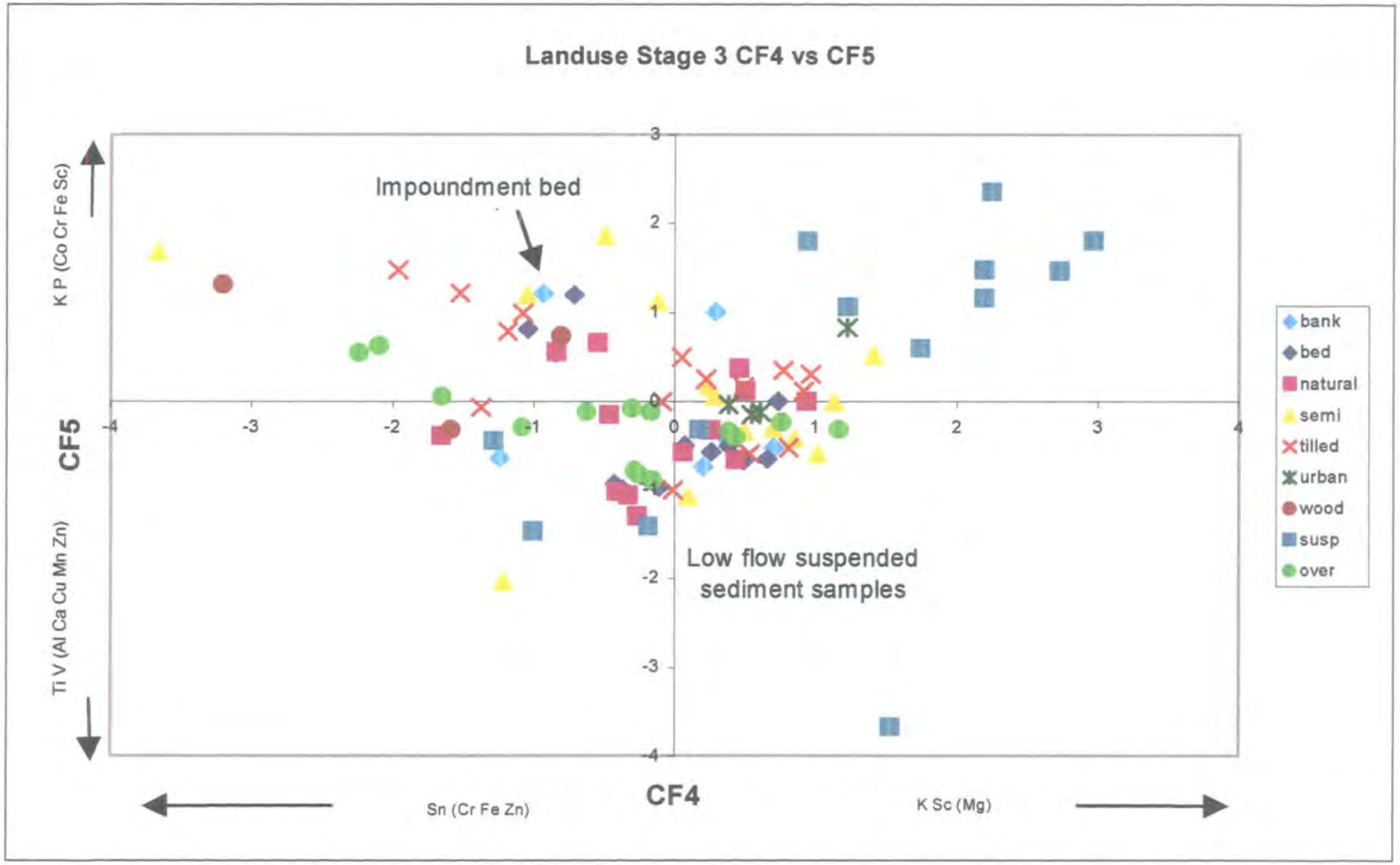


Figure 7.8 Stage 3 CF4 v CF5

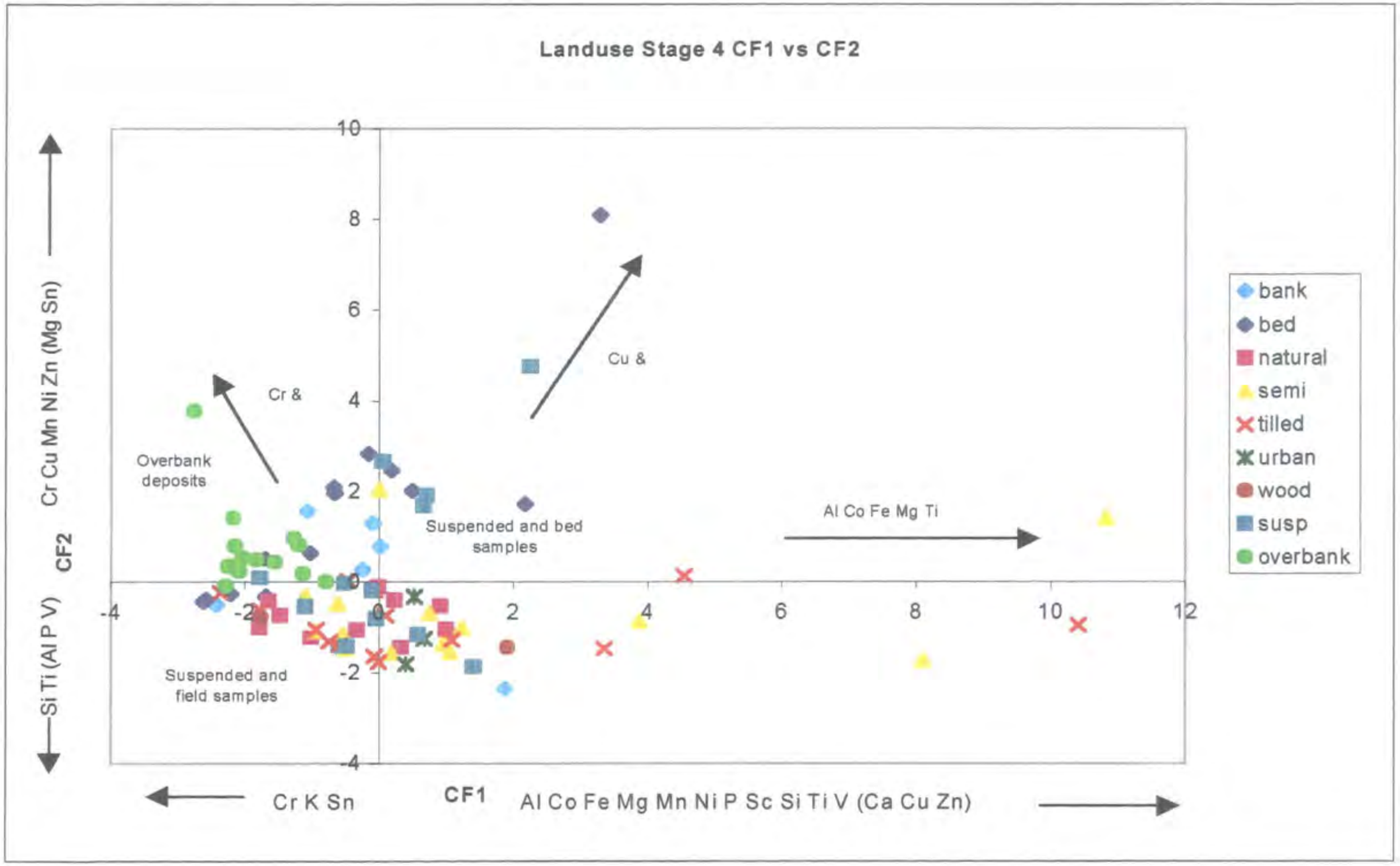


Figure 7.9 Stage 4 CF1 v CF2

7.4.4 Stage 4 Extraction

The first five factor components in stage 4 explain the variance in 75% of the data as shown in Appendix F, Table F.4. The first principal component axis is positively correlated with all elements except Cr, K and Sn, whilst the second is positively correlated with Cr, Cu, Mn, Ni and Zn (positive) and Si and Ti control the negative axis. The third component axis is controlled by Cr, Mg and Sn (positive axis) and Cu and Zn (negative axis), whilst the fourth component is explained only by Cr (on the positive axis) and Ca, K and Mg (negative axis). The fifth component axis is positively controlled by Ca, Mn, P and Sc and negatively by Al.

The first component factor shows little discrimination between the groups, but picks out the field samples that are higher in Al, Co, Fe, Mg, Ti and Zn than the general trend. The non-separation of suspended sediment from the rest of the data indicates that organic bonding sites are not as important for the metals analysed in the suspended sediment as in the previous stages. On the second component axis the field and suspended sediment tend to plot away from the overbank, bed and bank sediment samples, giving an indication that they have lower values of Cr, Cu, Sn and Zn. The third component factor axis is similar to the second, but separates samples high in Cr-Sn from those high in Cu-Zn, with the rest of the data showing little variation. The only information gleaned from the fourth component axis is that M7 is distinct from the rest of the data due it its high Ca and Mg. The fifth component factor shows no variation in the different groups, but picks out some minor outliers due to high P contents.

7.4.4.1 CF1 v CF2

Figure 7.9 shows that some of the suspended sediment samples are similar in chemistry to field samples whilst some are similar to bed and bank samples. Suspended sediment samples W11, W35, W36 and W37 plot with samples taken from river beds, whilst the remainder of the suspended sediments plot with field data. Suspended sediment sample W35 may be affected by a bed sample from Eggleshope Burn (D8), which was taken downstream of a major mining area, where high values of Cu, Ni and Zn were found. This area was found to have values of up to 20% Pb in a previous study (Novis, 1999).

Further graphs of component factor axis using stage 4 extraction results do not show any clear evidence of being able to discriminate between groups and show samples that outlie the general trend. Component factor axis plots CF1 v CF3 (in Appendix G) and CF2 v CF3 show bed sample D8 (Cu, Ni and Zn) and overbank sample OV4 (Cr and Sn) to be outliers. CF1 v CF4 (in Appendix G) shows OV4 and M7 (Ca, K and Mg) to be outliers. A component graph plot of CF1 v CF5 shows suspended sediment sample W35 (Cu, Ni and Zn) plotting close to river bed sample D8 as seen in CF1v CF2. Component plot CF2 v CF5 show similar results to CF1 v CF2 with 4 suspended samples close to field samples and the rest linked to field samples of varying landuses. Suspended sediment sample W35 again looks to be of similar chemistry to the river bed sample D8.

7.4.5 Stage 5 Extraction

After the removal of outlier field samples M8 and M10, the first five component factors explained the variance in 75% of the data. Results are shown in Appendix F, Table F.5. The first component axis was found to be positively correlated with Al, Co, Fe, Ni, P, Sc and Ti, whilst high values of Ca, K and Mg were highlighted on the negative axis (i.e. suspended sediment samples). The second component axis was positively correlated with Co, Mn and Zn. Chromium (Cr) and Sn controlled the positive axis in the third component and the negative axis in the fourth component. The fifth component axis was generally related to Si and V (positive) and Cu (negative). Sample plots with M8 and M10 included are shown in the appendices.

The first component separates suspended sediment samples from the field samples with slight overlap between them, as shown in Figure 7.10. The river bed samples plotted in this overlap between field and suspended sediment samples. Bed, bank and overbank sediments are chemically more similar to the field samples, as the suspended sediment samples contain high concentrations of Ca, Mg, K and Si. There are no major outliers identified on the first component, although suspended sediment samples W7, W9 and W11 tend to plot slightly adrift from the rest of the data. Field and suspended sediments have similar values on the second component, although the field samples overlap bed, bank and overbank whilst the suspended sediment samples do not. The bed, bank and overbank sediments tend to have a higher concentration of Co, Mn and Zn than field and suspended sediment samples. The third component shows little variation in the bulk of the samples and serves to highlight river bed sample D6 (taken in the middle Tees catchment - high in Co, Cu, Mn and Zn) and overbank sample OV4 (taken at Yarm in the lower Tees - high in Cr and Sn). CF4 also shows OV4 to outlie the rest of the data. All the points are scattered on the CF5 axis, with no outliers and is shown plotted against CF1 in Figure 7.11.

7.5 All stages analysed together

All the data (stages 1-5) were analysed together to determine if there was any variation in the overall chemical composition between the different stages. As a whole the samples in the dataset had similar ranges of values, with the exception being outliers, particularly in stage 3.

The first five components explained 79% of the data when all stages were analysed together. PCA results are shown in Appendix F, Table F.6. The first component axis was related to all elements except Ca, K and Mg, whilst the second component axis was controlled by Ca, K and Mg along with Cu, Si and Zn (all these elements are often found in suspended sediment in large concentrations). The third component axis is also influenced by K and Mg along with Ti and V on the positive axis whilst Co, Cu, Mn and Zn increase along the negative axis. The fourth component axis is controlled only by Cr and Sn, whilst the fifth component axis is controlled by Co, K, Mg and Mn (on the positive axis) and Cu and Zn (on the negative axis). The fifth component is positively correlated with Fe, P and Sc and negatively correlated with Al, Mn, Ti and V.

The first component factor axis is controlled by all elements except Ca, K and Mg, the primary constituents of water. Stage 3 extraction had the greatest variation on this axis due to suspended sediment, whilst stage 1 had the least. A stage 3 extraction sample taken from a riverbed in the river Leven (W5) plotted separately from the majority of the data points owing to its high Al, Fe, P, Sc, Ti and V contents. A suspended sediment sample, W11 - a stage 3 extraction sample from the Skerne, also plotted away from the main cluster of sample points, owing to its high concentration of Cu, Si and Zn. Samples from Stage 2 & 3 extraction have the most variation on the second component axis. The same samples were responsible for the highest recorded value in each stage (W11, due to high Ca, Cu, Si and Zn). The suspended sediment data is split on the third component, with its location on the component plot dictated by high K and Mg (extraction stages 1 and 5) or high Co, Cu, Mn and Zn (stage 3). Again suspended sediment sample W5 outlies the rest of the data due to its high Ti and V content. This is shown in Figure 7.12.

There is little variation on the fourth component with most samples lying on the axis. This component shows two outliers from the same location - OV4 in stages 4 and 5. These two samples have significantly higher values of Cr and Sn. The fifth component splits the outlying data according to high Cu and Zn (on the negative axis) or high Co and Mn and/or high K and Mg. When the fifth component is plotted against the first component three distinct patterns can be seen, those with high Cu and Zn (stages 2, 3 & 4), high Co and Mn (stages 3 & 5) or high K and Mg (stage 5).

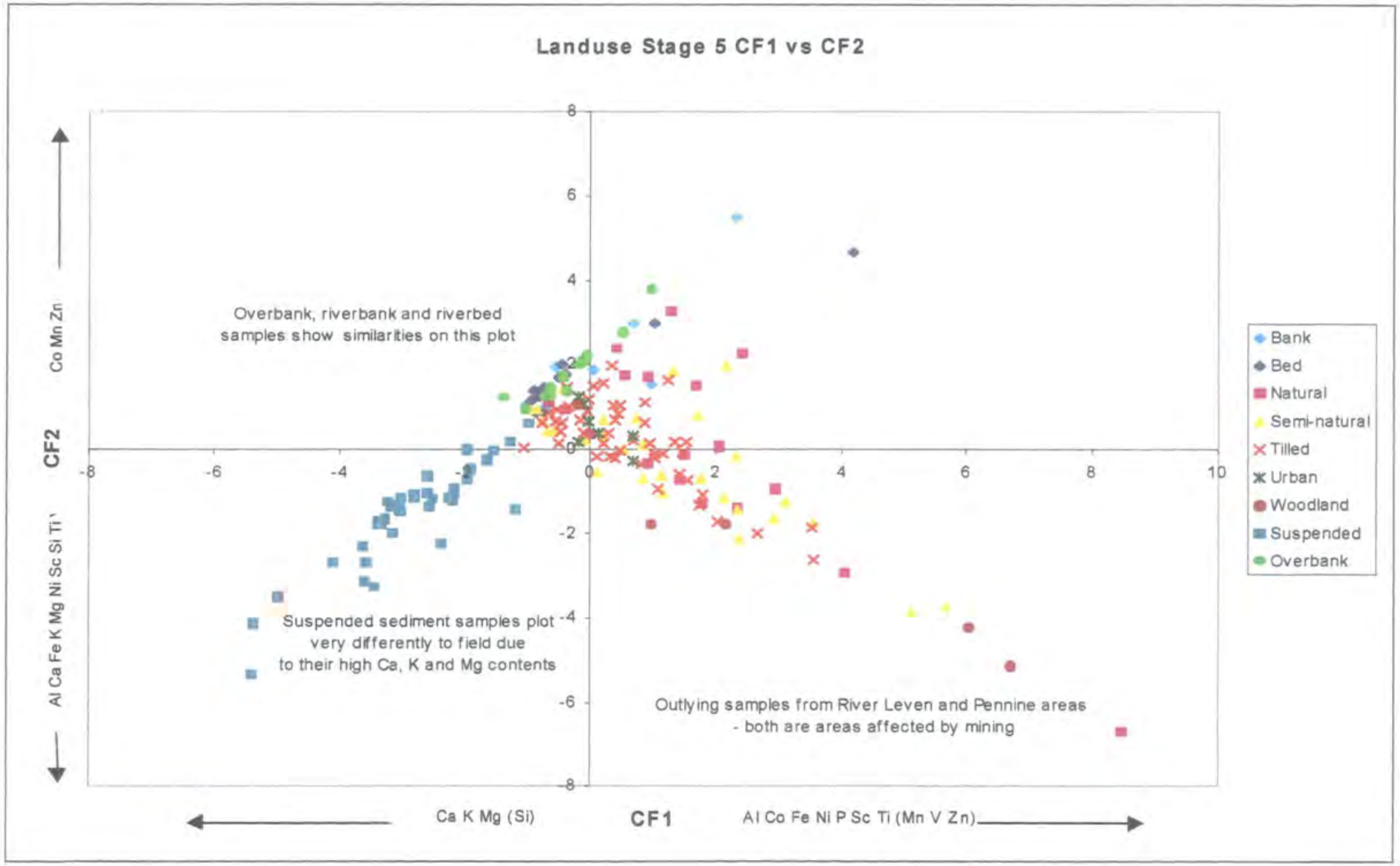


Figure 7.10 Stage 5 CF1 vs CF2

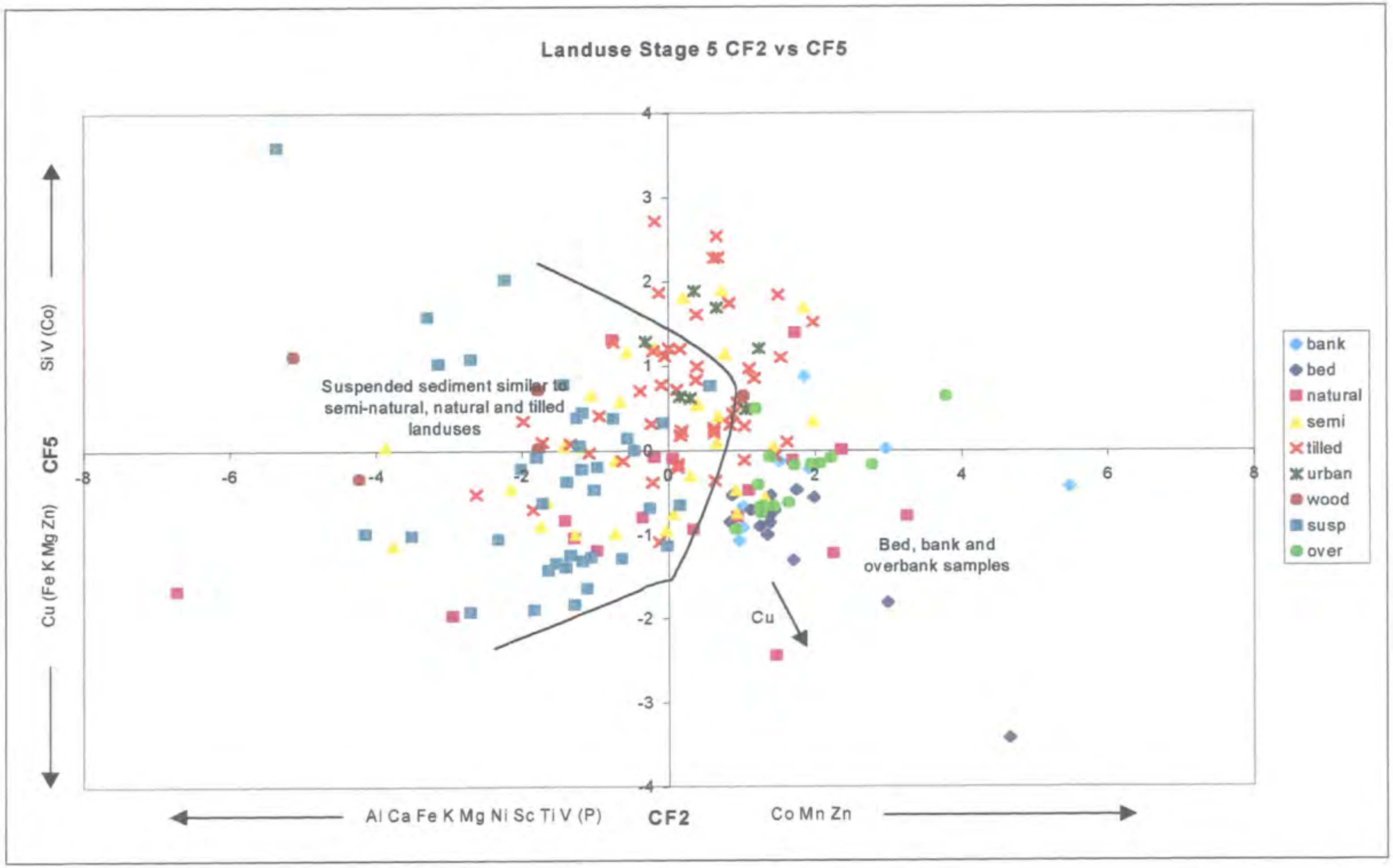


Figure 7.11 Stage 5 CF2 vs CF5

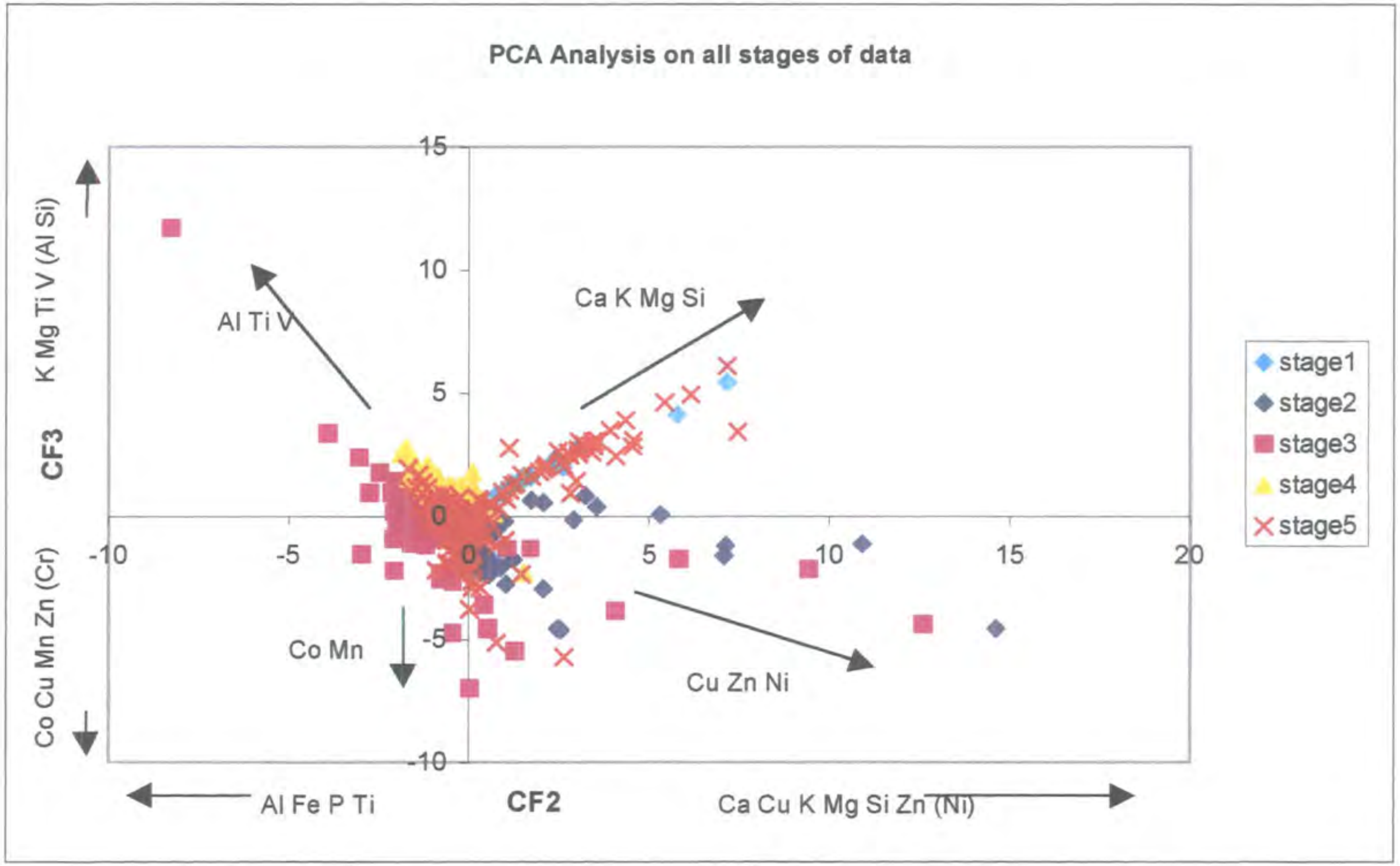


Figure 7.12 Stage 1-5 CF2 v CF3

7.6 Loss on Ignition

Loss on ignition (LOI) was conducted on all bed, bank, field and overbank samples. However, there were insufficient suspended sediment samples for LOI. As can be seen from Table 7.2, there is little difference between the average values for all field sediment groups, as seen in landuse column when bed and bank material are ignored. However, bed and bank sediments were consistently lower in their organic carbon content than the field data. This is probably due to conditions in the river, with organic material being removed.

Table 7.2 Loss on ignition results

Landuse	LOI %	Geology	LOI %	Subcatchment	LOI %
Bed	3.1	Arg	11.7	Upper Tees	11.3
Bank	4.4	Arsd	12.2	Lower Tees	8.8
Natural	8.4	Dldo	9.7	Skerne	9.6
Semi-natural	11.0	Lmst	8.4	Leven	9.3
Tilled land	9.8	Mgac	12.6		
Urban	11.8	Sdst	9.5		
Woodland	13.0				

Geology and subcatchment LOI values do not include bed & bank data

There is no positive correlation with LOI and metal content in any of the stages analysed, indicating that there is no relation between metal concentrations and organic contents in the samples. No account could be allowed for the organic content of the samples, as the suspended sediment samples could not be normalised with regards to organic content in the source samples. This was due to the sample size taken being insufficient for LOI analysis to be performed upon it.

7.7 Particle size distribution of suspended sediment

Particle size distributions were conducted on five suspended sediment samples, for which adequate material was collected for this to be undertaken. As can be seen in Figure 7.13 the sediment size distribution of all rivers is similar, apart from the Skerne, which has a larger percentage of smaller particles. Over 90% of the grains in each sample were below 63μm. Analysis of field samples was conducted on this section to accommodate this. Generally over 50% of the suspended sediment is below 8μm.

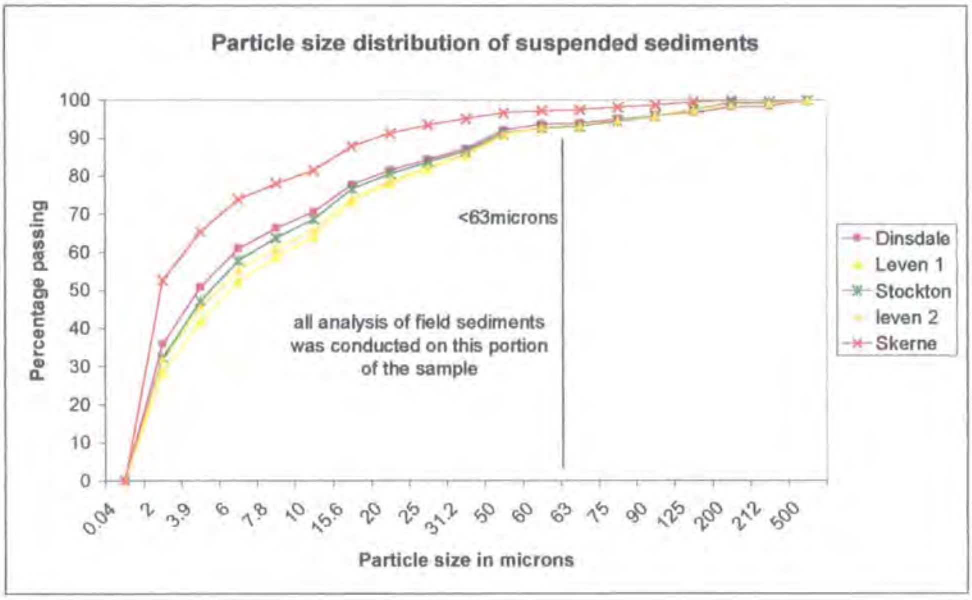


Figure 7.13 Particle size distribution of suspended sediments

Differences between metal concentrations in the source (field) samples and suspended sediment concentrations may be a result of possible differences in particle size. Although the field data was sieved to below 63μm, the suspended sediment may contain a higher percentage of smaller particles - which are known to be attractive to metal ions due to their large surface area and charge density.

7.8 Discussion

Determining the importance of each extraction stage as a percentage of the overall chemical composition of each sample showed that extraction stage 3 was the most important. Extraction stage 3, the phase where metals are bound to oxyhydroxides, was the bonding site most preferentially bound to in all samples from field through to suspended sediment samples.

The principal component plots were very useful in looking at the relationship between the different samples, particularly as they allowed the overall composition of each sample to be included. Samples could be seen to plot in groups and the effects of field or bed samples on the composition of suspended sediments could be identified.

Stage 1 of the sequential extraction stage and stage 5 total extraction are unlikely to be able to fingerprint sediment sources in this catchment, as the influence of water chemistry is too strong in these samples as a result of suspended sediment extraction procedure. The suspended sediment samples were extracted from the river water by evaporation, causing the dissolved solids in the water to be extracted also.

The removal of outlier field samples M8 and M10 from stage 5 significantly enhanced the visual interpretation of the data. A component plot with these samples can be seen in Appendix G. Several other samples often outlay the majority of the data but as they were analysed by sequential extraction and therefore duplicated, the high values were found in more than one stage of analysis.

Iron-Manganese oxyhydroxides are the dominant bonding phase for all metals, as has been identified previously in this catchment by Hudson-Edwards et al (1997). However, the importance of carbonates as a bonding site for metals in the upper limestone dominated areas has not been found in this work.

Suspended sediment samples provide most of the outliers in all stages except 4. Extraction stage 4 is the only phase where the first component does not segregate field from suspended sediment samples. The prominence of suspended sediment samples in most stages as outliers could be due to the size fraction of the material analysed. The size fraction of suspended sediment is likely to be significantly smaller than the field samples. Metals are known to preferentially adhere to the smallest particles (Horowitz, 1991). The analysis of only material below 63µm in this study may not have overcome this. However, the three suspended sediment samples that constantly outlie the dataset were found to be sandy in character during preparation. These samples did not need to be crushed before the next analysis stage, unlike the majority of samples analysed.

Phosphorus (P) is generally absent or low in the bed, bank and overbank sediment samples (especially in stages 1 & 2). This is possibly due to the high mobility of P - it is possible that it is simply washed away. The P content of suspended sediment is often similar to that of field samples, indicating that the P in the water is coming directly from field runoff.

Bed, bank and overbank samples are found to be higher in Co, Fe, Mn and Sn than field or suspended sediment samples in stages 2 and 3 of the sequential extraction process. In these two stages the suspended sediment is chemically similar on the component plots to field samples, particularly tilled and semi natural. It is difficult to distinguish between the upper Tees catchment and the River Leven catchment as both these areas have high metal concentrations due to previous mining works. Riverbed samples taken downstream from the Pennine mining areas in the upper to middle Tees catchment are distinctively different from River Leven bed samples. The bed samples taken from the barrage impoundment (sink samples) appear to be correlated with bed material in stage 2, but field samples in stage 3.

Suspended sediment samples from the Skerne catchment are higher in K and P (in stage 2) and the samples are seen to plot together. The Skerne is a predominantly tilled catchment and the higher K and P values could be a result of fertiliser use.

Suspended sediment samples taken at low river flow plot very differently from all other samples, owing to their exceptionally high metal concentrations. These samples are possibly sourcing their sediment from the riverbed. Heavy metals often form deposits in river beds or overbank during floods, as when the discharge decreases any load carried by the water column will be deposited irrespective of its whereabouts. Hydraulic sorting and settling velocities mean that metals settle out first owing to their high densities.

In stage 4 some suspended sediment samples can be identified as being similar to riverbed material rather than field material as seen in stage 2. Suspended sediment sample W35 (River Tees at Blackwell Bridge) is often seen to plot closer to bed material than other suspended sediment samples. It contains high concentrations of Cu and Zn - the same as a bed sample from an upstream tributary. It is possible that this sample was affected by a reactivation of the mine spoil heaps in the steep sided Hudeshope Beck subcatchment.

High values of Cr are seen in overbank samples, particularly overbank sample OV4 at Yarm Railway Bridge. A major Chromium production factory is situated in the middle of the Tees catchment and could be a major source of Cr in the middle and lower catchment areas.

When all stages are plotted together on a principal component diagram, extraction stage 3 of the extraction process shows the most variable range in data values, reinforcing its dominance as the major bonding phase in the catchment. In all plots it is predominantly the suspended sediment samples that form the outliers from the main cluster. In extraction stages 2, 3 and 4 this is due to high metal concentrations, whilst in extraction stages 1 and 5 it is due to high concentration of Ca, K and Mg in the water.

Summary of Main Points:

- Extraction stage 3 is the most important bonding site for metals.
- Extraction stages 1 and 5 are unlikely to be able to fingerprint sediment samples due to the influence of the water chemistry.
- Suspended sediment samples are outliers in all extraction stages except the fourth.
- Bed, bank and overbank samples contain higher concentrations of Co, Fe, Mn and Sn than field and suspended sediment samples, probably due to the deposition of these metals from the mining works upstream.
- It can be difficult to determine the difference between the two mining areas in the catchment – in the Upper Pennine area and the Cleveland Hills in the River Leven catchment.
- The River Skerne catchment contains the highest concentrations of K and P, probably due to the high proportion of tilled land in the catchment and the use of fertilisers.

- Suspended sediment samples taken at low flow tend to contain higher concentrations of metals.

Chapter 8 Analysis of River Water Data

8.1 Introduction

The river water samples taken alongside suspended sediment samples during events were analysed by Principal Components Analysis, in the same manner as the suspended sediment samples. The river water was analysed in order to determine if the water chemistry changed throughout the Tees Catchment and whether there was a change in river water chemistry between events. The river water was also studied to identify any changes in chemistry between samples taken during high and low flow events. The water samples were all taken during storm events as more suspended sediment tends to be carried in high flows.

8.2 River Water Data

River water samples taken alongside but separately from the suspended sediment samples were analysed to determine the chemical signature of the water itself. The samples sites are shown in Figure 8.1 and the details of all samples are shown in Table 8.1. Principal Component Analysis (PCA) was carried out on all elements that Minitab would allow, i.e. all elements where the value was non zero or non-constant. The elements used were Al, Ca, Cu, Fe, K, Mg, Mn, P, Si, Ti and Zn, the results are shown in Appendix I. The first component was positively correlated with all the elements analysed except Zn, which was negatively correlated. The second component was split according to two sources - heavy metals (Al, Cu, Fe, Mn and Ti) were negatively related to the component factor, whilst the positive axis was indicative of the water source (Ca, K, Mg and P). The final component was controlled by Cu, Zn and Ca on the negative axis and could be expected to pinpoint upstream Pennine mining sources and (Mn) controlled the positive axis.

When the first component axis is plotted against the second (Figure 8.2) and also against the third (Figure 8.3), different water chemistries throughout the catchment are immediately apparent. The Tees upstream of the Skerne is very different from the downstream Tees and tributaries (as if depleted in all metals/cations). The Skerne and Leven are fairly similar to each over with the Leven plotting closer to the Upper Tees catchment. The Stockton and Dinsdale samples plot in between Skerne/Leven and upper Tees indicating a degree of mixing between the two distinct sources. There is more variability in the data on component three than the second component.

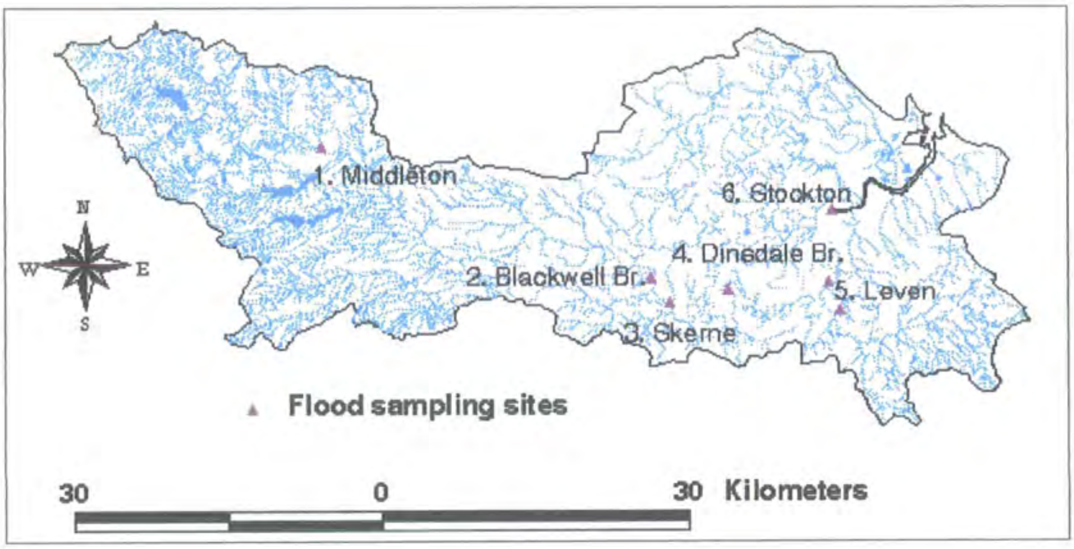


Figure 8.1 Showing locations of water samples

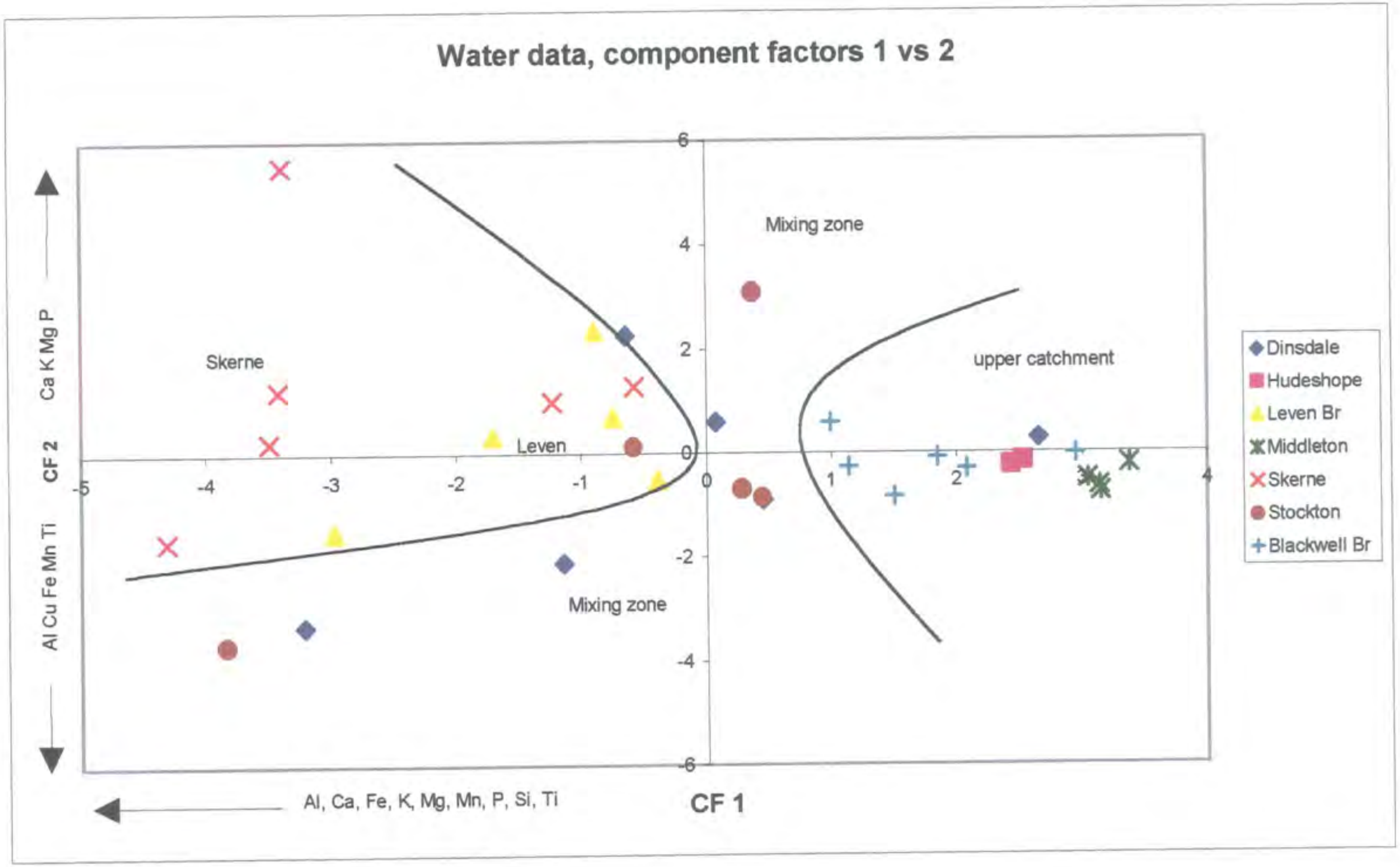


Figure 8.2 Water data CF1 v CF2

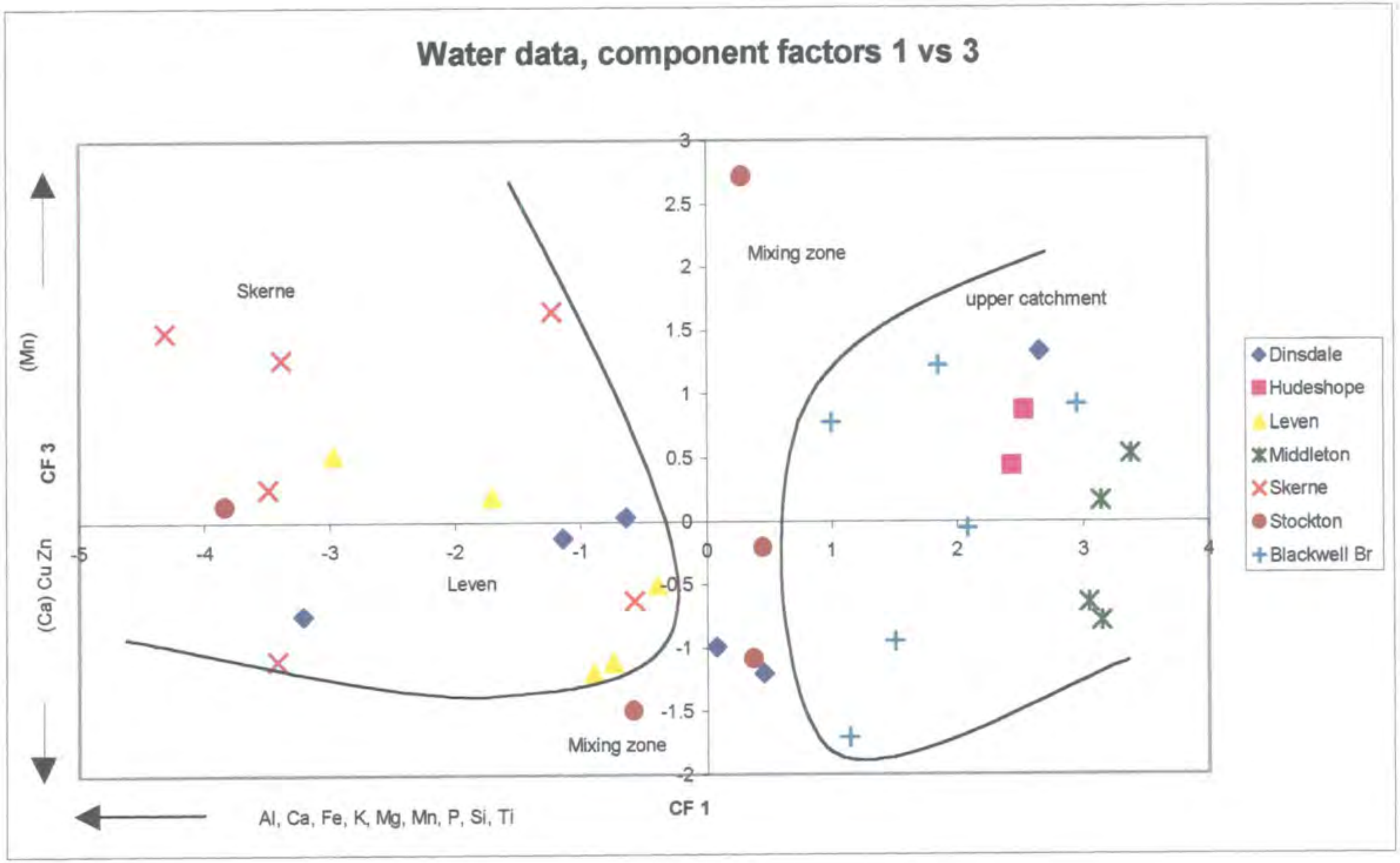


Figure 8.3 Water data CF1 v CF3

8.3 Study of the Individual Storms Sampled

In this section the samples taken at each site for a particular flow event will be studied to determine any relationship of the water chemistry with rainfall over the catchment, intensity of rainfall and any differences in water chemistry between flow events. The sample and flow details are shown in Table 8.1 and the flow events are marked on Figure 8.4 (CF1 vs CF2) and Figure 8.5 (CF1 vs CF3).

8.3.1 Storm event on the 11th October 2000

In this storm the River Skerne sample has the highest value on the second component axis than all other samples (Figure 8.4). This sample was taken before the flood peak and contains relatively high values of Ca, Mg, K and P, when compared with the other water samples. The sample taken from the River Tees at Dinsdale shows a strong upper catchment signal, which is consistent with the rainfall over the most westerly side of the catchment. In this rain event the Pennines received twice the amount of rainfall than that encountered at Barnard Castle in the middle catchment. The Dinsdale sample was taken on a falling limb, whilst the River Skerne was taken on a rising limb - indicating that the River Skerne peaked later than the River Tees.

8.3.2 Storm event on the 30th October 2000

The chemistry of the water in the Tees at Dinsdale is very different from the River Skerne, possibly indicating that the River Tees rose quicker than the River Skerne (Figure 8.4). This sample, taken on the 30th October was a very intense rainfall event, as 70mm of rain had fallen since the 27th October in the Pennine areas. The middle catchment also received a substantial amount (~46mm) of rainfall. The River Leven sample also plots very close to these points, but owing to their locations these samples cannot be related unless it is the chemical signature from the rainfall itself. On the third component axis (Figure 8.5) the positions of the samples from the River Leven and the River Tees at Stockton are similar.

8.3.3 Storm event on the 3rd November 2000

All the samples were taken three to twelve hours after the flood peaks, see Table 8.1 for exact times, on the recession limb. This is the only event sampled when the storm was concentrated on the eastern side of the catchment. The River Tees sample from Stockton shows a similarity with samples from the upper catchment. It is possible that the flood peak from the River Leven had passed Stockton by the time of sampling, therefore its influence is not seen here. The water sample from the River Skerne has a similar chemical composition to the previous flood. The River Leven sample is very depleted in metals and was also taken at the highest sampled flow. It is possible that the sample is predominantly rainwater or that the metal concentration was diluted due to the size of the flood – a supply limited suspended sediment sample.

8.3.4 Storm event on the 6th February 2001

These samples were taken in after a heavy downpour event (>70mm in 3 days in the upper catchment) but the peak flow delay is greater than that seen on the 30th October flood. This is explained by the preceding conditions in the catchment. In the 30 days before the flood on the 30th October there had been 5 days without rain, whilst in the 30 days preceding the flood on the 6th February there had been 12 days without rain. This could mean that the ground absorbed a greater proportion of the rainfall before runoff was generated during the flood on the 6th February.

The sample from the River Skerne is depleted in metals but high in K and P. The samples taken from the River's Leven, Skerne and the Tees at Stockton samples plot very close together, indicating that both the Skerne and the Leven are influencing the chemistry in the barrage. The river water sample from the River Tees at Low Moor is intermediate between these samples and the upper catchment.

8.3.5 Storm event on the 8th February 2001

All these river water samples were taken 10 to 27 hours after the flood peak. The samples from the River Tees at Dinsdale Bridge and Stockton plot close together, possibly indicating a flood dominated by the upper catchment.

8.3.6 Storm event on the 7th March 2001

The Stockton sample is intermediate between the Dinsdale and Blackwell Bridge samples on the first component, indicating a chemical signature similar to that in the middle catchment. The preceding rainfall before sampling on 7th March was mostly in the upper catchment, which was twice that in the lower catchment. Overall, however, it was a small rainfall event. On the second component axis the River Tees sample taken at Stockton sample is very similar to the Dinsdale sample. The sample taken from the River Skerne has no resemblance to the sample taken at Stockton, when shown on the second component, but does when plotted on the third component. There is no water sample from the River Leven sample as the data was lost during ICP-AES analysis.

8.4 Chemistry of Water as a Function of the Flow Rate at Time of Sampling

The River Leven samples appear to have higher negative values on the second component at higher flow rates, meaning a higher concentration of dissolved metals in the samples. This trend is also seen to a lesser degree in the River Tees samples from Blackwell Bridge and the River Skerne samples. No evidence of this is seen in the River Tees samples from Stockton or Dinsdale, as shown in Figure 8.4. The scatter of points from Skerne, Leven, Dinsdale, Stockton and Blackwell all form triangles, as seen in Figure 8.5. The river water chemistry from the Tees at Stockton never overlaps with the samples from the upper catchment - due to distance and the mixing with effects of the Rivers Leven and Skerne. The River Tees at Dinsdale data often plots closer to the Skerne than the upper catchment – possibly due to timing of samples or strong Skerne chemistry.

No connection can be found between the size of flow at the time of sampling and chemistry of the water samples taken. Samples from two different flood events can be seen to be showing similar chemistry as indicated in Figure 8.5.

8.5 Chemistry of Water as a Function of Sampling on Rising/Falling Limb

In chapters 6 and 7, samples could be seen to be plotting in groups depending on whether the sample was taken on a rising limb or a falling limb. This is not the case for the water chemistry as shown in Figure 8.6 and Figure 8.7.

8.6 Comparison of suspended sediment with water data

Where heavy metal concentration peaks are seen in suspended sediment samples, a corresponding rise in that element in the water sample is not seen. Phosphorus (P) and Zn are rare in suspended sediment but are generally present in the water samples, whilst Co, Cr, Ni and V are absent in water but often present in suspended sediment samples. Tin (Sn) is always absent in both suspended sediment and water samples.

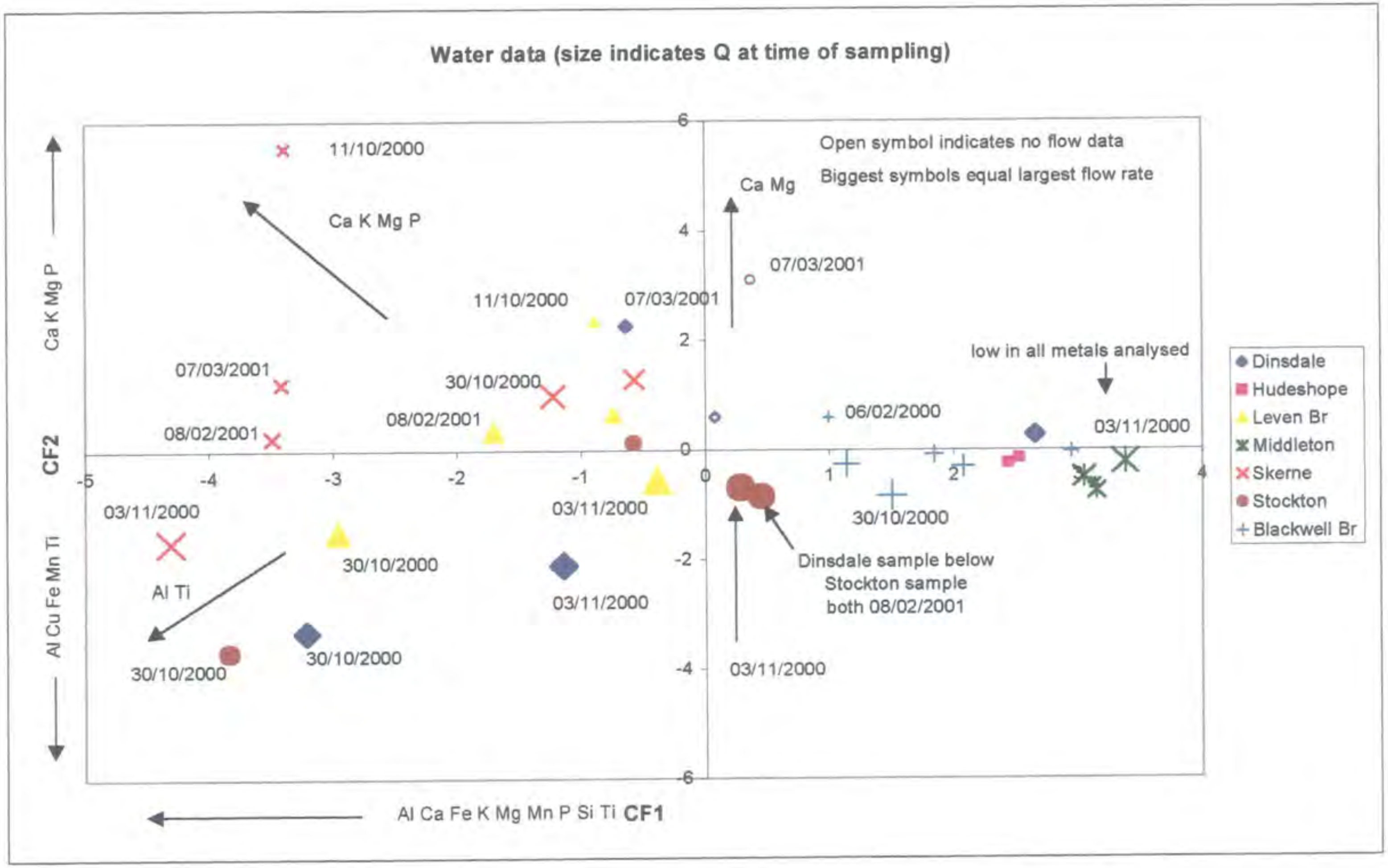


Figure 8.4 Water data with regards to flow at time of sampling CF1 v CF2

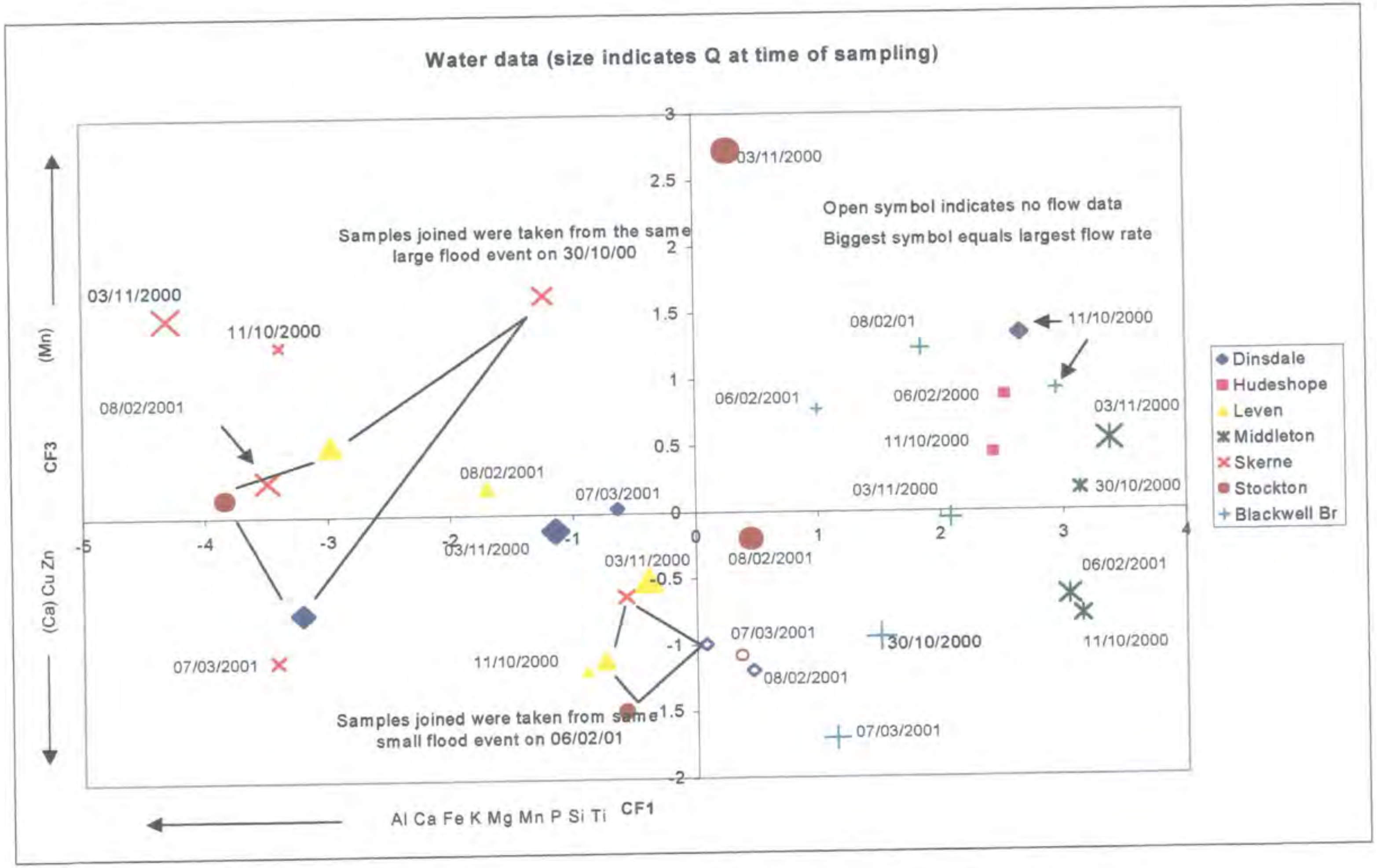


Figure 8.5 Water data with regards to flow at time of sampling CF1 v CF3

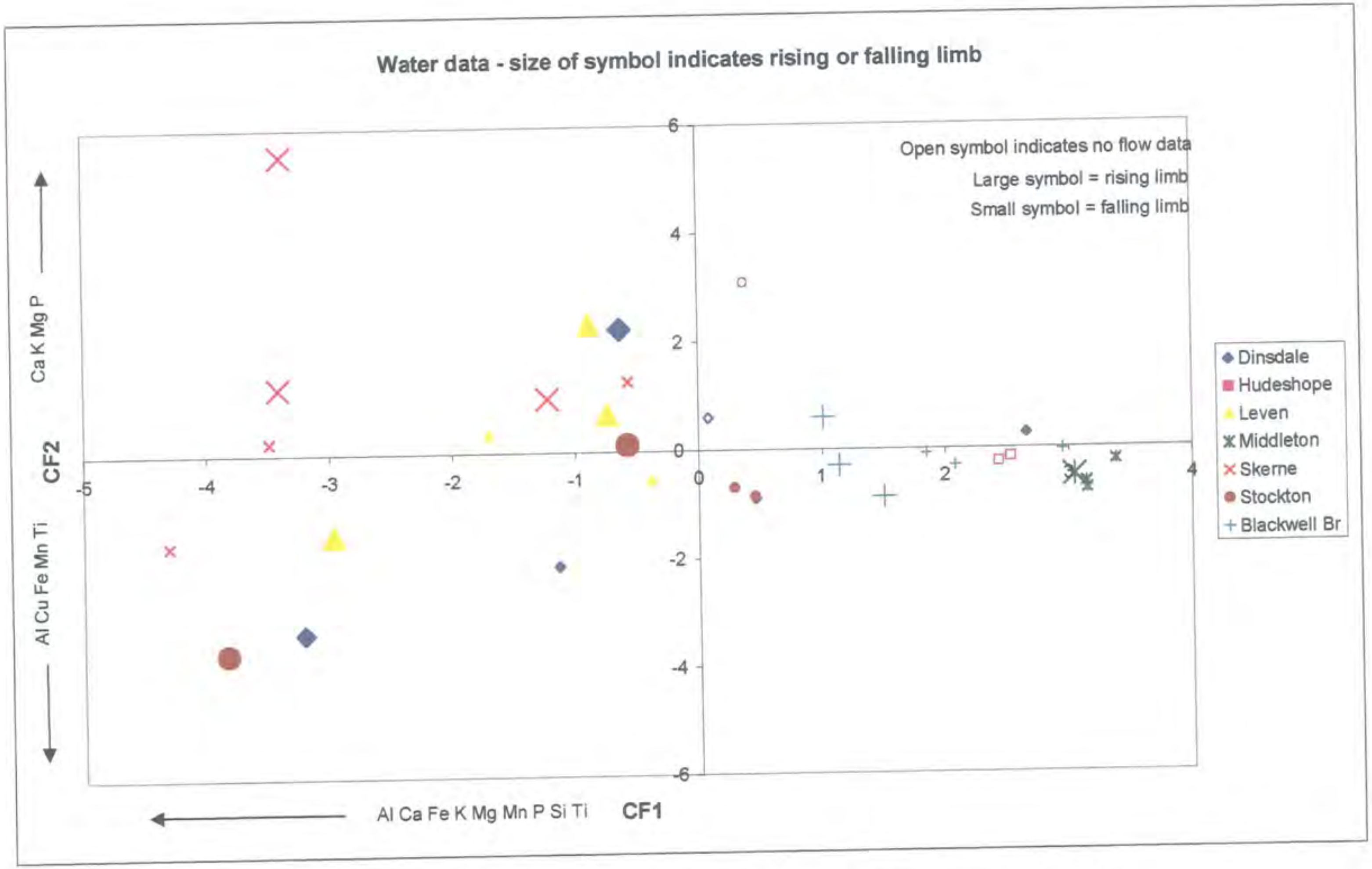


Figure 8.6 Water data showing sampling on rising/falling limb CF1 v CF2

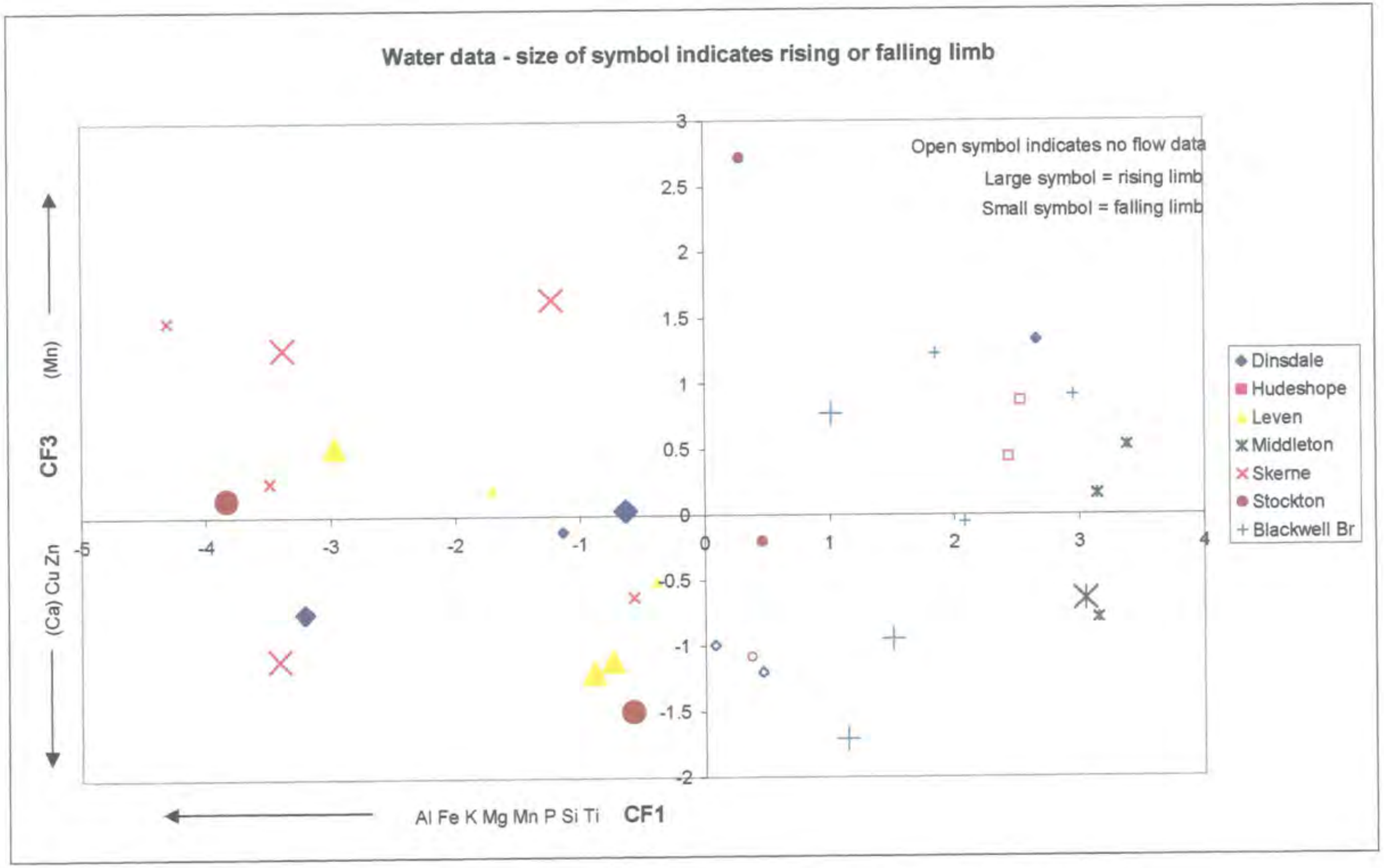


Figure 8.7 Water data showing sampling on rising/falling limb CF1 v CF3

Table 8.1 Sample details for water and suspended sediment samples

water id	susp id	river	date samp	Q sample	Qs time	Q peak	Qp time	Qs/Qp	fall/rising	Time betw Qs & Qp
t1	W07	mid	11/10/2000	17.36	12.00	69.685	20.15	-0.10	falling	15.75
t3	W08	bla	11/10/2000	40.58	13.50	108.127	00.45	-0.38	falling	13.00
t4	W09	ske	11/10/2000	2.22	14.00	7.661	07.15	0.29	rising	17.25
t5	W10	low	11/10/2000	66.063	14.15	104.191	07.15	0.63	rising	7.00
t6	W11	lev	11/10/2000	7.077	15.45	12.755	19.15	0.55	rising	3.50
t12	W12	sto	30/10/2000	251.92	16.30	338.64	06.15	0.74	rising	14.25
t8	W13	bla	30/10/2000	157.453	14.00	157.684	12.30	1.00	peak	1.50
t10	W14	low	30/10/2000	182.66	14.30	244.931	20.00	0.75	rising	5.50
t11	W15	lev	30/10/2000	45.166	16.05	53.65	21.00	0.84	rising	5.00
t9	W16	ske	30/10/2000	22.521	14.10	25.329	12.00	0.89	rising	2.25
t18	W17	sto	03/11/2000	329.16	17.00	490.1	06.45	-0.67	falling	9.25
t17	W18	lev	03/11/2000	52.601	16.20	124.582	07.45	-0.42	falling	8.50
t16	W19	low	03/11/2000	476.376	14.20	538.866	11.45	-0.88	falling	2.50
t15	W20	ske	03/11/2000	25.019	13.40	33.807	06.15	-0.74	falling	7.50
t14	W21	bla	03/11/2000	92.928	13.25	553.316	01.00	-0.17	falling	12.25
t13	W22	mid	03/11/2000	24.891	11.55	179.01	21.15	-0.14	falling	14.75
t19	W23	mid	06/02/2001	18.746	11.15	175.778	06.45	0.11	rising	19.50
t21	W25	bla	06/02/2001	35.212	13.00	530.373	11.45	0.07	rising	22.75
t22	W26	ske	06/02/2001	21.006	13.10	21.587	11.30	-0.97	falling	2.25
t23	W27	low	06/02/2001	n/a						

t24	W28	lev	06/02/2001	13.16	14.00	13.619	12.30	0.97	rising	1.50
t25	W29	sto	06/02/2001	46.24	14.30	729.02	15.00	0.06	rising	24.50
t26	W30	bla	08/02/2001	51.14	15.05	530.373	11.45	-0.10	falling	27.15
t27	W31	ske	08/02/2001	11.01	15.20	25.481	16.30	-0.43	falling	23.75
t28	W32	low	08/02/2001	n/a						
t29	W33	lev	08/02/2001	8.29		24.751		-0.33	falling	
t30	W34	sto	08/02/2001	261.9	17.10	785.5	03.30	-0.33	falling	10.25
t31	W35	bla	07/03/2001	122.43	15.50	151.28	18.15	0.81	rising	2.50
t32	W36	ske	07/03/2001	9.762	16.00	10.083	17.15	0.97	rising	1.25
t33	W37	low	07/03/2001	40.796	16.15	163.848	00.15	0.25	rising	8.00
t34	W38	lev	07/03/2001	16.75	16.45	22.891	09.45	-0.73	falling	7.00
t2		hud	11/10/2000	n/a						
t7		mid	30/10/2000							
t20		hud	06/02/2001	n/a						

<u>Explanation of river codes</u>

Mid	River Tees at Middleton	Bla	River Tees at Blackwell Bridge
Low	River Tees at Low Moor	Sto	River Tees at Stockton
Ske	River Skerne	Lev	River Leven
Hud	Hudeshope Beck (tributary upstream of the sampling site at Middleton	Q	discharge (m^3sec^{-1})

8.6 Conclusion

When river water data is plotted as component plots, the river water can be seen to separate into 2 distinct groups:

1. The Upper River Tees catchment.
2. Rivers Skerne and the River Leven.

The middle and lower Tees catchment river water samples plot in between, showing a degree of mixing between the upper river water sources. River water samples taken from the Rivers Skerne, Leven and the Tees at Stockton show high values of metals compared with those taken in the upper catchment. Water samples taken during higher flows have been found to contain higher Al & Ti concentrations (**Figure 8.4**). There appears to be no direct relation between the timing of the sample with reference to the flood peak, although samples taken on a rising limb do appear to plot more in the 3rd and 4th quadrants, indicating higher metal contents.

As a general trend the right side of the component plots show the upper, most westerly catchment whilst the left side contains the lower, easterly area of the catchment.

Chapter 9 Conclusions and Recommendations for future work.

9.1 Conclusions

Principal Components Analysis (PCA) has proved to be more successful in determining sediment sources in the Tees catchment than the idea of using multivariate statistics to produce an 'un-mixing' model. Through PCA there appear to be three main source areas that are chemically distinct from one another, and these have been identified in several extraction stages. These three sediment sources appear to be:

1. Areas subjected to mining in the past (this includes the Upper Tees/Pennines area and the Cleveland Hills in the Leven catchment).
2. The bed and bank material – particularly that in the middle to upper Tees catchment; these sediments tend to be high in Co and Mn.
3. The middle to lower catchment where there is little variability in the data. These samples do not generally contain high metal contents, which marks them as different from the two previous sources.

The suspended sediment samples taken appear to be from a mixture of these sources. Different extraction stages and principal component plots place the suspended sediments in different places with respect to the land samples. Some suspended sediment sources appear to be dominated by bed & bank, whilst many are dominated by the middle catchment area. Only occasionally do suspended sediment samples tend to represent the mining areas.

In several component plots the suspended sediment samples can be segregated according to whether they were sampled at a low flow, high flow, rising limb or falling limb. Low flow samples tend to be higher in metals, probably due to the sediment being removed from the riverbed. Higher flows tend to contain more K; this can be interpreted as runoff from agricultural land (which dominates the middle and lower catchment). Potassium (K) is often applied to fields in the form of fertiliser. It has been shown to be virtually absent in bed and bank material, possibly as a result of its high mobility.

Samples taken on a rising limb are generally higher in heavy metals, possibly due to the remobilisation of bed and bank sources. The falling limb samples, however, are high in K, particularly in extraction stage 3.

The metal concentrations vary significantly within groups; this variability is seen in all the groups. The concentrations of metals in different groups normally have different mean values, but the variability within each group is similar. This indicates that it is difficult to classify different areas of the catchment on the basis of the geochemistry alone. The Tees catchment is covered by a thick blanket of drift – therefore masking the different chemistries of the geological stratum below. The glacial drift also covers all the different tributaries in the catchment therefore disallowing subcatchment chemistry from being used as a basis for producing different source areas. Subcatchment did however show more of a difference between the groups than geology.

The best indicator of sediment sources in the catchment was landuse, but it is still too variable within groups and similar throughout the catchment to be used as a reliable method for discriminating between different sediment sources.

Extraction stage 3, which extracted material bound to iron-manganese oxyhydroxides is the most important phase in the Tees catchment, with 50-90% of metals being bonded to or within the oxyhydroxides. Iron-manganese oxyhydroxides are said to be the last stage in the weathering process (Garrels & Christ, 1965) and therefore could be an indicator of the amount of weathering that has taken place in the soils samples. No link between heavy metal content and organic matter was found in this study, which agrees with work done by Davies et al (1991), although the absence of organic contents of suspended sediment may have affected this result.

Analysis of the river water samples taken alongside the suspended sediments showed that there are distinct differences between the water chemistry in the upper catchment and in the lower tributaries of the Rivers Skerne and Leven. The water chemistries of the Rivers Skerne and Leven are very similar when viewed on a component plot. The upper catchment has low concentrations of all metals, whilst the samples taken from the River Tees in the middle catchment and at Stockton generally plot within the two end members (upper catchment area against the Rivers Skerne and Leven). A relation with rainfall over the catchment can be identified from the component plots with samples taken from the River Tees at Dinsdale and Stockton during and after high rainfall events in the Pennines plotting closer to the upper catchment sources.

The extreme flow events of 2000 and 2001 have been shown to have caused a change in the typical sediment transport response of the River Tees to runoff events (White et al 2002). Prior to these events the River Tees contained lower concentrations of suspended sediment per unit runoff, and the relative timing of the flow and concentration peaks appeared to be related to event size. Following Autumn 2000, events have been characterised by higher sediment concentration per unit runoff, and a tendency for the concentration peak to lead the flow peak regardless of event size. There is much greater non-flow-related variability in concentration during events than previously (White et al 2001). As can be seen in Figure 8.5 this change in sediment response is not seen in the chemistry of the suspended sediment.

At higher river flow the water samples taken from the Leven appear to contain higher metal concentrations. During some storm events, samples from Stockton, Dinsdale, Skerne and Leven can be shown as having similar chemistries. No correlation between river water chemistry during a rising or falling limb can be found in the data collected here. No links between heavy metal concentrations in suspended sediment and the appropriate river water samples were found.

The Kruskall-Wallis technique identified several metals in the field sediment samples as being able to distinguish between the selected groups. However, when the results were input into the multi discriminant function analysis, the metals failed to be reliable in identifying between groups. An attempt at using suspended sediments to construct a mixing model also failed when Kruskall-Wallis identified only one element as capable of classifying the data.

The mixing model approach to identify sediment sources has been used successfully throughout the UK and abroad. Its failure here is possibly due to the limited number of source samples taken for analysis. In order to produce a mixing model, a large number of source materials are needed. The small number of suspended sediment samples was not an issue in this study as the mixing model failed to produce composite fingerprints for each source group. This study has shown, however, that where the data fails the two-stage statistical test, results may still be obtained from PCA analysis.

It is possible to get reliable chemical information from small suspended sediment samples (2-5 grams from 10 litres of water) using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES). However, larger volumes of suspended sediment samples are needed if a wider range of techniques is to be used.

The two-step statistical process on the river water data was more successful; the discriminant function identified K and P as being able to distinguish between groups. The Wilk's Lambda values were high, but lower than those returned by the field or suspended sediment, so it was decided to use this information to construct a mixing model for the water data. The mixing model clearly failed to unmix the samples, as one of the constraints on the model was that each source would provide between 0 and 100 percent of the sample. The failure of the model is possibly due to a number of factors; the similarity in the chemistry of the Skerne and the Leven or insufficient samples to construct a robust model.

9.2 Use of Principal Components Analysis

Principal Components Analysis (PCA) has proven to be a reliable choice for determining patterns and sources of sediment within a catchment when limited sample material is available. The PCA plots show visually the similarities and differences between each sample and each source group – a mixing model can not do this.

Whereas a mixing model can show an estimated breakdown of the source groups for each suspended sediment sample, PCA shows all the suspended sediment samples and their relationship to each other and all source materials. This makes it easier for trends and differences to be identified.

Principal Components Analysis could be used as a preliminary tool in sediment source identification as it can show where the outliers and general trends lie, the results from this could be used to direct further sampling needs. In studies where there is limited sample data available and therefore a mixing model is not a viable option, PCA can be used to produce viable results.

When using PCA, the same set of results can be plotted as any of the source groups, the plot can be redrawn with a new key/legend to show landuse or geology etc.

9.3 Recommendations for Future Work

In order to improve the number of elements that pass the 2-step statistical procedure and therefore make a mixing model viable, a greater number of source samples need to be taken throughout the Tees Catchment. More samples will give a more thorough coverage of the catchment, which may reduce the effect of 'outlier values' on the mean source group values. More samples need to be taken from each specific source group type (e.g. natural landuse types) to give a more accurate average concentration values of the elements analysed, and less variance around the mean value. A larger number of bank and bed samples need to be taken, as these are important sediment sources. It was difficult to take a substantial number of bed and bank samples in the lower Tees due to their inaccessibility. In any future research, sampling from a boat could yield a greater number of samples. Bank and bed samples should ideally be taken at roughly regular intervals down each tributary and the River Tees itself. The bank samples in this study have identified a trend, indicating that Co and Mn increase upstream. A more in-depth study of the bed and bank source may enhance such trends and allow the identification of how far the mining effects have reached downstream.

In an ideal world a greater number of suspended sediment samples would be taken. This could be done in two ways, firstly sample more floods in general (if nature allows) as the results from this research have shown that in the same river the sediment concentration can vary widely between storm events. More storm sampling may reveal whether this is due to runoff factors i.e. more rain over a certain areas of the catchment or river source areas i.e. activation of new sources within the riverbed. Secondly, collect multiple samples from the same location throughout a storm event to identify any changes in sediment source behaviour during a storm event.

Larger volumes of water and suspended sediment would need to be taken to allow full analysis of all parameters in the sample. In order to improve source identification, particularly if a mixing model was to be used, a wider range of properties could be analysed. The use of Cs^{137} profiling or mineral magnetics may provide some useful insight. For this study in particular the analysis of a greater number of elements, particularly lead (Pb) may have helped to distinguish between the two mining sources – the upper Tees catchment and the Leven catchment. Some preliminary samples were analysed using X-ray diffraction (before the equipment was taken out of operation), showed that some Pennine samples contained up to 20% Pb. Lead (Pb) has been mined previously in the Pennine area of the catchment. These two areas of mining in the catchment have different origins – igneous/geothermal (in the Pennines) and sedimentary deposit (in the Cleveland Hills), but their chemistries appear similar in the range of metals analysed here.

The method of retrieving the sediment from water also needs to be modified to remove the effects of suspended solids in the water. Other authors have used centrifugation, but this technique was not available in Durham. The samples themselves need to be analysed for a wider range of determinants. It was hoped that by sequential extraction and therefore splitting the metals into different phases that the different environmental controls on the samples would be accounted for.

Methods other than sequential extraction could also be considered. It has been shown by some authors (Xiangdong et al, 2001) to not achieve complete and selective dissolution and recovery. It was found that some solutions may not be strong enough to completely break down the samples and also that re-absorption may occur in later stages.

An important factor not covered here to the full extent is the importance of particle size. All samples were analysed on the <63μm portion, but the suspended sediment fraction can be at the finest end. Also some heavy metals have been shown to preferentially absorb onto the finest particles, e.g. <20μm (Moalla, 1997). No account of the organic material has been made in this data. Loss on ignition was undertaken on all the field samples, but limited amounts of suspended sediment samples would not allow this for the suspended sediment samples. The relationship between organic matter and element concentration is complex and difficult to generalise (Walling et al, 1999).

Appendices

These appendices are ordered as they appear in the main text of this work, and are as follows:

- A Field sample data (Chapter 3)
- B ICP calibration information (Chapter 4)
- C ANOVA results (Chapter 6)
- D PCA result tables (Chapter 6)
- E Extra PCA plots (Chapter 6)
- F PCA results tables (Chapter 7)
- G Extra PCA plots (Chapter 7)
- H Boxplots – landuse, geology and subcatchment (Chapter 7)
- I PCA results table – water data (Chapter 8)
- J Basic elemental data for each extraction stage, shown on the floppy disc provided

Appendix A

Table A.1 Locations of all soil samples taken in the River Tees Catchment

Site	x cood	y cood	Location	HOST	Landuse	Geology
B1	382500	532500	Harwood Beck	n/a	bank	n/a
B2	399500	513200	Greta	n/a	bank	n/a
B3	439000	510400	Tees, Low Worsall	n/a	bank	n/a
B5	430500	515800	Skerne, Darlington	n/a	bank	n/a
B7	428800	512300	Skerne	n/a	bank	n/a
B8	445700	509500	Leven	n/a	bank	n/a
B9	398500	528780	Tees, Eggleshope Bridge	n/a	bank	n/a
D1	445600	519000	Tees, waterski jump	n/a	bed	n/a
D2	444800	519100	Tees, minesweeper boat	n/a	bed	n/a
D3	442900	512600	Tees, Yarm	n/a	bed	n/a
D4	452700	586000	Leven, Stokesly	n/a	bed	n/a
D6	416500	516700	Tees, Gainford	n/a	bed	n/a
D7	396300	525080	Tees, Stotley	n/a	bed	n/a
D8	398500	528780	Tees, Eggleshope Bridge	n/a	bed	n/a
D9	400940	520060	Tees-Balder confluence	n/a	bed	n/a
D10	401270	520600	Tees, Shipley Wood	n/a	bed	n/a
D11	430300	519300	Skerne, Farmland	n/a	bed	n/a
D12	445700	509500	Leven	n/a	bed	n/a
D13	394700	526550	Hudeshope Beck	n/a	bed	n/a
D14	390710	528400	Bowlees, picnic site	n/a	bed	n/a
D15	385050	532980	Langdon, Green Lords Seat	n/a	bed	n/a
D16	434600	511400	Tees, Low Dinsdale	n/a	bed	n/a
D17	399650	523270	Tees, Eggleton Bridge	n/a	bed	n/a
G1	408100	513000	Roman Fort	5	tilled	sdst
G2	405200	512200	Moor House Cottage	24	semi	sdst
G4	402400	508500	Stang Foot	26	rough	lmst
G5	401200	512600	Plover Hall	24	tilled	lmst
G7	392800	512400	Valley Farm/Bowe	29	dune	arsd

G8	388800	507900	Polly Moss	12	dune	arsd
G9	395800	510600	Sleighthome	26	tilled	lmas
G10	391200	507400	Path	12	heath	arsd
H1	383700	532300	Bowes Close	26	semi	lmst
H2	383300	531100	Peghorn cattlegrid	26	dune	mgac
H3	382500	532400	Mashes Gill	24	semi	mgac
H4	382300	534300	Rough Rigg	29	dune	lmst
H5	380900	535500	Ashgill Head	29	dune	lmst
H6	380900	534100	Herdship	26	semi	lmst
H8	379400	535000	Spitley Tongue	29	dune	lmst
L1	399200	529000	Middle End	5	heath	sdst
L2	399500	525000	Blackton	24	dune	sdst
L3	397000	523800	Mickleton	5	tilled	lmst
L4	399300	522200	Romaldkirk	5	semi	sdst
L6	399100	515900	Nova Scotia	24	semi	arsd
L7	405000	515300	Thorsgill	5	tilled	lmst
L8	404800	521400	Kinninvie	24	tilled	sdst
L9	409500	518700	Stretlam	24	dune	arsd
L10	412500	512500	Hutton	5	tilled	lmas
L11	416300	517000	Barforth Hall	24	tilled	arsd
L12	415800	521000	Grainger Barn	24	tilled	arg
L13	419300	519500	Killerby	2	semi	dldo
L14	419300	512600	Carlton	24	tilled	arsd
L15	423100	509000	Barton	24	semi	lmas
L16	426500	511800	Stapleton	8	wood	dldo
L17	428500	509500	Croft on Tees	24	urban	arg
L18	432100	508700	Eryholme	8	tilled	sdst
L19	433600	506000	Low Entercommon	24	tilled	sdst
L20	434400	509100	Black Wood	24	semi	sdst
L21	435500	512100	Middleton One Row	24	tilled	sdst
L22	422600	517100	Ulnaby Hall	5	tilled	sdst
L23	422200	513400	Manfield	24	tilled	dldo
L24	397000	520500	Gill House	26	semi	arsd
L27	411300	514000	Van Farm	5	tilled	lmst

L27b	411300	514000	Van Farm	6	tilled	lmst
L29	424000	514900	Merrybent	24	semi	dldo
L30	435300	512000	Over Dinsdale Grange	24	tilled	sdst
L31	407900	523600	Cragg Top	24	semi	arg
L31b	407900	523600	Cragg Top	25	semi	arg
L32	412500	517750	Little Newsham	24	tilled	arsd
L33	420600	508400	Middle Lavien	6	tilled	lmst
L34	413800	519500	East Bell House	24	tilled	arg
L35	411800	514000	woodland	5	tilled	lmst
L36	433300	507400	Docking Slack Plantation	24	tilled	sdst
L38	413400	520500	Staindrop	24	urban	arg
L39	415500	513600	Caldwell	24	dune	lmst
L40	436400	510500	Low Moor Farm	24	tilled	sdst
IBG1	437200	507200	West Worsall	24	tilled	sdst
IBG2	441400	507050	Picton Grange	24	semi	sdst
IBG3	443100	509900	Kirklevington School	24	urban	sdst
IBG4	439300	510000	Low Worsall	24	tilled	sdst
IBG5	441500	513700	Egglescliffe School	24	urban	sdst
IBG6	444900	515250	Thornaby Way	24	tilled	mgac
IBG7	442900	515900	Preston Hall	24	semi	sdst
M1	395500	529300	Marl Beck	26	dune	arsd
M2	393900	527500	Hardberry Farm	24	dune	arsd
M3	391300	529750	Moor House	26	dune	lmst
M4	390000	532700	Black Hill	29	dune	arsd
M5	388500	530450	High Beck Head	26	semi	lmst
M6	385300	530700	Hunt Hall	24	semi	lmst
M7	385900	534300	Langdon Fell	29	dune	arsd
M8	381600	528800	Cauldron Snout	29	heath	mgac
M9	379800	527500	Maize Beck	29	heath	mgac
M10	385800	529100	Cronkley	24	dune	arg
M13	390400	527000	Holwick	5	semi	mgac
M14	393700	525200	Crossthwaite	6	semi	mgac
M15	394800	526300	High Dyke	24	wood	lmst
OV1	443000	512900	Tees, downstream of Leven	n/a	overbank	n/a

			confluence (North bank)			
OV2	439500	510400	Tees, Low Worsall (N)	n/a	overbank	n/a
OV3	443400	512900	Leven	n/a	overbank	n/a
OV4	441700	513200	Tees, Yarm Rail Br (S)	n/a	overbank	n/a
OV5	444500	516200	Tees, The Holmes (S)	n/a	overbank	n/a
OV6	443900	515700	Tees, Pipe Br (N)	n/a	overbank	n/a
OV7	444300	516300	Tees,Basselton Wd (N)	n/a	overbank	n/a
OV8	443200	515800	Tees, (S)	n/a	overbank	n/a
OV9	436400	510600	Tees, Low Moor steps (S)	n/a	overbank	n/a
OV10	385200	530900	Langdon Beck	n/a	overbank	n/a
OV11	394700	525100	Tees, Middleton (S)	n/a	overbank	n/a
OV12	434600	511400	Tees, Dinsdale (S)	n/a	overbank	n/a
OV13	439000	510400	Tees, Low Worsall (S)	n/a	overbank	n/a
OV14	444600	512100	Leven, Leven Br (N)	n/a	overbank	n/a
OV15	443000	515700	Tees, Preston Hall (N)	n/a	overbank	n/a
S1	428700	526700	Woodham	24	tilled	dldo
S2	424400	521500	Cross Lane - Heighinton	24	tilled	dldo
S3	434300	532900	Camp House	2	tilled	dldo
S4	438000	531400	Bridge House	24	tilled	dldo
S5	433800	528400	Brakees Farm	5	tilled	dldo
S6	430600	530600	Chilton	5	tilled	dldo
S7	426400	531000	Merrington Grang	2	tilled	dldo
S8	431000	524000	Preston le Skerne	24	urban	dldo
S9	429500	520700	Brafferton	24	semi	dldo
S10	433500	518600	Dales House	24	tilled	dldo
S11	431800	516000	Haughton le Skerne	24	semi	arg
S12	429700	510800	Hill Top	24	tilled	arg
S13	427000	518200	Whessoe Grange	24	tilled	dldo
S14	423300	524200	Red House	24	tilled	arg
S15	436600	533400	Trimdon House	24	tilled	dldo
S16	430500	527400	Little Isle	11	urban	dldo
S17	432700	526500	Mardon	24	semi	dldo
S18	434400	515400	Street House	18	tilled	arg
S19	429900	512900	East Skerne Park	24	semi	arg

S20	427500	516400	Faverdale	25	urban	dldo
S21	424950	528050	Eldon	5	tilled	dldo
V1	449700	503200	Faceby	24	semi	arg
V2	455300	505500	Great Broughton	24	tilled	arg
V3	444700	512200	Leven Bridge	24	tilled	sdst
V5	447200	508500	Indian Farm	18	tilled	arg
V6	449600	509700	Seamer Carrs	18	tilled	arg
V7	445700	505700	Hutton Rudby	24	semi	arg
V8	450600	506800	Busby House	9	tilled	arg
V9	452100	503400	Busby Moor	20	wood	sdst
V10	457700	503600	Hasty bank	24	wood	sdst
V11	459100	504200	Woods Farm	24	semi	arg
V12	458100	508800	Easby	24	semi	arg
V13	453700	508100	Stokesly	9	tilled	arg
V14	453000	512000	Tunstall	24	semi	arg
V15	457900	514400	Pinchinthorpe Hall	24	tilled	arg
V17	459100	511100	E. Ayton Banks	20	semi	arg
V18	450100	500450	Sparrow Wood	24	wood	arg
V19	459600	506100	Bank Foot	20	wood	arg

Appendix B

Table B.2 Correlation coefficients for ICP Calibration

Analyte and wavelength	Correlation coefficient
Al 308.215	0.9982
Al 396.153	0.9985
Ca 315.887	0.9939
Ca 317.933	0.9939
Ca 422.673	0.9967
Co 230.786	0.9986
Co 231.160	0.9986
Cr 205.560	0.9987
Cr 283.563	0.9988
Cu 221.459	0.9988
Cu 324.752	0.9987
Fe 234.349	0.9930
Fe 259.939	0.9936
K 404.721	0.9956
K 766.490	0.9976
Mg 279.077	0.9945
Mg 285.213	0.9863
Mn 293.305	0.9987
Mn 257.610	0.9987
Na 330.237	0.9964
Na 588.995	0.8768
Na 589.592	0.9579
Na 330.298	0.9964
Ni 227.022	0.9987
Ni 341.476	0.9971
P 214.914	0.9990
P 213.617	0.9990
S 180.669	0.9885
S 181.975	0.9942

Sc 424.683	0.9988
Sc 361.383	0.9988
Sc 357.634	0.9987
Si 251.611	0.9977
Si 252.851	0.9983
Sn 235.485	0.9980
Sn 189.927	0.9985
Sn 283.998	0.9988
Ti 336.121	0.9988
Ti 368.519	0.9988
V 310.230	0.9986
V 270.093	0.9987
Zn 334.501	0.9940
Zn 334.558	0.9900
Zn 213.857	0.9986

Appendix C

Explanation of Anova results and tabulated Anova results

Landuse 5 groups (natural, semi-natural, tilled, urban and woodland)

The woodland samples are high in Al, Co, Cr, Cu, Fe, Ni, Sn and V. Seventy five percent of the woodland samples are from the Cleveland Hills, which have been mined extensively for Fe. Urban areas are high in Ca, K, Mg and Si - many of the urban locations are situated on magnesium limestone, which has already been proved to contain high levels of Mg and Si. Zinc (Zn) is high in the natural soils, which are generally in the upper Tees catchment. This area has been mined in the past for its zinc ores (Johnson, 1995).

Landuse 6 groups (bed/bank, natural, semi-natural, tilled, urban and woodland)

With six groups the average values (of metal concentration) for the field samples were unchanged, but the bed and bank material often displayed higher average values. Aluminium (Al), Fe, K, Ni, Si, Ti and V were often present only in low concentrations in bed and bank samples in various stages. Potassium (K) and Si could be expected to be mobile and therefore removed by water flow. Titanium (T) and V are rare in soils, often present only where humans have introduced them. The mobility of Al, Fe and Ni will depend on the charge of the ion and the pH of the water, which influences the solubility. The bed and bank materials displayed higher levels of Co, Cu, Mn, Sc and Zn. The zinc levels were particularly high in the upper catchment, which is due to zinc mining. These elements are denser and therefore less mobile.

Geology

Only three elements could distinguish between the geological groups with 95% confidence - Mg, Si and Ti. Dolomitised limestone (Dldo) contained high levels of Mg (twice that of any other geological type), which can be expected as this rock type is composed of magnesium limestone ($CaMgCO_3$). Sandstone was also fairly high in Mg - probably due to impurities or interbedded limestones. Igneous material Mgac was very low in the Mg. Igneous rocks are not likely to contain carbonate material and any Mg present is likely to be fixed into the lattice. There was little difference between differentiated argillaceous rocks (arsd) and limestone (lmst), whilst argillaceous rocks (arg) had lower concentrations of Mg. The Ti content of mgac was double that of all other rock types. It is possibly released by weathering of igneous material.

Differentiated argilaceous rocks (arsd) were high in Fe and Al in the total extraction (stage 5); this will be due to the Cleveland Hills, as this rock type is prevalent in the Leven catchment. Igneous rock (mgac) was also high in Fe and Al, which are common rock forming minerals in igneous rocks. Aluminium (Al) and Fe contents increased from arg to lmst to sandstone (sdst) rock types, Al would normally be expected to be higher in clays than sdst and lmst. Chromium (Cr) is highest in arg and arsd rocks, possibly due to substitution in the clay matrix. The same Mg trend is seen stage 5 extraction as in extraction stage 2 with dldo showing the highest concentrations and mgac the lowest.

Subcatchment

The variability of the elements within a subcatchment was generally very high. Cobalt (Co) and Cr were the only elements with low variabilities with respect to their mean values in stage 2, as was Cr in stage 3. Many of the elements selected by Anova in stage 2 are metals; which are found to be high in the Leven, owing to the effect of mining in the Cleveland Hills. Cobalt (Co), Cr, Fe and Ni have high values in the Leven, but show little diversity across the rest of the catchment. Potassium (K) is highest in the Skerne and lower catchment, possibly due to the mostly agricultural use of the land in this area. Magnesium (Mg) is two and a half times higher in the Skerne catchment than elsewhere which is likely to be as a results of the dolomitised limestone (dldo). Silica (Si) was highest in the Skerne also.

In extraction stage 3 the Leven was again shown to have elevated levels of metals, including Cr, Fe and Sn. The upper catchment was also high in Fe. The Pennines have been extensively mined in the past, mostly for Cu, Pb and Zn, but some Fe was mined there also. Potassium (K) was found by Anova to be very low in concentration in the upper catchment, which is predominantly pasture, whilst lower areas of the Tees are used for crops. Fertilisers added to fields are likely to elevate K levels. Again high Mg was found in the Skerne catchment.

Table C.1 ANOVA results for Landuse with five source groups

Landuse Groups: natural, semi-nat, tilled, urban & woodland					
	Stage 1	**Stage 2**	**Stage 3**	**Stage 4**	**Stage 5**
Al	**9.414**	**5.331**	0.804	0.627	**5.508**
Ca	**2.832**	0.820	1.386	0.299	**2.646**
Co	**14.849**	0.329	1.079	0.966	1.514
Cr	**9.036**	**11.120**	**4.209**	0.454	1.320
Cu	**4.943**	**4.896**	0.374	0.683	1.289
Fe	**9.685**	**12.526**	1.153	0.550	**5.952**
K	1.810	0.487	**2.527**	0.616	1.984
Mg	**5.595**	1.804	1.247	0.457	**7.661**
Mn	1.621	2.080	0.441	0.587	0.495
Ni	**16.136**	**10.146**	**7.772**	0.532	**8.670**
P	2.119	1.671	0.201	0.782	0.514
Sc	n/a	**3.367**	0.701	0.805	1.886
Si	1.080	**14.801**	1.173	1.076	**3.155**
Sn	n/a	**6.941**	2.433	0.607	0.380
Ti	**5.505**	**4.229**	0.593	0.623	**3.479**
V	n/a	n/a	**2.606**	0.464	**4.421**
Zn	n/a	0.344	0.826	0.612	**2.825**
Fcritical	2.584	2.584	2.589	2.619	2.460
Stage 1 Sc, Sn, V & Zn, sums and averages = 0 Stage 2 V, sums and averages = 0					

Table C.2 ANOVA results for landuse with six source groups

Landuse Groups: bed&bank, natural, semi-nat, tilled, urban & woodland					
	Stage 1	**Stage 2**	**Stage 3**	**Stage 4**	**Stage 5**
Al	**11.577**	**5.566**	1.900	1.887	**10.876**
Ca	1.854	1.191	0.419	0.775	1.940
Co	0.889	**5.804**	**6.228**	0.988	0.803
Cr	**9.877**	**7.941**	1.107	0.399	1.995
Cu	**4.133**	**3.946**	**5.477**	1.369	1.461
Fe	**11.122**	**7.100**	0.849	1.060	**7.846**
K	2.093	**3.673**	**2.612**	0.924	**2.289**
Mg	2.060	2.001	1.341	0.406	**5.286**
Mn	0.372	**6.967**	**4.620**	1.200	1.138
Ni	**13.609**	**9.787**	**6.479**	0.495	**7.983**
P	**4.082**	**3.616**	1.272	**2.676**	1.440
Sc	n/a	**2.929**	0.486	1.498	**4.302**
Si	1.067	**12.584**	0.814	1.984	**6.930**
Sn	n/a	**5.264**	**3.105**	1.270	0.477
Ti	**6.786**	**7.252**	1.095	**4.769**	**5.473**
V	n/a	n/a	**5.770**	**3.411**	**13.782**
Zn	0.897	**7.510**	**3.835**	0.589	1.912
Fcritical	2.360	2.356	2.360	2.377	2.287
Stage 1 Sc, Sn & V, sums and averages = 0 Stage 2 V, sums and averages = 0					

Table C.3 ANOVA results for Geological group sources

Geological Groups: arg, arsd, dldo, lmst, mgac & sdst					
	Stage 1	**Stage 2**	**Stage 3**	**Stage 4**	**Stage 5**
Al	0.507	1.317	1.321	1.596	**4.602**
Ca	0.218	0.594	0.641	0.280	0.863
Co	1.918	0.350	1.847	1.209	0.667
Cr	0.945	0.357	2.254	0.990	**3.468**
Cu	0.590	0.571	1.474	1.555	0.825
Fe	0.887	2.002	2.138	1.197	**3.582**
K	1.511	2.312	2.151	0.623	1.939
Mg	1.703	**4.314**	1.986	0.459	**5.355**
Mn	1.689	1.039	0.985	0.476	1.638
Ni	1.701	1.723	1.471	0.938	1.039
P	1.281	1.773	1.609	1.690	0.562
Sc	n/a	0.972	0.816	1.750	1.120
Si	1.370	**4.735**	1.799	1.285	2.275
Sn	n/a	0.676	1.931	0.890	1.011
Ti	0.376	**2.708**	1.527	1.020	2.151
V	n/a	n/a	1.601	1.641	2.042
Zn	n/a	0.549	1.238	**3.182**	1.366
Fcritical	2.432	2.432	2.432	2.470	2.303
Stage 1 Sc, Sn, V & Zn, sums and averages = 0 Stage 2 V, sums and averages = 0					

Table C.4 ANOVA results for subcatchment source groups

Subcatchments: Upr Tees, Lwr Tees, Skerne & Leven					
	Stage 1	**Stage 2**	**Stage 3**	**Stage 4**	**Stage 5**
Al	1.078	2.527	2.773	0.487	2.564
Ca	2.140	0.794	1.309	1.481	1.549
Co	0.164	**5.258**	1.276	0.954	1.549
Cr	2.051	**3.386**	**4.171**	0.153	2.384
Cu	0.356	0.970	0.517	0.865	0.627
Fe	2.119	**4.622**	**4.282**	0.907	2.311
K	**3.597**	**4.502**	**3.283**	0.290	**3.492**
Mg	1.347	**5.249**	**4.059**	0.484	2.311
Mn	0.925	1.917	2.080	1.256	1.850
Ni	2.619	**3.846**	2.569	1.103	2.317
P	**5.189**	1.075	0.207	2.289	0.664
Sc	n/a	2.150	1.820	1.332	0.108
Si	0.805	**6.177**	1.023	0.959	1.810
Sn	n/a	1.870	**3.303**	1.407	0.538
Ti	0.772	1.189	0.965	0.477	1.082
V	n/a	n/a	1.684	0.408	**4.740**
Zn	n/a	0.498	0.687	1.160	0.796
F critical	2.812	2.811	2.802	2.839	2.689
Stage 1 Sc, Sn, V & Zn, sums and averages = 0 Stage 2 V, sums and averages = 0					

Appendix D

Table D.1 PCA results for landuse stage 2

Eigenanalysis of the correlation matrix					
	CF1	**CF2**	**CF3**	**CF4**	**CF5**
Eigenvalue	4.2905	2.1302	1.7232	1.2081	0.7727
Proportion	0.358	0.178	0.144	0.101	0.064
Cumulative %	0.358	0.535	0.679	0.779	0.844
Variable	**CF1**	**CF2**	**CF3**	**CF4**	**CF5**
Al-st2	*0.071*	*-0.137*	0.455	0.379	0.298
Co-st2	0.259	-0.301	-0.340	0.367	*0.086*
Cr-st2	0.407	*0.092*	0.276	*-0.146*	*-0.115*
Cu-st2	0.417	*0.037*	*-0.105*	*-0.174*	*0.110*
Fe-st2	*0.188*	-0.526	*0.219*	*0.019*	*-0.237*
Mn-st2	*0.193*	*-0.180*	-0.461	0.497	*0.069*
Ni-st2	0.410	*0.173*	*0.121*	*-0.108*	*0.034*
P-st2	*-0.005*	0.356	*0.135*	0.486	-0.687
Si-st2	0.391	0.326	*0.106*	*0.167*	*-0.031*
Sn-st2	*0.080*	-0.547	*0.151*	*-0.189*	-0.444
Ti-st2	*-0.041*	*-0.094*	0.503	0.273	0.373
Zn-st2	0.432	*0.028*	*-0.107*	*-0.189*	*0.081*

Table D.2 PCA results for landuse stage 3

Eigenanalysis of the correlation matrix				
	CF1	**CF2**	**CF3**	**CF4**
Eigenvalue	2.9539	1.9931	1.6485	0.7509
Proportion	0.369	0.249	0.206	0.094
Cumulative %	0.369	0.618	0.824	0.918
Variable	**CF1**	**CF2**	**CF3**	**CF4**
Co	*-0.221*	*0.198*	-0.623	*-0.211*
Cu	-0.503	*0.156*	*0.232*	*0.262*
K	-0.326	*-0.041*	*0.241*	-0.869
Mn	*-0.171*	*0.308*	-0.609	*-0.022*
Ni	-0.508	*-0.12*	*0.097*	*0.036*
Ti	*-0.12*	-0.619	*-0.287*	*0.14*
V	*-0.178*	-0.642	*-0.154*	*-0.009*
Zn	-0.509	*0.173*	*0.116*	*0.332*

Table D.3 PCA results for landuse stage 5

Eigenanalysis of the correlation matrix			
	CF1	**CF2**	**CF3**
Eigenvalue	3.5023	1.3048	0.9447
Proportion	0.438	0.163	0.118
Cumulative %	0.438	0.601	0.719
Variable	**CF1**	**CF2**	**CF3**
Al	-0.456	*0.133*	*-0.116*
Fe	-0.496	*0.147*	*-0.044*
Ni	-0.318	*-0.154*	*0.299*
Sc	-0.389	*0.024*	*-0.151*
Si	*0.019*	-0.718	*0.125*
Sn	*0.074*	0.424	0.834
Ti	-0.484	*0.075*	*0.02*
V	*-0.232*	-0.485	*0.401*

Table D.4 PCA results for Geology stage 2

Eigenanalysis of the correlation matrix		
	CF1	**CF2**
Eigenvalue	1.9655	0.9999
Proportion	0.655	0.333
Cumulative	0.655	0.988
Variable	**CF1**	**CF2**
Mg	-0.707	*0.001*
Si	-0.705	*0.077*
Ti	*0.055*	0.997

Table D.5 PCA results for Geology stage 5

Eigenanalysis of the correlation matrix			
	CF1	**CF2**	**CF3**
Eigenvalue	1.9695	1.0155	0.8036
Proportion	0.492	0.254	0.201
Cumulative	0.492	0.746	0.947
Variable	**CF1**	**CF2**	**CF3**
Al	-0.659	0.095	*-0.174*
Cr	*0.087*	0.943	*0.321*
Fe	-0.627	0.195	*-0.335*
Mg	0.406	0.254	-0.869

Table D.6 PCA results for subcatchment stage 2

Eigenanalysis of the correlation matrix			
	CF1	**CF2**	**CF3**
Eigenvalue	4.2804	1.4383	0.6643
Proportion	0.611	0.205	0.095
Cumulative	0.611	0.817	0.912
Variable	**CF1**	**CF2**	**CF3**
Co	*-0.135*	0.616	0.748
Cr	-0.438	*0.115*	-0.374
Fe	*-0.069*	0.726	-0.498
K	-0.403	*-0.215*	*0.162*
Mg	-0.467	*-0.144*	*0.014*
Ni	-0.439	*0.044*	*-0.087*
Si	-0.461	*-0.106*	*0.138*

Table D.7 PCA results for subcatchment stage 3

Eigenanalysis of the correlation matrix			
	CF1	**CF2**	**CF3**
Eigenvalue	2.2761	1.2445	0.7502
Proportion	0.455	0.249	0.15
Cumulative	0.455	0.704	0.854
Variable	**CF1**	**CF2**	**CF3**
Cr	-0.586	*0.057*	*0.263*
Fe	*-0.254*	0.587	-0.725
K	-0.451	-0.381	-0.392
Mg	-0.508	-0.425	*0.053*
Sn	-0.361	*0.57*	*0.498*

Appendix E

Extra PCA plots (Chapter 6)

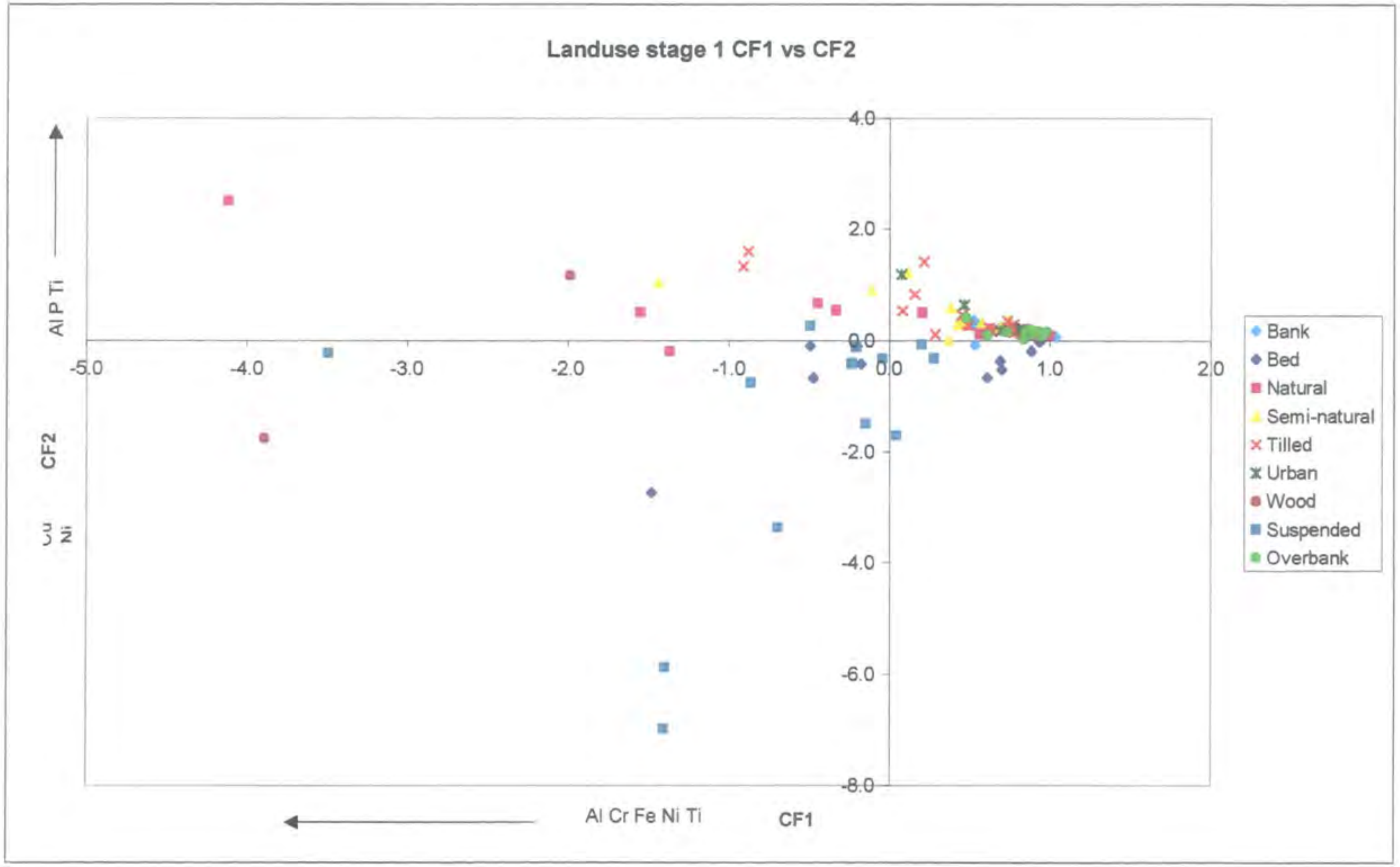


Figure E.1 (ANOVA) Landuse stage 1 CF1 vs CF2

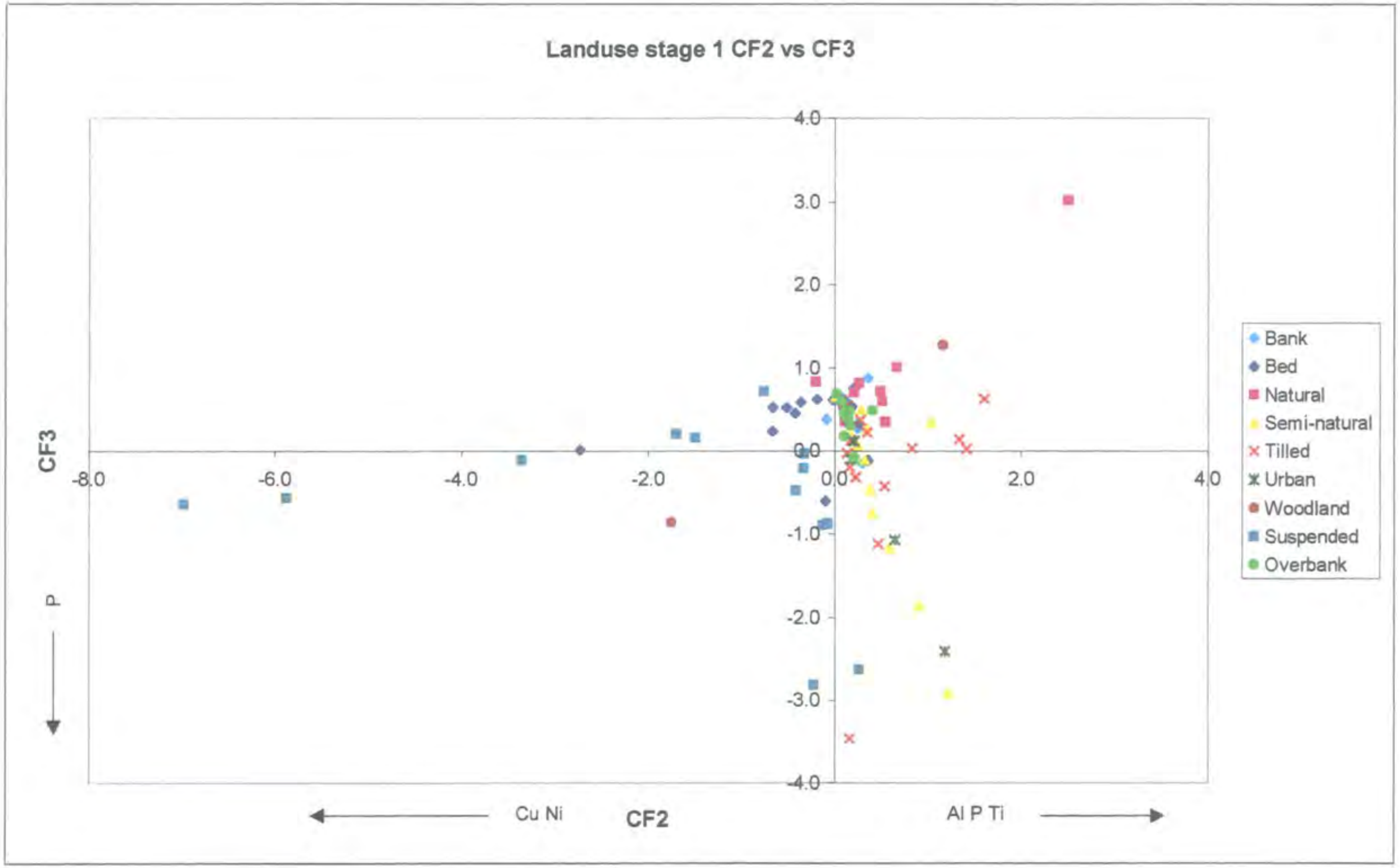


Figure E.2 (ANOVA) Landuse stage 1 CF2 vs CF3

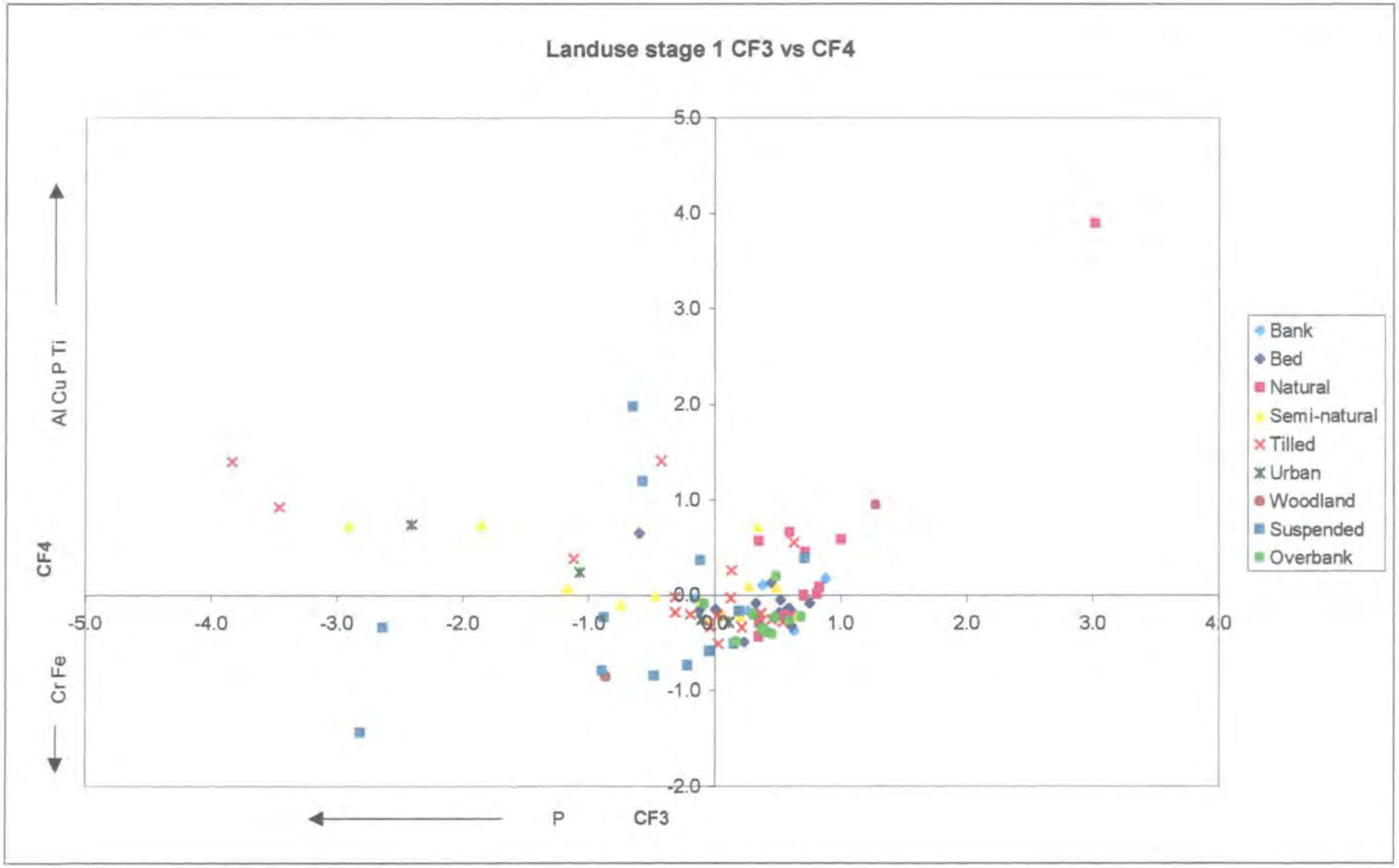


Figure E.3 (ANOVA) Landuse stage 1 CF3 vs CF4

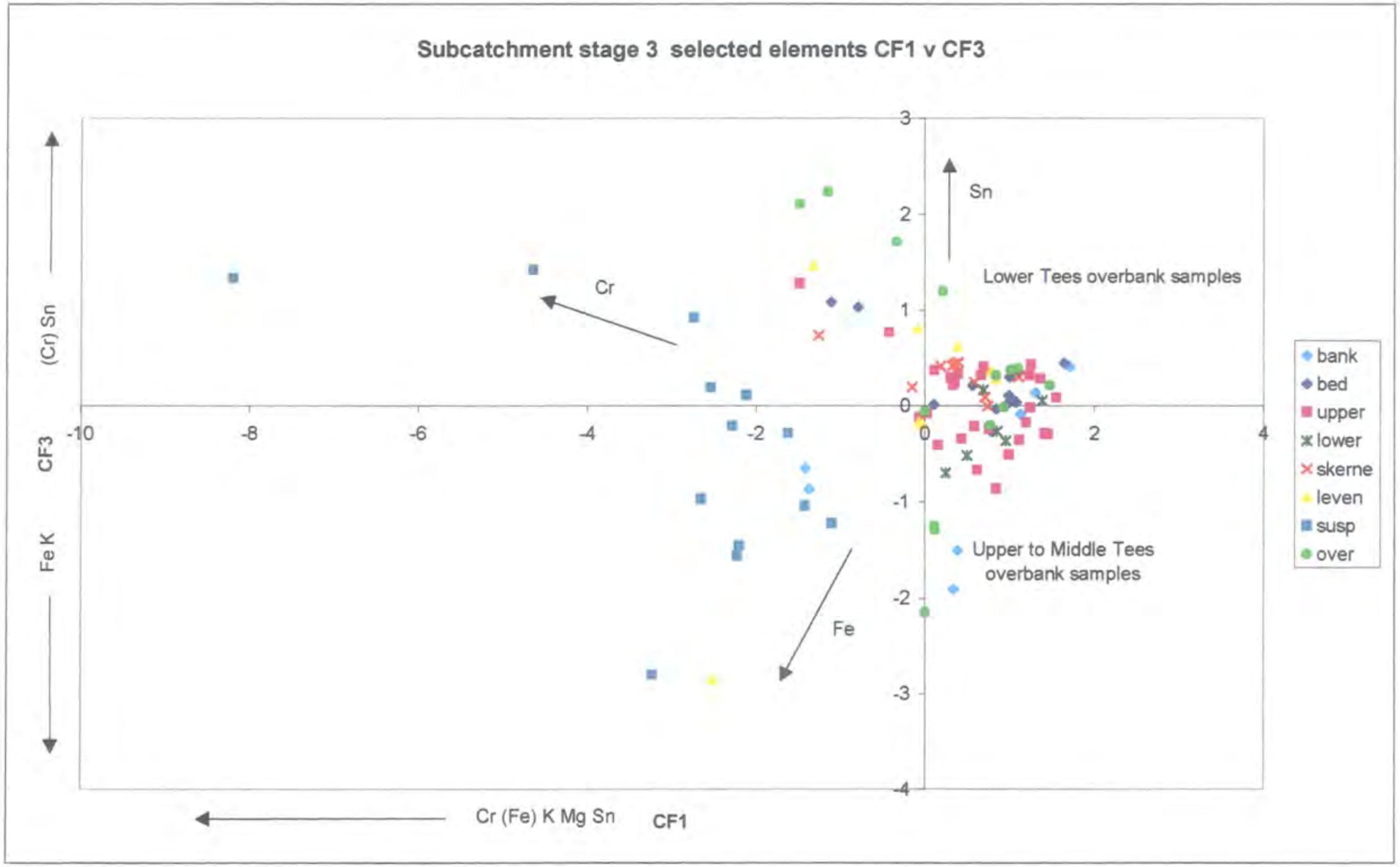


Figure E.4 (ANOVA) Subcatchment stage 3 CF1 vs CF3

Appendix F

Table F.2 Stage 1 PCA results for full dataset

Eigenanalysis of the Correlation Matrix				
	CF1	**CF2**	**CF3**	**CF4**
Eigenvalue	5.9304	4.4284	2.7752	1.0967
Proportion	0.349	0.26	0.163	0.065
Cumulative	0.349	0.609	0.773	0.837
Variable	**CF1**	**CF2**	**CF3**	**CF4**
Al	*0.114*	0.397	*-0.132*	*-0.116*
Ca	0.331	*-0.146*	*0.06*	*0.212*
Co	*0.126*	*0.169*	0.51	*0.03*
Cr	0.232	0.332	*-0.09*	*0.135*
Cu	0.342	*-0.157*	*0.063*	*-0.205*
Fe	*0.142*	0.421	*-0.105*	*-0.043*
K	0.363	*-0.179*	*-0.077*	*0.015*
Mg	0.36	*-0.184*	*-0.06*	*-0.089*
Mn	*0.037*	*0.103*	0.561	*0.049*
Ni	0.329	*0.16*	*0.051*	*-0.023*
P	*0.021*	*0.06*	*-0.079*	0.91
Sc	0.208	*-0.044*	*-0.087*	*0.101*
Si	0.325	*-0.134*	*-0.027*	*0.085*
Sn	*0.118*	0.402	*-0.133*	*-0.096*
Ti	*0.092*	0.39	*-0.109*	*-0.055*
V	0.349	*-0.185*	*-0.086*	*-0.102*
Zn	*0.074*	*0.081*	0.564	*0.004*

Table F.2 Stage 2 PCA results for full dataset

Eigenanalysis of the Correlation Matrix					
	CF1	**CF2**	**CF3**	**CF4**	**CF5**
Eigenvalue	6.885	2.6666	1.926	1.471	0.9364
Proportion	0.405	0.157	0.113	0.087	0.055
Cumulative	0.405	0.562	0.675	0.762	0.817
Variable	**CF1**	**CF2**	**CF3**	**CF4**	**CF5**
Al	*-0.079*	*0.098*	-0.524	*0.115*	-0.337
Ca	-0.354	*-0.131*	*-0.029*	*0.009*	*-0.062*
Co	*-0.125*	0.385	*0.176*	0.434	*0.037*
Cr	-0.333	*0.056*	*-0.117*	*-0.187*	*0.211*
Cu	-0.297	*0.174*	*0.23*	*-0.172*	*-0.177*
Fe	*-0.071*	0.473	*-0.246*	*-0.095*	0.312
K	-0.272	-0.253	*-0.145*	*0.22*	0.273
Mg	-0.362	*-0.156*	*0*	*-0.011*	*0.056*
Mn	*-0.089*	0.273	0.265	0.57	*-0.046*
Ni	-0.336	*0.016*	*-0.001*	*-0.058*	*0.063*
P	*-0.074*	-0.342	*-0.112*	0.264	0.468
Sc	-0.233	*0.129*	-0.319	*0.149*	-0.404
Si	-0.359	*-0.135*	*-0.003*	*0.102*	*0.07*
Sn	*0.028*	0.459	*-0.142*	*-0.244*	0.448
Ti	*0.015*	*0.016*	*-0.507*	*-0.015*	*-0.089*
V	-0.202	*-0.089*	*0.165*	-0.397	*-0.124*
Zn	-0.305	0.185	*0.237*	*-0.168*	*-0.119*

Table F.3 Stage 3 PCA results for full dataset

Eigenanalysis of the Correlation Matrix					
	CF1	**CF2**	**CF3**	**CF4**	**CF5**
Eigenvalue	6.5284	3.5486	1.9518	1.2945	0.8896
Proportion	0.384	0.209	0.115	0.076	0.052
Cumulative	0.384	0.593	0.708	0.784	0.836
Variable	**CF1**	**CF2**	**CF3**	**CF4**	**CF5**
Al	-0.211	-0.414	*-0.037*	*0.03*	*-0.207*
Ca	-0.293	0.257	*-0.117*	*-0.065*	*-0.211*
Co	*-0.066*	*-0.065*	0.651	*-0.01*	*0.155*
Cr	-0.312	*0.087*	*-0.133*	*-0.23*	*0.128*
Cu	-0.294	0.288	*0.071*	*-0.085*	*-0.206*
Fe	*-0.166*	-0.35	*0.147*	*-0.212*	*0.153*
K	-0.23	*0.063*	*-0.027*	0.465	0.413
Mg	-0.314	*0.177*	*-0.078*	*0.191*	*-0.048*
Mn	*0.002*	*0.017*	0.668	*-0.041*	*-0.128*
Ni	-0.335	*0.048*	*0.061*	*-0.032*	*0.002*
P	*-0.157*	-0.229	*-0.048*	*0.027*	0.375
Sc	-0.229	*-0.189*	*0.083*	0.453	*0.175*
Si	-0.371	*0.092*	*-0.026*	*0.101*	*-0.014*
Sn	*-0.149*	*-0.042*	*-0.094*	-0.612	0.486
Ti	*-0.151*	-0.433	*-0.035*	*-0.109*	-0.316
V	-0.205	-0.398	*-0.12*	*0.02*	-0.282
Zn	-0.297	0.25	*0.163*	*-0.178*	*-0.172*

Table F.4 Stage 4 PCA results for full dataset

Eigenanalysis of the Correlation Matrix					
	CF1	**CF2**	**CF3**	**CF4**	**CF5**
Eigenvalue	5.5968	2.5731	1.9257	1.5335	1.0505
Proportion	0.329	0.151	0.113	0.09	0.062
Cumulative	0.329	0.481	0.594	0.684	0.746
Variable	**CF1**	**CF2**	**CF3**	**CF4**	**CF5**
Al	0.366	*-0.125*	*0.019*	*0.092*	-0.274
Ca	*0.159*	*0.051*	*0.181*	-0.443	0.372
Co	0.328	*0.21*	*0.036*	*-0.009*	*-0.047*
Cr	*-0.042*	0.279	0.55	0.301	*-0.056*
Cu	*0.178*	0.43	*-0.276*	*-0.033*	-0.133
Fe	0.36	*-0.105*	*-0.09*	*0.143*	*-0.012*
K	*0.06*	*-0.071*	*0.181*	-0.533	*-0.055*
Mg	0.203	*0.198*	0.355	-0.312	*0.101*
Mn	0.192	0.342	*-0.175*	*0.083*	0.327
Ni	0.252	0.296	*0.146*	*-0.044*	*-0.213*
P	0.247	*-0.204*	*0*	*0.17*	0.519
Sc	0.352	*-0.106*	*-0.072*	*0.146*	0.291
Si	0.246	-0.252	*0.06*	*0.064*	-0.421
Sn	*-0.08*	*0.18*	0.444	0.429	*0.089*
Ti	0.294	*-0.3*	*0.022*	*0.184*	*0.023*
V	0.255	*-0.161*	*0.233*	*-0.141*	*-0.194*
Zn	*0.15*	0.388	-0.328	*0.029*	*-0.142*

Table F.5 Stage 5 PCA results for full dataset

Eigenanalysis of the Correlation Matrix					
	CF1	**CF2**	**CF3**	**CF4**	**CF5**
Eigenvalue	4.3952	3.0794	2.2553	1.9274	1.1089
Proportion	0.259	0.181	0.133	0.113	0.065
Cumulative	0.259	0.44	0.572	0.686	0.751
Variable	**CF1**	**CF2**	**CF3**	**CF4**	**CF5**
Al	0.376	-0.188	*0.023*	*0.021*	-0.039
Ca	-0.28	-0.266	-0.287	*-0.084*	0.121
Co	0.215	0.302	-0.312	-0.111	0.29
Cr	*-0.052*	*-0.036*	0.229	-0.664	0.005
Cu	*0.095*	*0.073*	-0.45	-0.204	-0.333
Fe	0.365	-0.301	*0.025*	*-0.018*	*-0.181*
K	-0.317	-0.287	*-0.216*	*-0.063*	*-0.211*
Mg	-0.323	-0.267	-0.228	*-0.078*	*-0.183*
Mn	*0.164*	0.367	-0.287	*-0.058*	*0.165*
Ni	0.224	-0.187	*-0.211*	*-0.149*	*0.097*
P	0.23	*-0.178*	-0.06	*-0.027*	*-0.032*
Sc	0.257	-0.254	*-0.057*	*0.002*	*-0.126*
Si	*-0.176*	-0.256	-0.319	*-0.061*	0.39
Sn	*-0.027*	*0.048*	0.278	-0.642	*0.018*
Ti	0.35	-0.313	*0.034*	*-0.015*	*-0.076*
V	*0.109*	-0.247	*0.004*	*-0.048*	0.658
Zn	*0.146*	0.244	-0.389	*-0.206*	*-0.183*

Table F.6 Stages 1 to 5 PCA results for full dataset

Eigenanalysis of the Correlation matrix					
	CF1	**CF2**	**CF3**	**CF4**	**CF5**
Eigenvalue	5.0062	3.1768	2.1264	1.8051	1.2546
Proportion	0.294	0.187	0.125	0.106	0.074
Cumulative	0.294	0.481	0.606	0.713	0.786
Variable	**CF1**	**CF2**	**CF3**	**CF4**	**CF5**
Al	-0.342	*-0.192*	*0.194*	*-0.092*	*-0.093*
Ca	*-0.087*	0.47	*0.058*	*-0.075*	*-0.093*
Co	-0.266	*-0.054*	-0.353	*-0.022*	0.454
Cr	*-0.103*	*0.087*	*0.117*	0.678	*0.047*
Cu	-0.21	0.34	-0.251	*0.019*	-0.3
Fe	-0.347	*-0.172*	*0.052*	*-0.019*	*0.129*
K	*0.051*	0.328	0.375	*-0.079*	0.445
Mg	*-0.003*	0.419	0.322	*-0.08*	0.351
Mn	*-0.14*	*-0.006*	-0.46	*-0.051*	0.452
Ni	-0.308	*0.199*	*-0.081*	*-0.018*	*-0.109*
P	-0.304	*-0.139*	*0.086*	*-0.049*	*0.097*
Sc	-0.349	*-0.103*	*-0.007*	*-0.038*	*0.1*
Si	-0.264	0.29	*0.116*	*-0.079*	*-0.139*
Sn	*-0.111*	*-0.007*	*0.042*	0.698	*0.049*
Ti	-0.274	*-0.202*	0.274	*-0.1*	*-0.181*
V	-0.305	*-0.118*	0.296	*-0.054*	*-0.022*
Zn	-0.219	0.307	-0.327	*0.003*	-0.237

Appendix G

Extra PCA plots (Chapter 7)

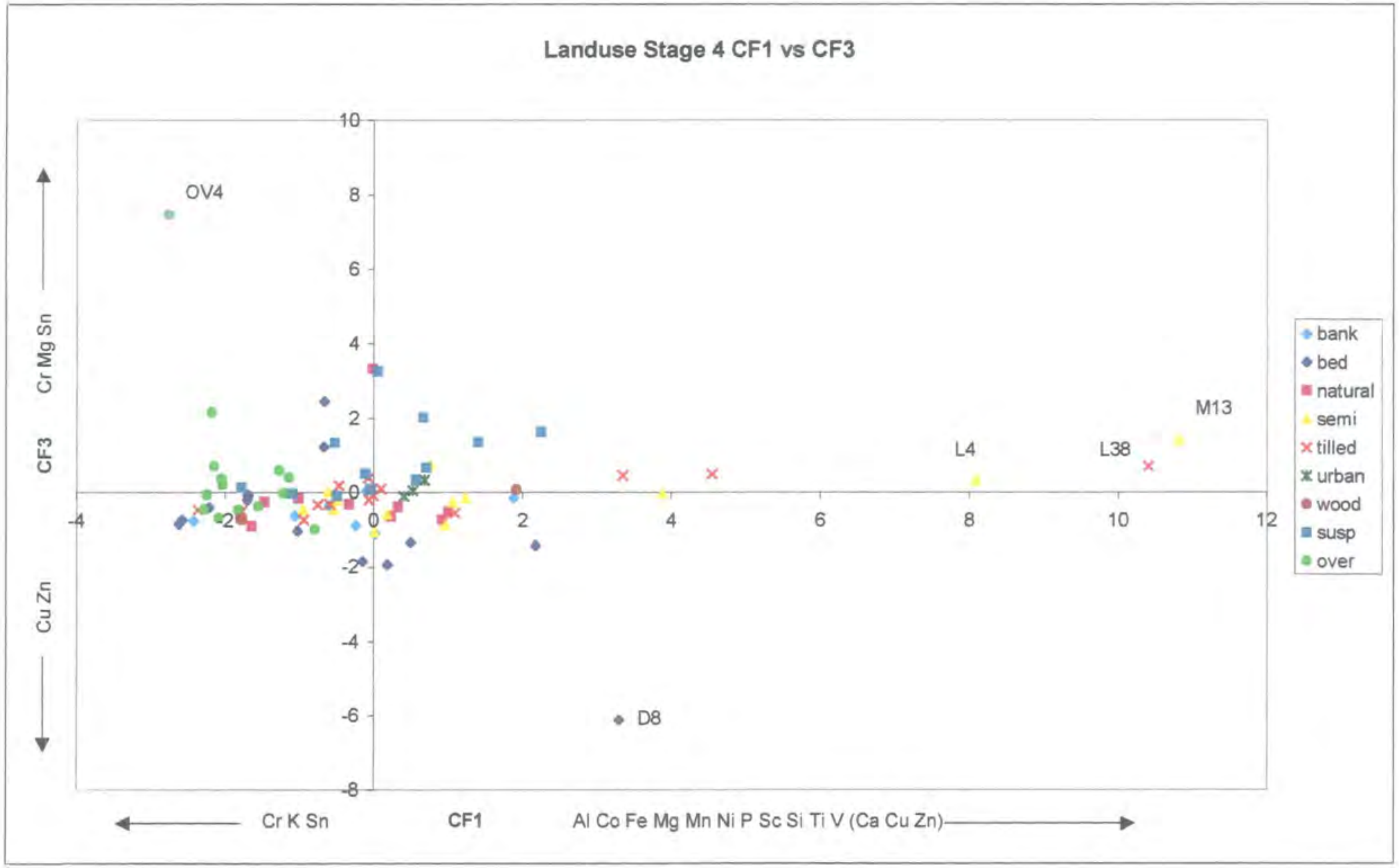


Figure G.1 PCA plot of all stage 4 data CF1 vs CF3

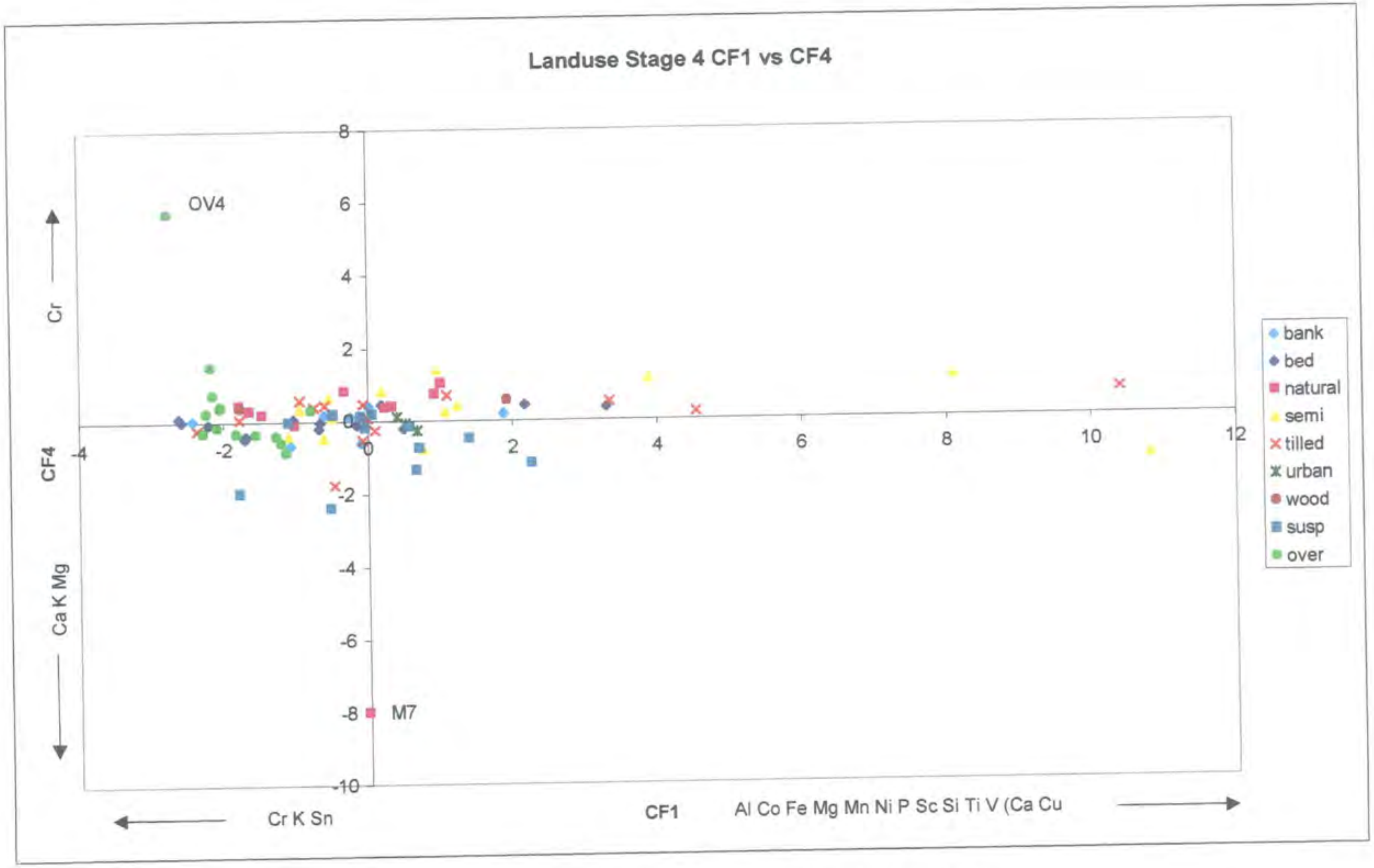


Figure G.2 PCA plot of all stage 4 data CF1 vs CF4

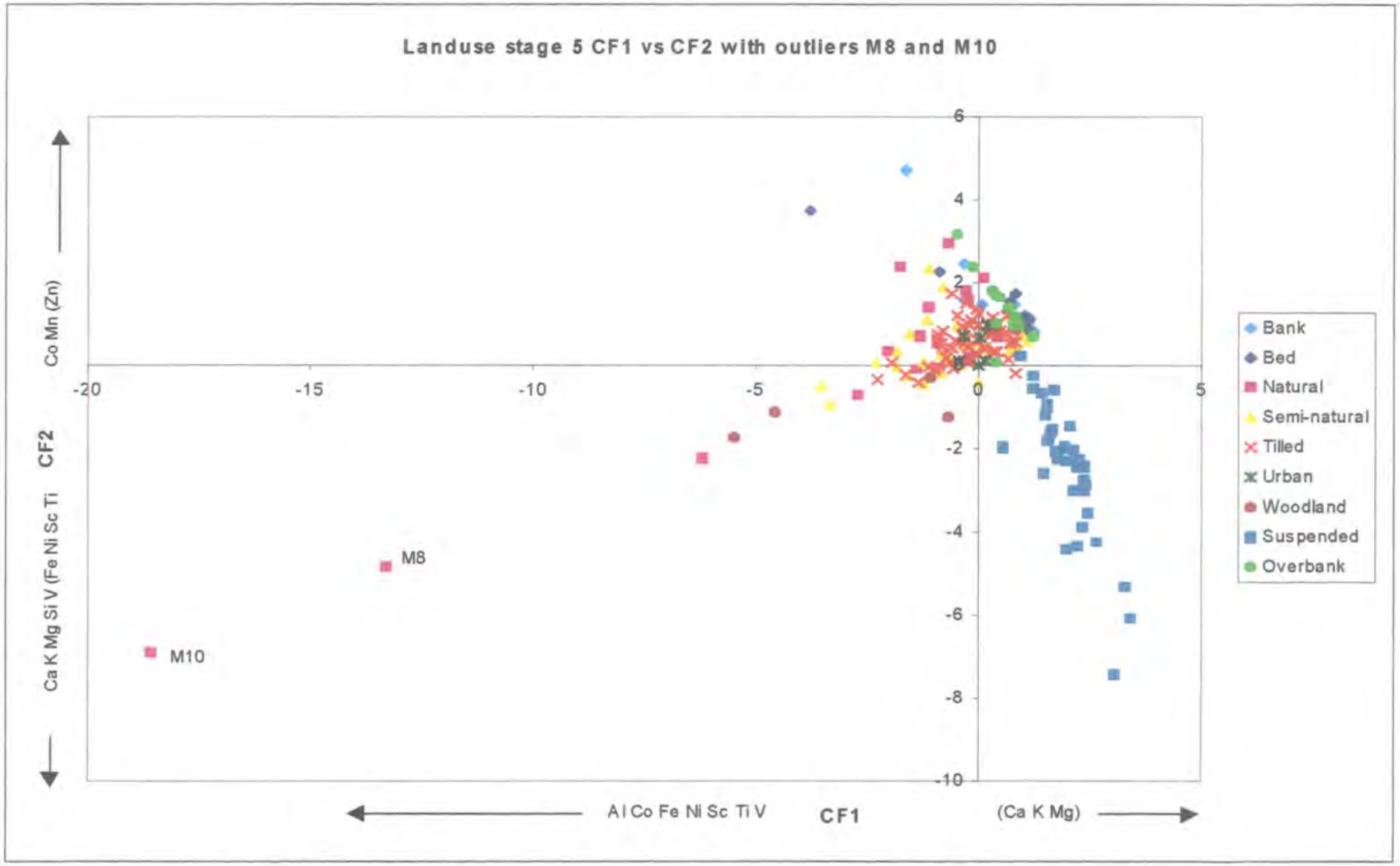
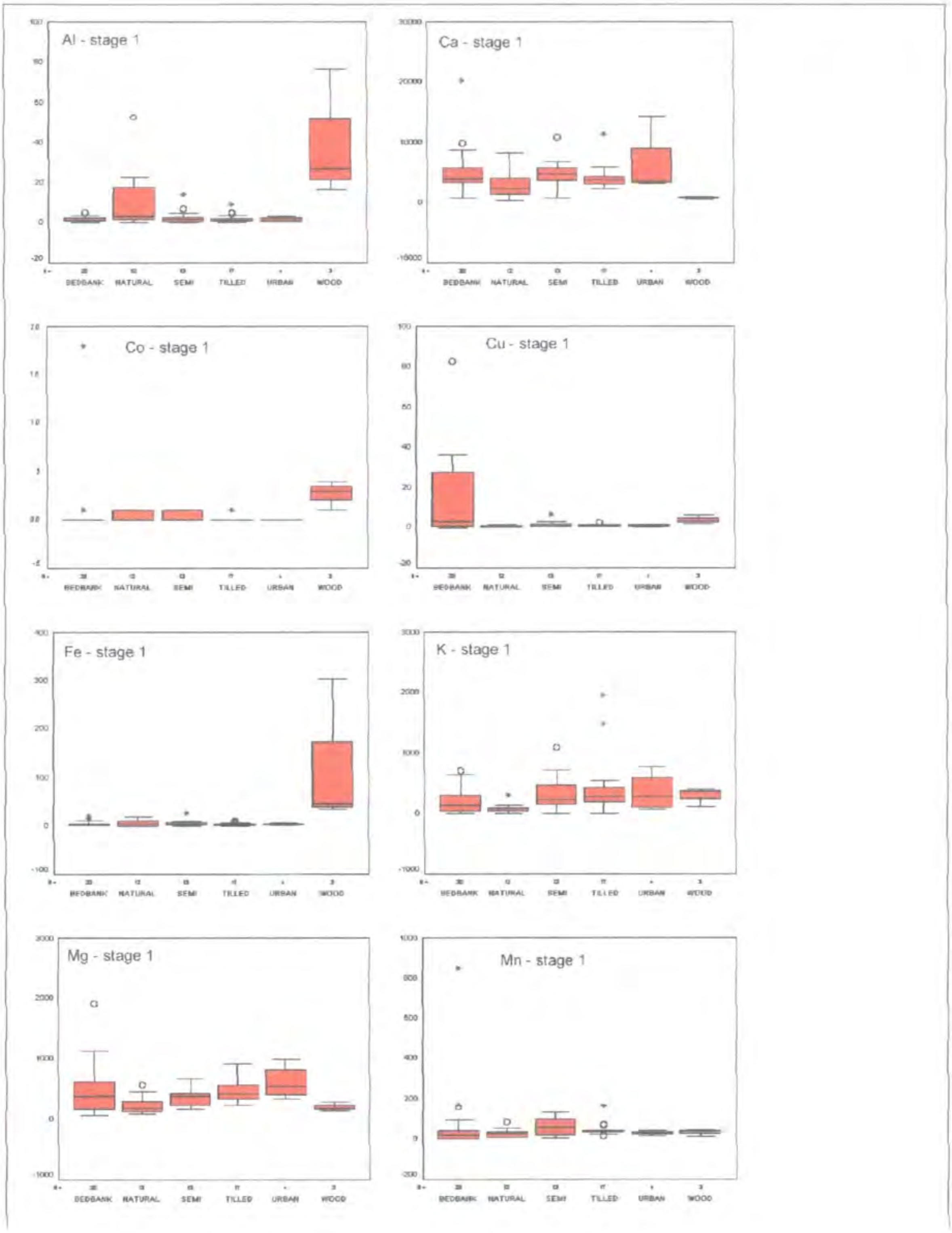


Figure G.3 PCA plot of all stage 5 data with outliers M8 and M10 included CF1 vs CF2

Appendix H

Boxplots – landuse, geology and subcatchment (Chapter 7)

Figure H.1 Boxplots Landuse stage 1



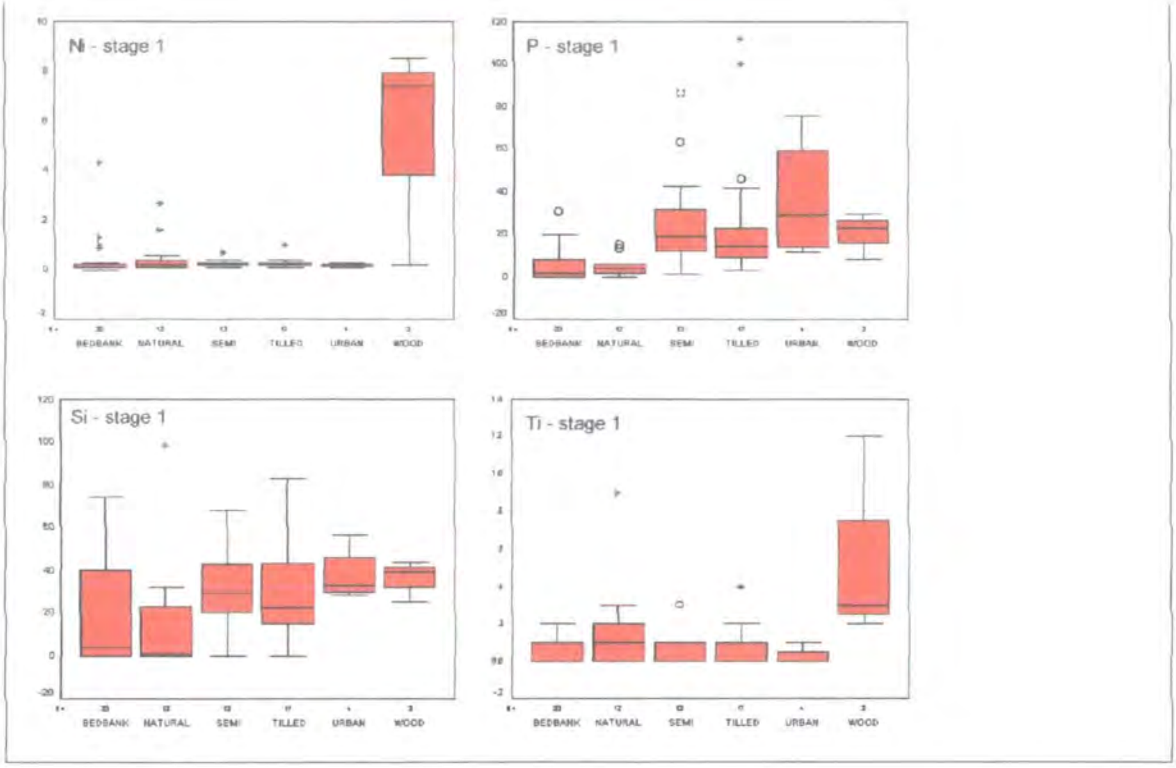
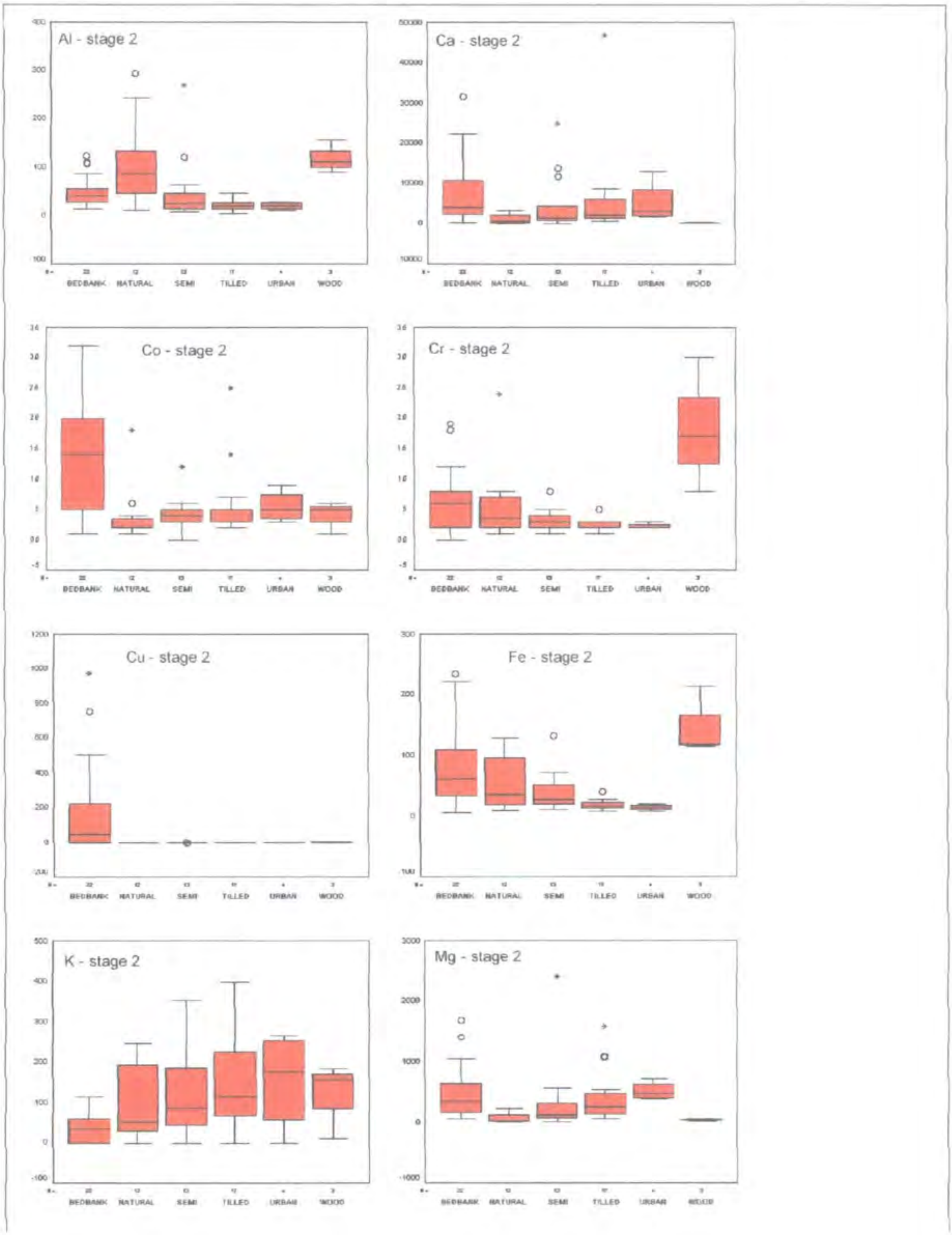

Ni - stage 1
P - stage 1
Si - stage 1
Ti - stage 1
BEDBANK
NATURAL
SEMI
TILLED
URBAN
WOOD
10
8
6
4
2
0
-2
120
100
80
60
40
20
0
-20

Figure H. 2 Boxplots Landuse stage 2



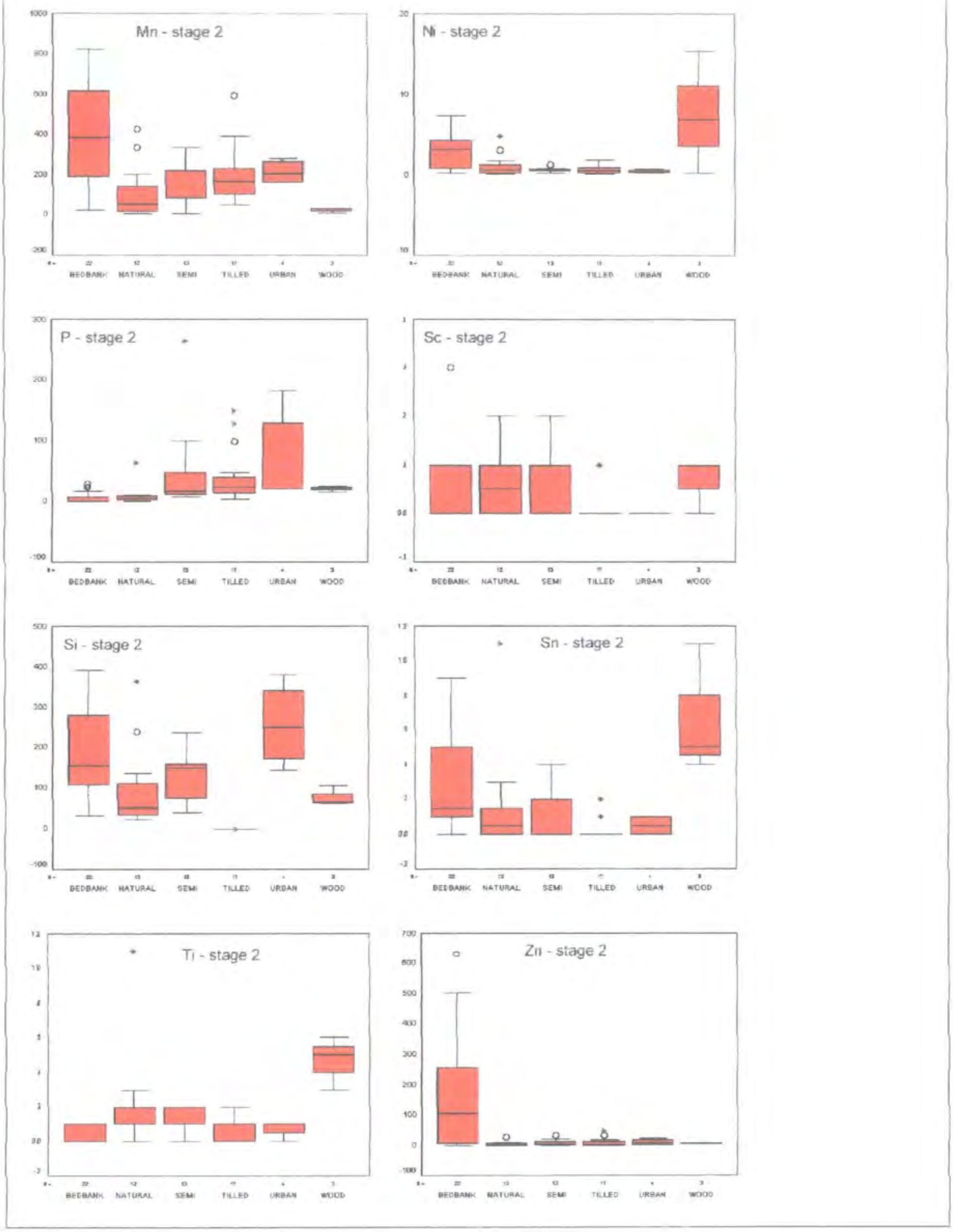
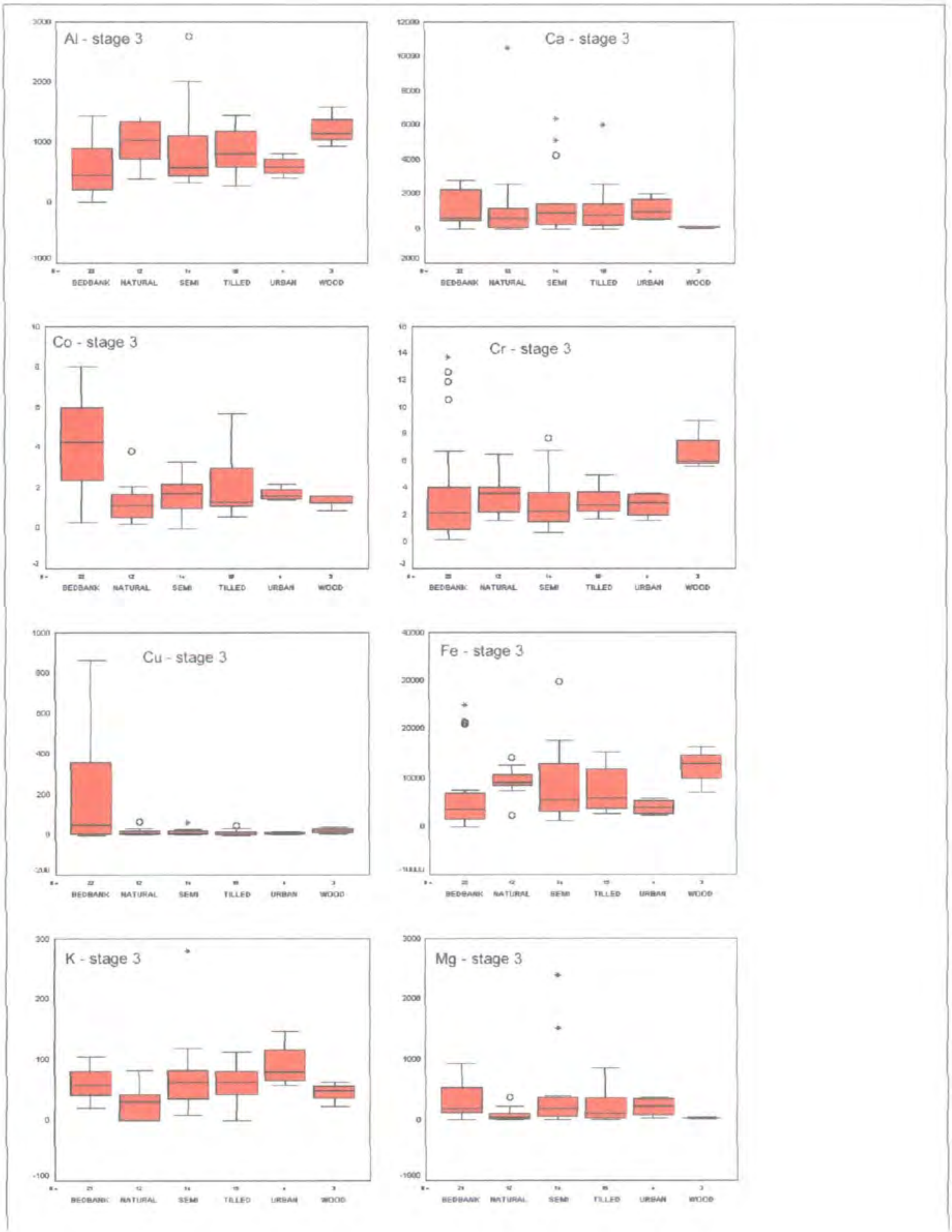
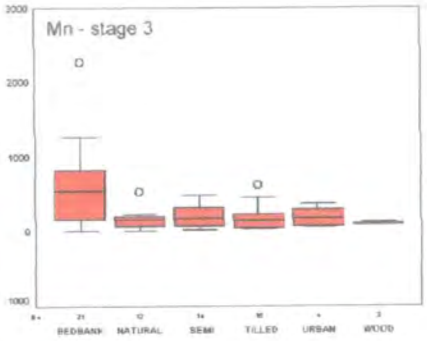
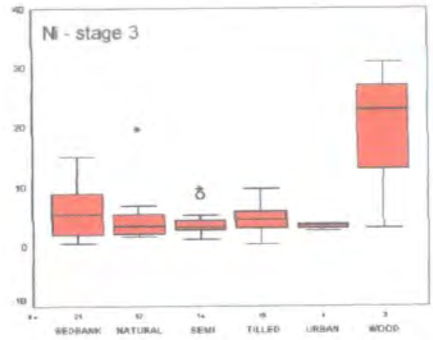
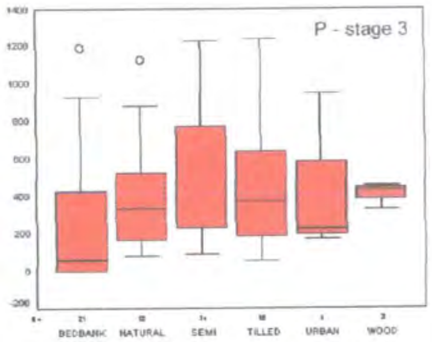

Mn - stage 2
1000
800
600
400
200
0
-200
BEDBANK
NATURAL
SEMI
TILLED
URBAN
WOOD
Ni - stage 2
20
10
0
BEDBANK
NATURAL
SEMI
TILLED
URBAN
WOOD
P - stage 2
300
200
100
0
-100
BEDBANK
NATURAL
SEMI
TILLED
URBAN
WOOD
Sc - stage 2
2
1
0.0
-1
BEDBANK
NATURAL
SEMI
TILLED
URBAN
WOOD
Si - stage 2
500
400
300
200
100
0
-100
BEDBANK
NATURAL
SEMI
TILLED
URBAN
WOOD
Sn - stage 2
12
10
0.0
BEDBANK
NATURAL
SEMI
TILLED
URBAN
WOOD
Ti - stage 2
12
10
0.0
BEDBANK
NATURAL
SEMI
TILLED
URBAN
WOOD
Zn - stage 2
700
600
500
400
300
200
100
0
-100
BEDBANK
NATURAL
SEMI
TILLED
URBAN
WOOD

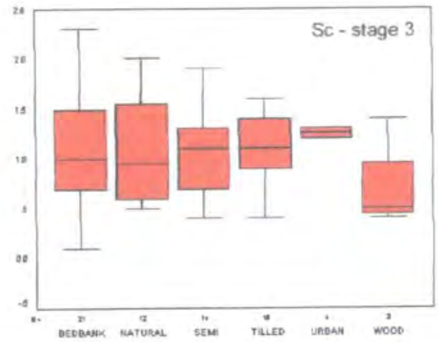
Figure H.3 Boxplots Landuse stage 3

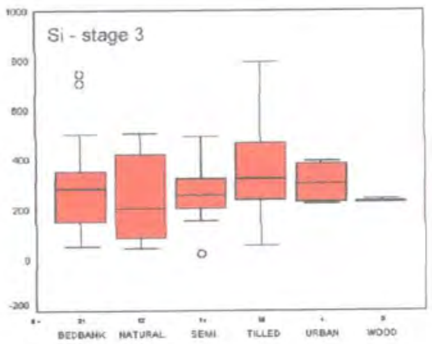


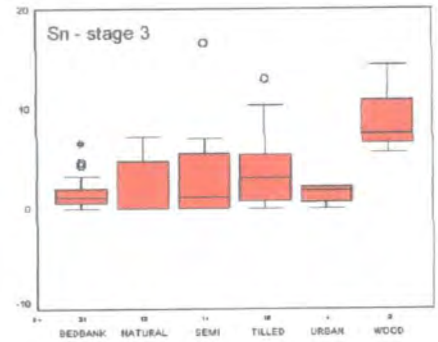

Mn - stage 3
3000
2000
1000
0
-1000
N =
21
12
14
15
4
3
BEDBANK
NATURAL
SEMI
TILLED
URBAN
WOOD

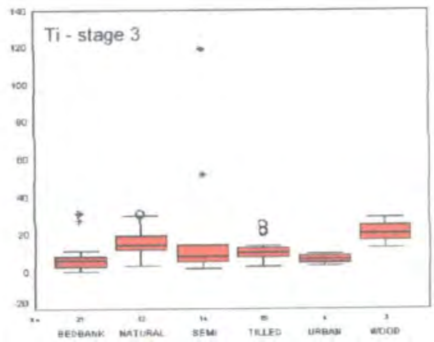

Ni - stage 3
40
30
20
10
0
-10
N =
21
12
14
15
4
3
BEDBANK
NATURAL
SEMI
TILLED
URBAN
WOOD

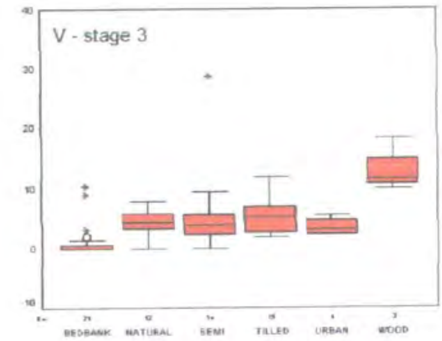

P - stage 3
1400
1200
1000
800
600
400
200
0
-200
N =
21
12
14
15
4
3
BEDBANK
NATURAL
SEMI
TILLED
URBAN
WOOD


Sc - stage 3
2.5
2.0
1.5
1.0
.5
0.0
-.5
N =
21
12
14
15
4
3
BEDBANK
NATURAL
SEMI
TILLED
URBAN
WOOD


Si - stage 3
1000
800
600
400
200
0
-200
N =
21
12
14
15
4
3
BEDBANK
NATURAL
SEMI
TILLED
URBAN
WOOD


Sn - stage 3
20
10
0
-10
N =
21
12
14
15
4
3
BEDBANK
NATURAL
SEMI
TILLED
URBAN
WOOD


Ti - stage 3
140
120
100
80
60
40
20
0
-20
N =
21
12
14
15
4
3
BEDBANK
NATURAL
SEMI
TILLED
URBAN
WOOD


V - stage 3
40
30
20
10
0
-10
N =
21
12
14
15
4
3
BEDBANK
NATURAL
SEMI
TILLED
URBAN
WOOD

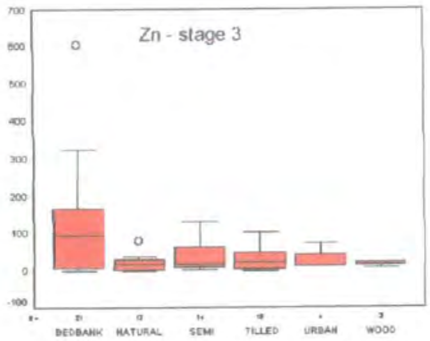
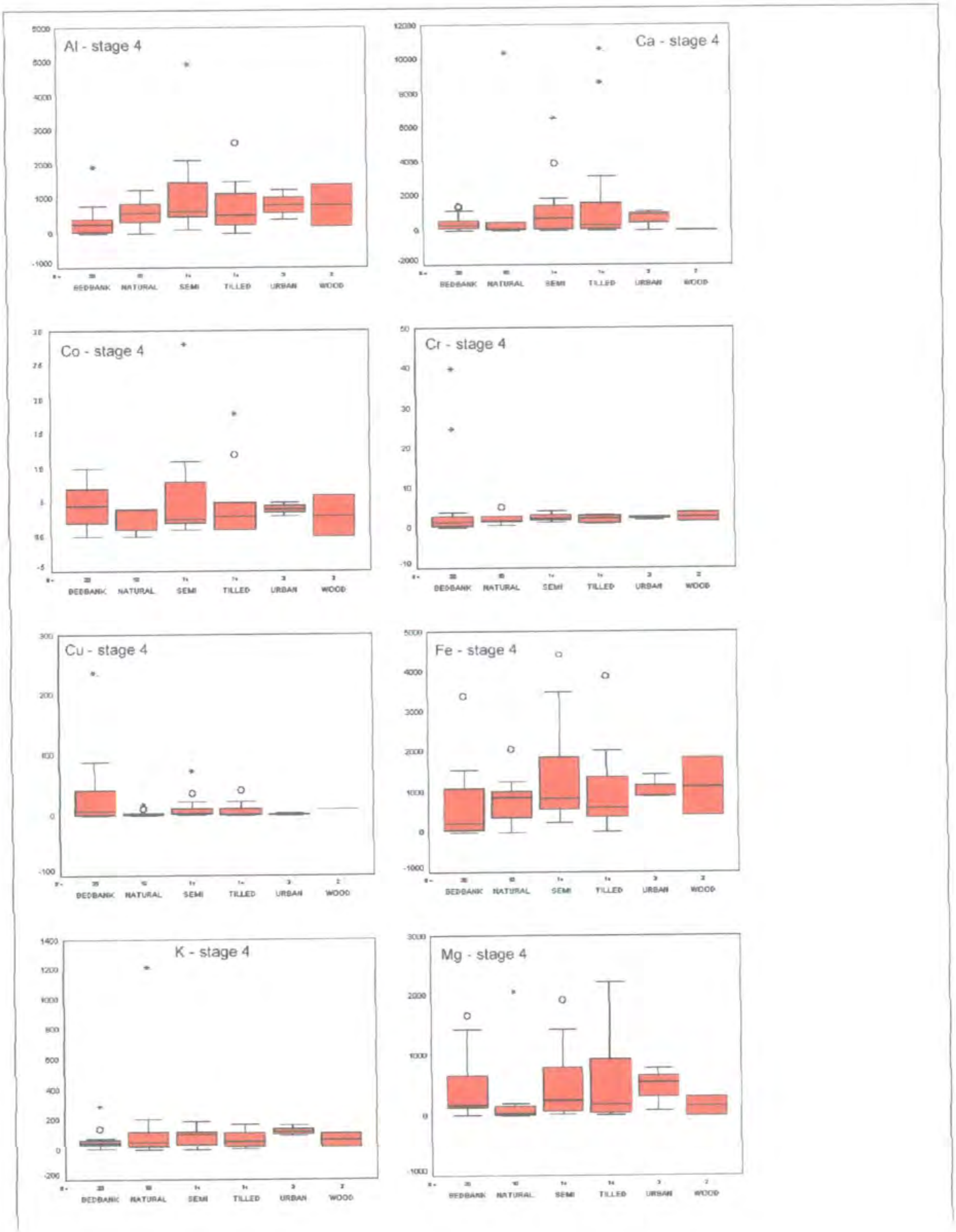

Zn - stage 3
700
600
500
400
300
200
100
0
-100
N =
21
12
14
15
4
3
BEDBANK
NATURAL
SEMI
TILLED
URBAN
WOOD

Figure H.4 Boxplots Landuse stage 4



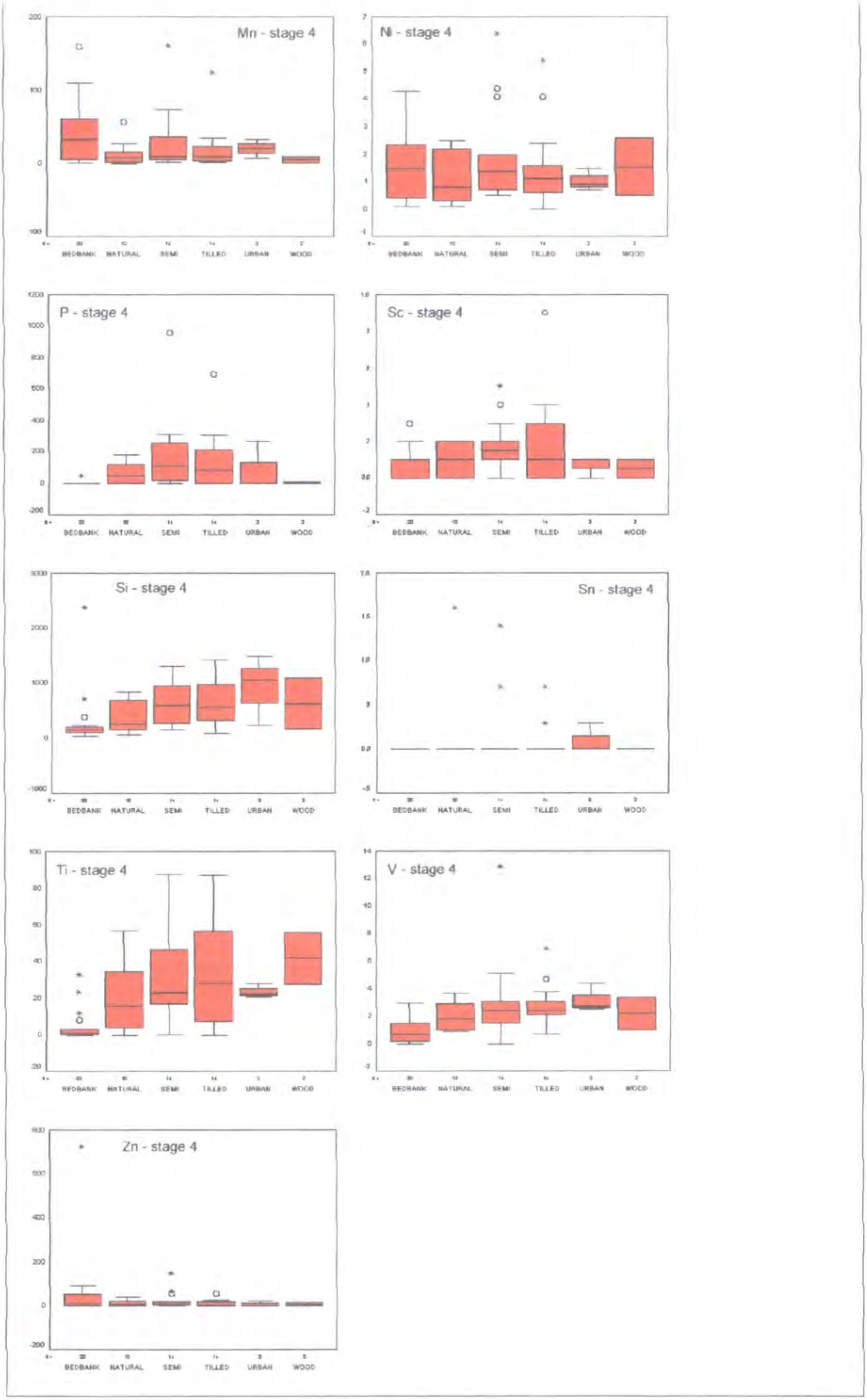
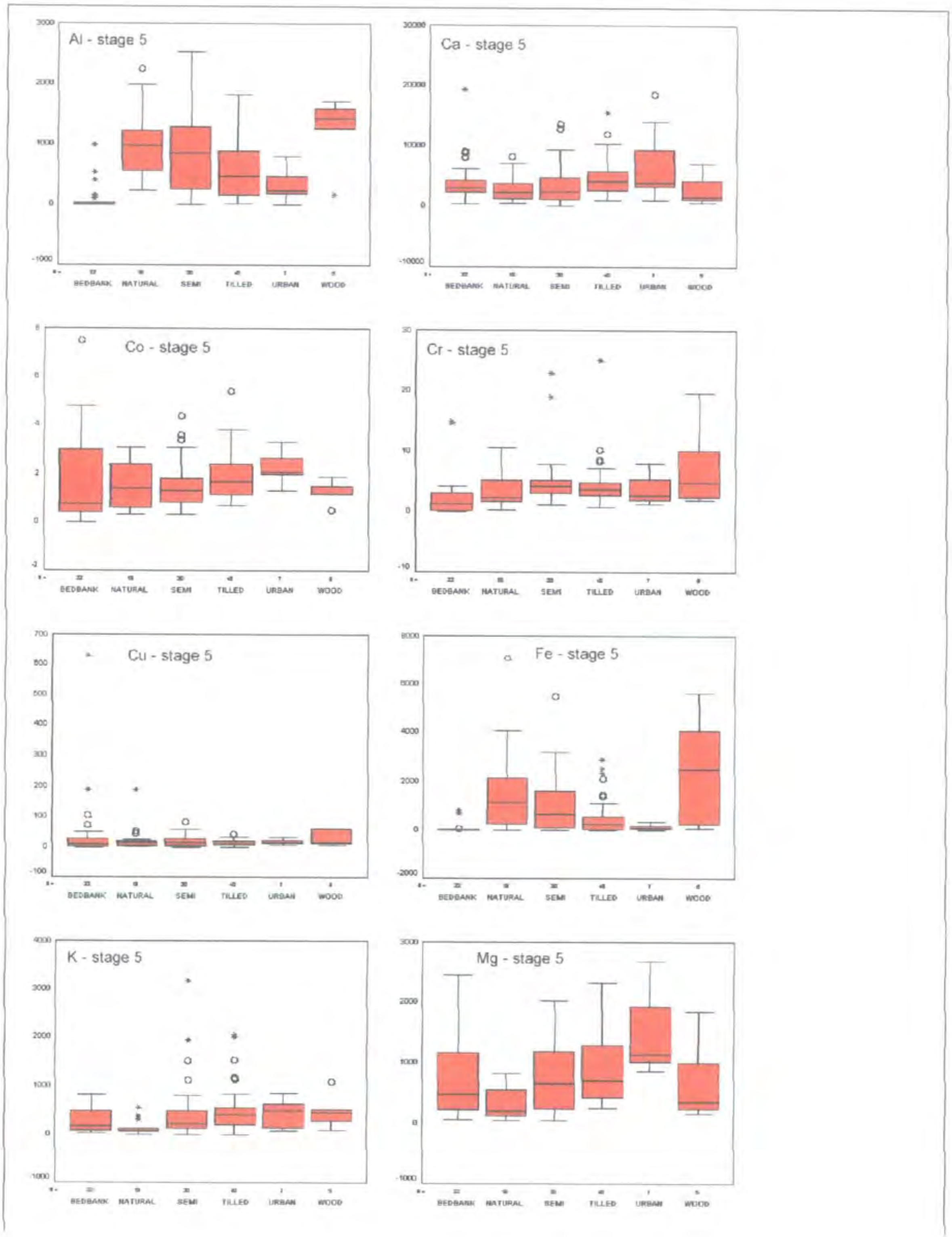
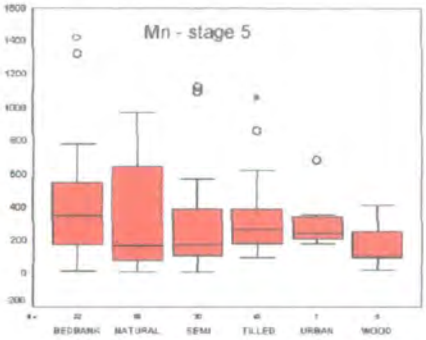
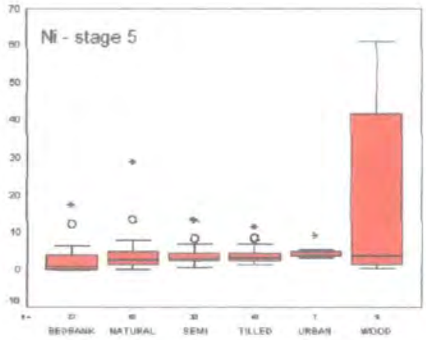
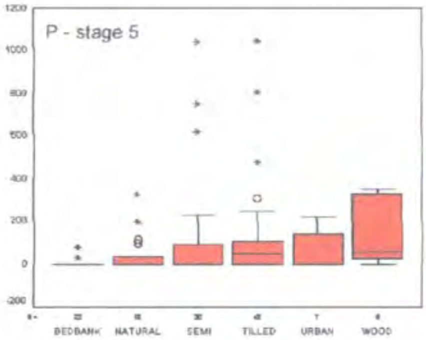

Mn - stage 4
Ni - stage 4
P - stage 4
Sc - stage 4
Si - stage 4
Sn - stage 4
Ti - stage 4
V - stage 4
Zn - stage 4
BEDBANK
NATURAL
SEMI
TILLED
URBAN
WOOD

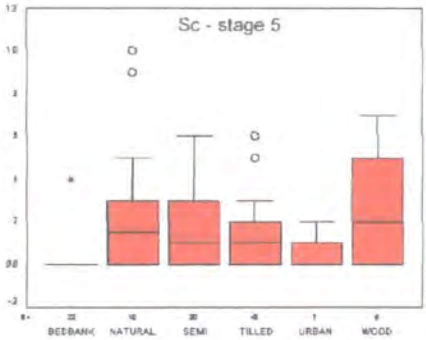
Figure H.5 Boxplots Landuse stage 5

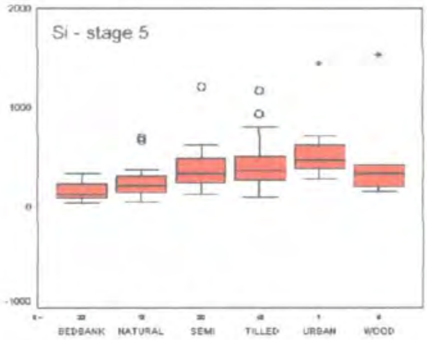


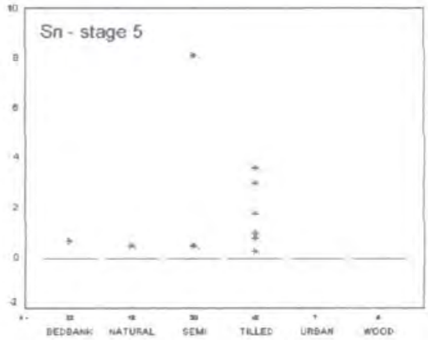

Mn - stage 5
1600
1400
1200
1000
800
600
400
200
0
-200
BEDBANK
NATURAL
SEMI
TILLED
URBAN
WOOD

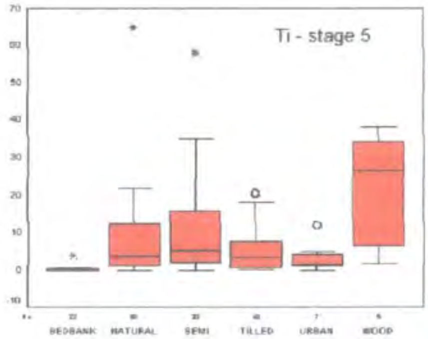

Ni - stage 5
70
60
50
40
30
20
10
0
-10
BEDBANK
NATURAL
SEMI
TILLED
URBAN
WOOD

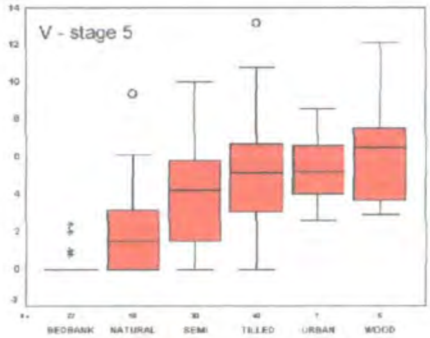

P - stage 5
1200
1000
800
600
400
200
0
-200
BEDBANK
NATURAL
SEMI
TILLED
URBAN
WOOD


Sc - stage 5
12
10
8
6
4
2
0
-2
BEDBANK
NATURAL
SEMI
TILLED
URBAN
WOOD


Si - stage 5
2000
1000
0
-1000
BEDBANK
NATURAL
SEMI
TILLED
URBAN
WOOD


Sn - stage 5
10
8
6
4
2
0
-2
BEDBANK
NATURAL
SEMI
TILLED
URBAN
WOOD


Ti - stage 5
70
60
50
40
30
20
10
0
-10
BEDBANK
NATURAL
SEMI
TILLED
URBAN
WOOD


V - stage 5
14
12
10
8
6
4
2
0
-2
BEDBANK
NATURAL
SEMI
TILLED
URBAN
WOOD

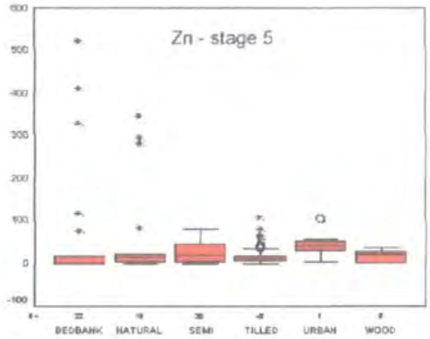
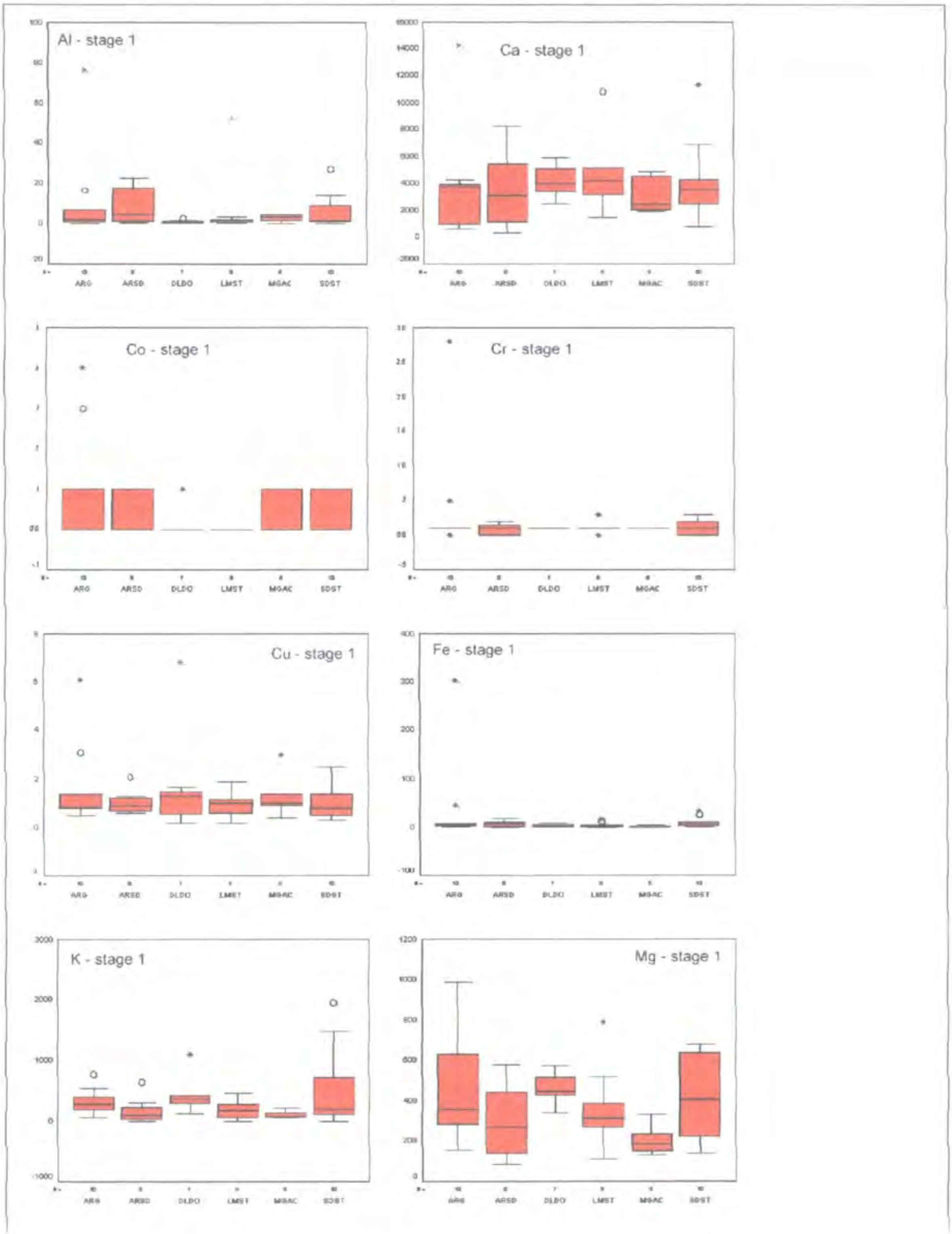
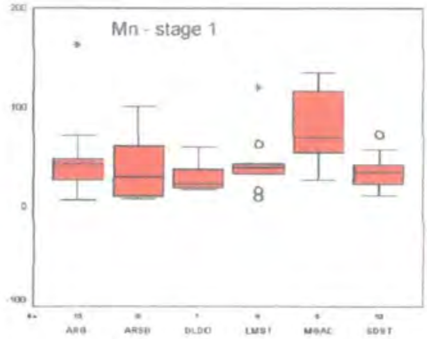
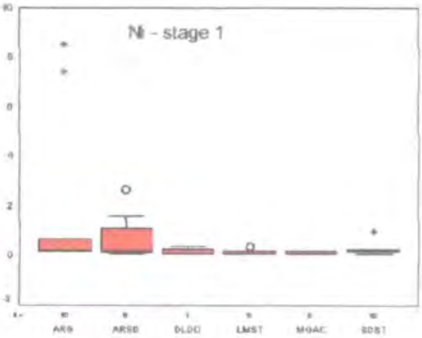
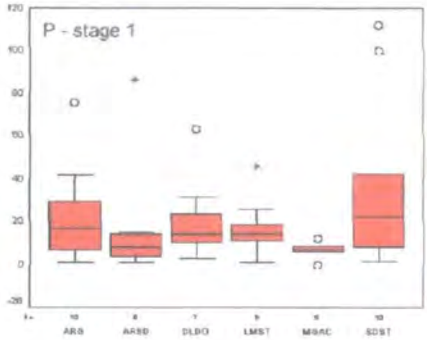

Zn - stage 5
600
500
400
300
200
100
0
-100
BEDBANK
NATURAL
SEMI
TILLED
URBAN
WOOD

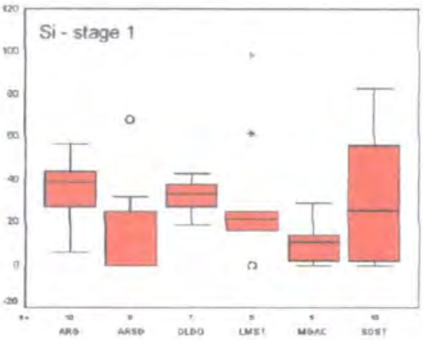
Figure H.6 Boxplots geology stage 1




Mn - stage 1
200
100
0
-100
ARG
ARSD
DLDO
LMST
MGAC
SDST


Ni - stage 1
10
8
6
4
2
0
-2
ARG
ARSD
DLDO
LMST
MGAC
SDST


P - stage 1
120
100
80
60
40
20
0
-20
ARG
ARSD
DLDO
LMST
MGAC
SDST


Si - stage 1
120
100
80
60
40
20
0
-20
ARG
ARSD
DLDO
LMST
MGAC
SDST

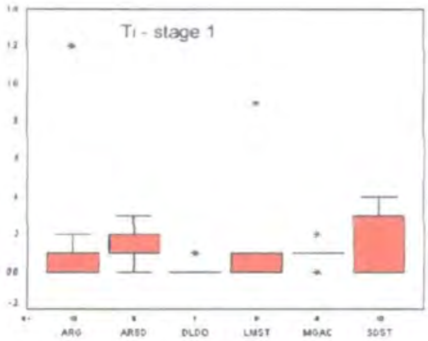
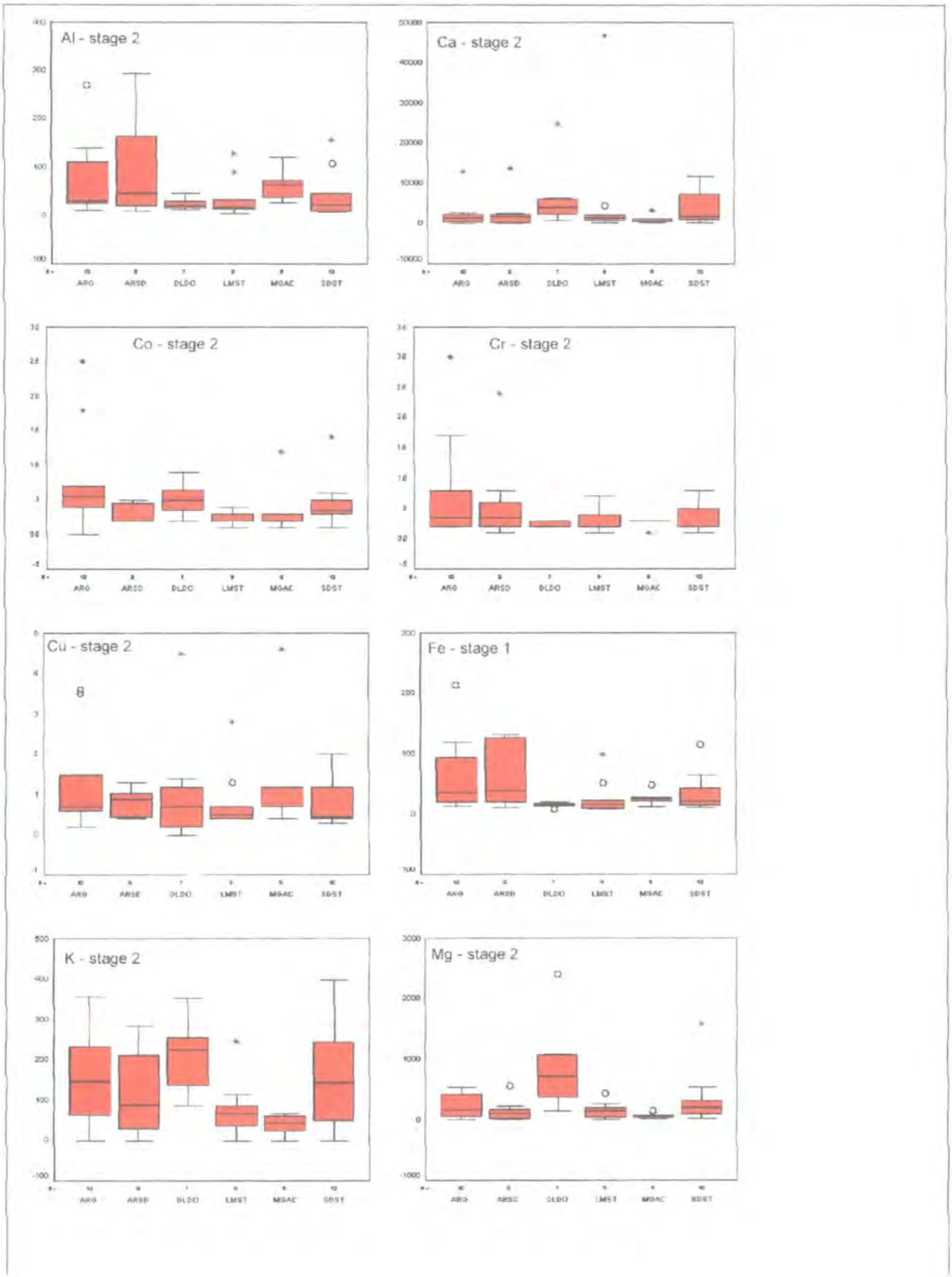

Ti - stage 1
14
12
10
8
6
4
2
0.0
-2
ARG
ARSD
DLDO
LMST
MGAC
SDST

Figure H.7 Boxplots geology stage 2



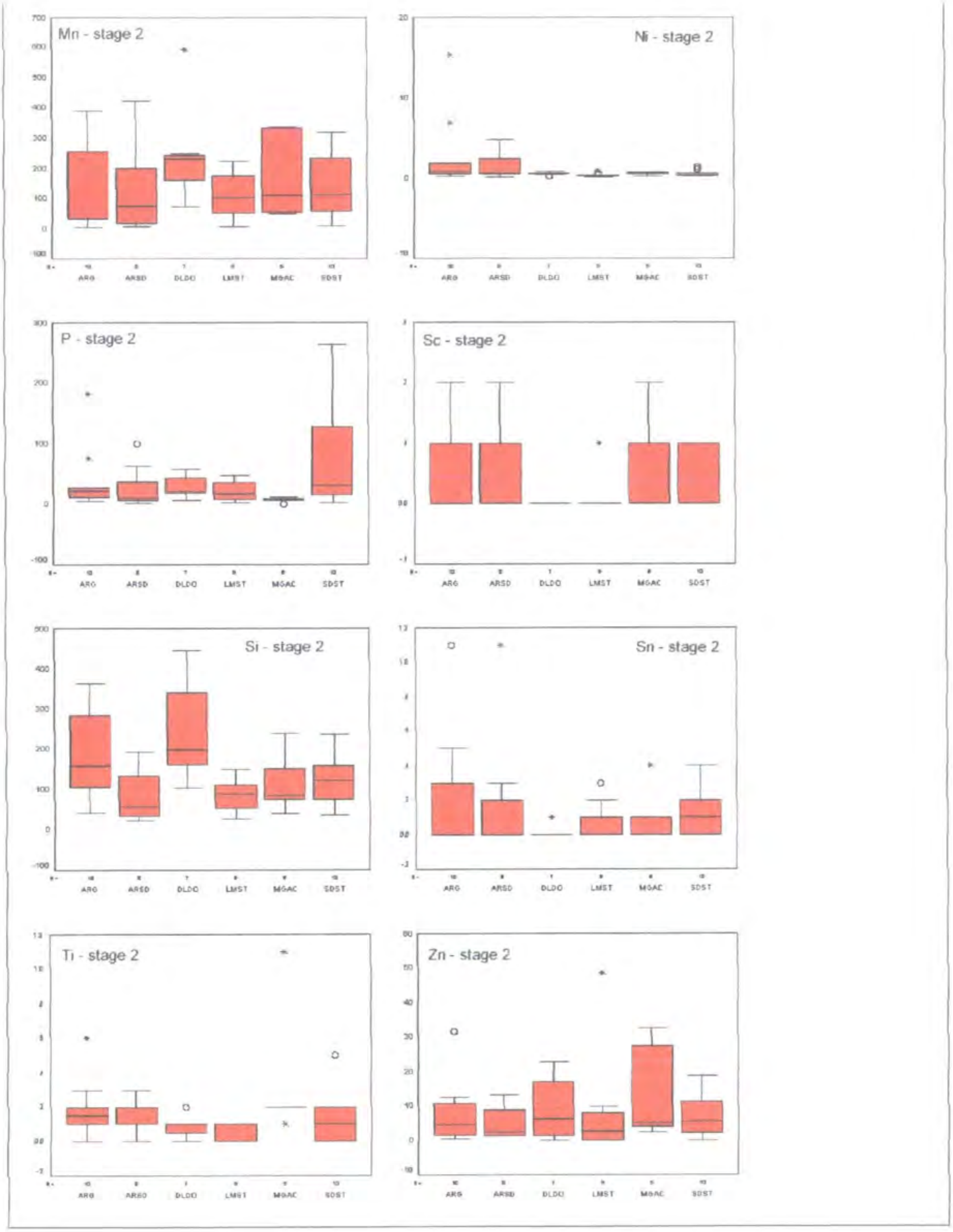
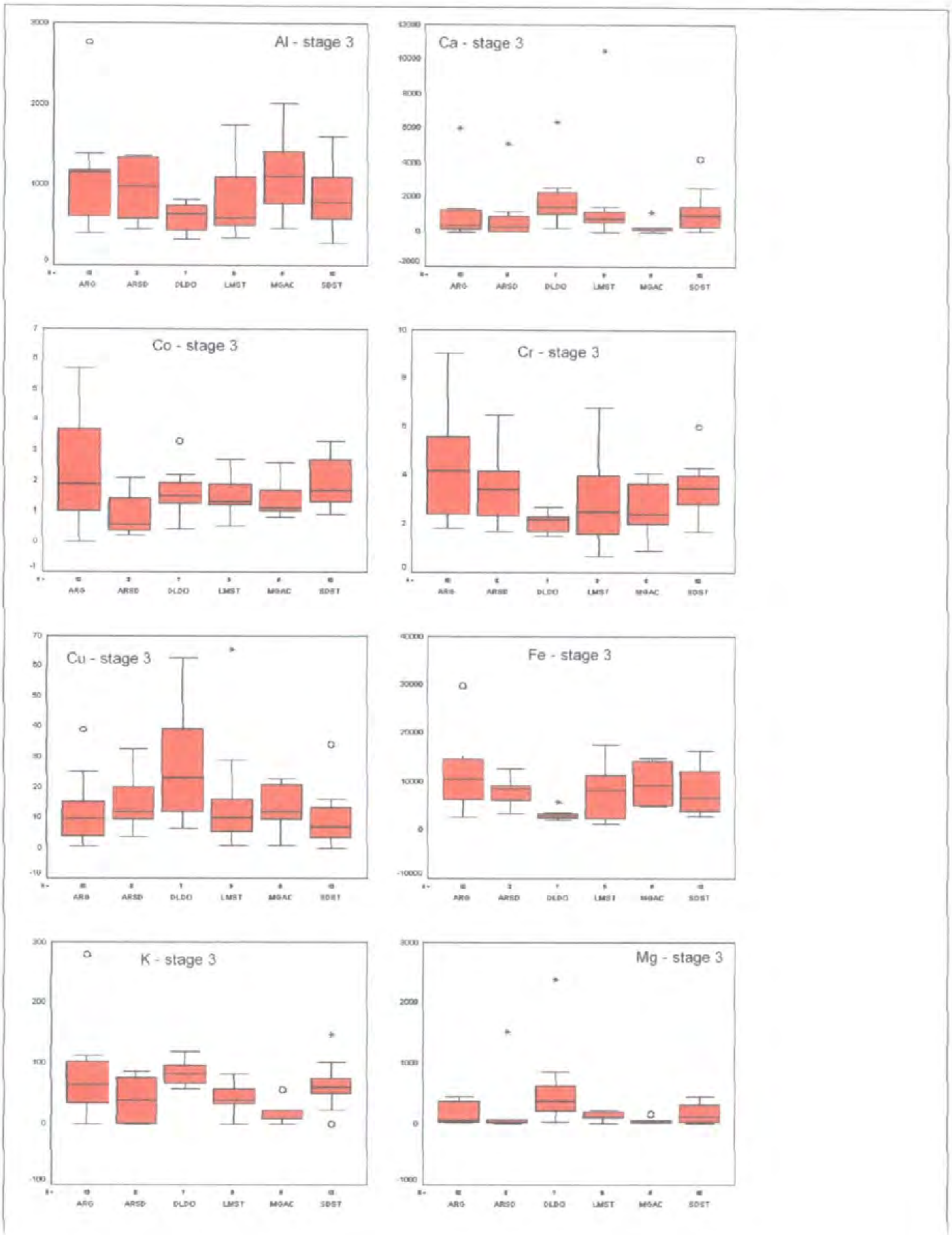
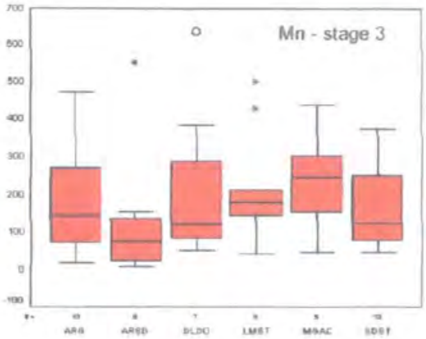
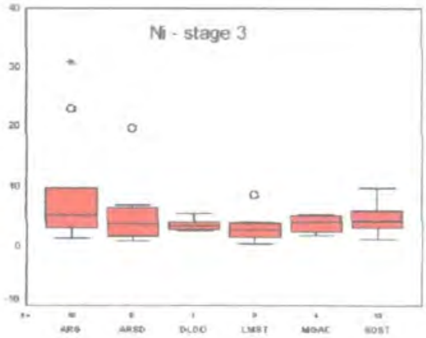
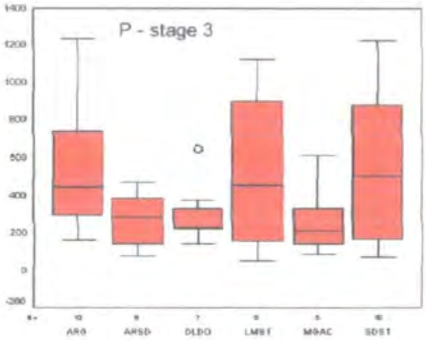

Mn - stage 2
Ni - stage 2
P - stage 2
Sc - stage 2
Si - stage 2
Sn - stage 2
Ti - stage 2
Zn - stage 2
ARG
ARSD
DLDO
LMST
MGAC
SDST

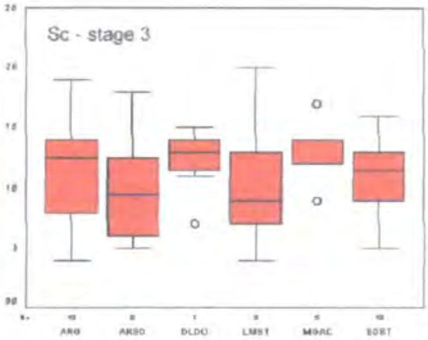
Figure H.8 Boxplots geology stage 3

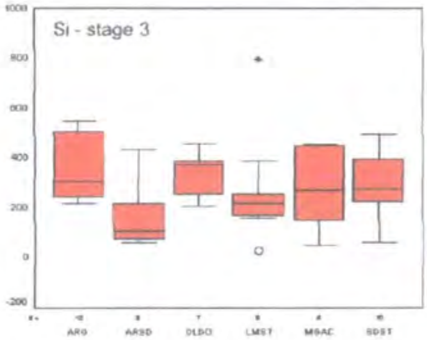


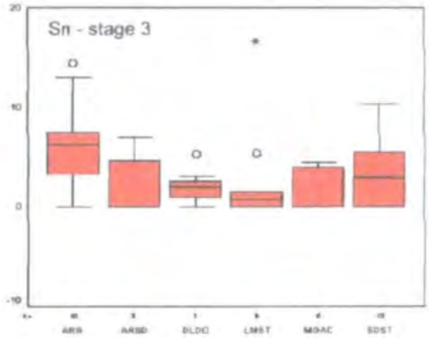

Mn - stage 3
700
600
500
400
300
200
100
0
-100
ARG
ARSD
DLDO
LMST
MGAC
SDST

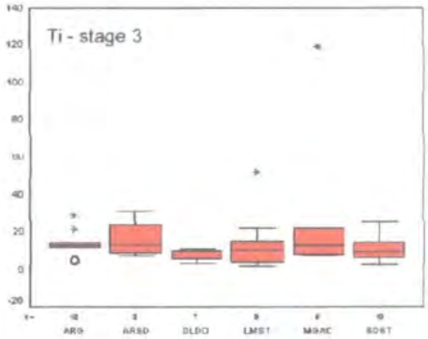

Ni - stage 3
40
30
20
10
0
-10
ARG
ARSD
DLDO
LMST
MGAC
SDST

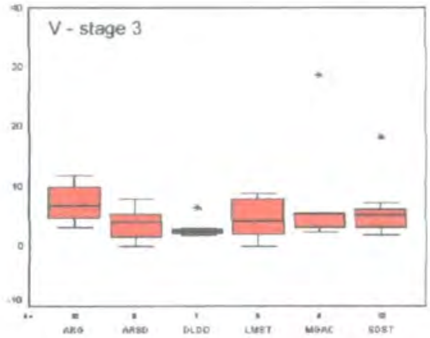

P - stage 3
1400
1200
1000
800
600
400
200
0
-200
ARG
ARSD
DLDO
LMST
MGAC
SDST


Sc - stage 3
ARG
ARSD
DLDO
LMST
MGAC
SDST


Si - stage 3
1000
800
600
400
200
0
-200
ARG
ARSD
DLDO
LMST
MGAC
SDST


Sn - stage 3
20
10
0
-10
ARG
ARSD
DLDO
LMST
MGAC
SDST


Ti - stage 3
140
120
100
80
60
40
20
0
-20
ARG
ARSD
DLDO
LMST
MGAC
SDST


V - stage 3
40
30
20
10
0
-10
ARG
ARSD
DLDO
LMST
MGAC
SDST

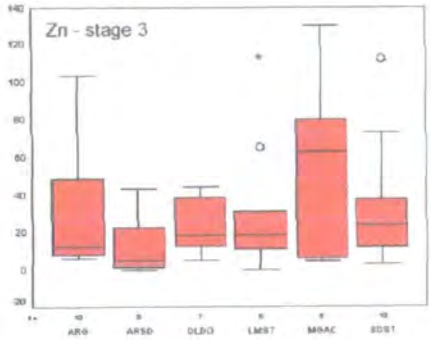
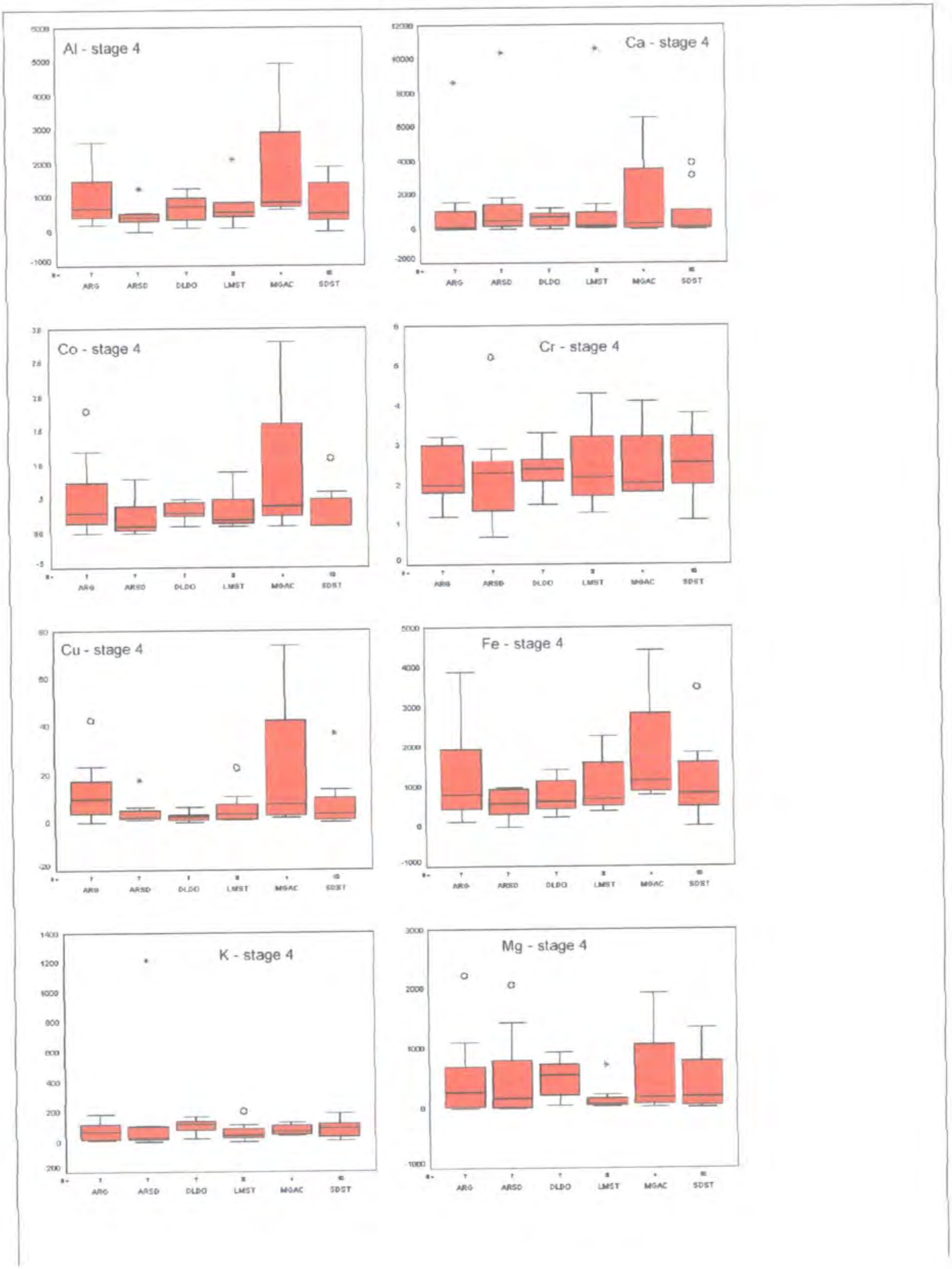
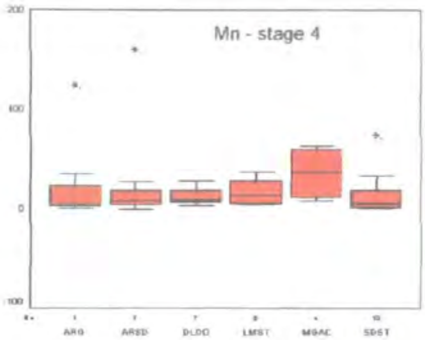
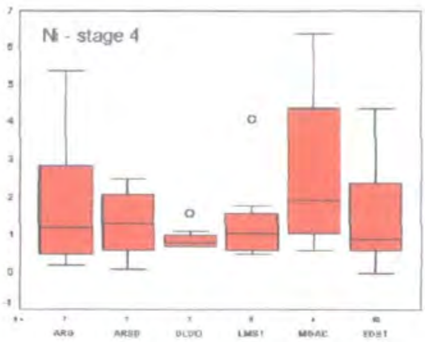
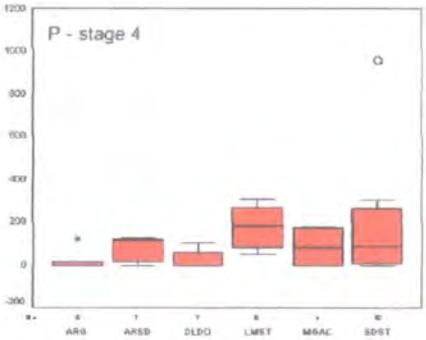

Zn - stage 3
140
120
100
80
60
40
20
0
-20
10
9
7
8
8
10
ARG
ARSD
OLDO
LMST
MGAC
SDS1

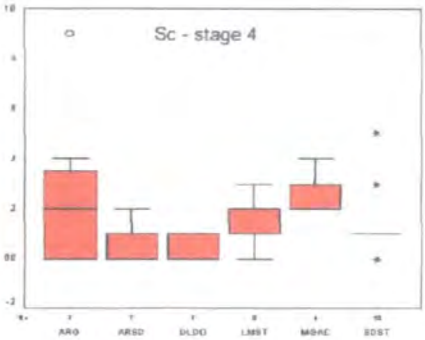
Figure H.9 Boxplots geology stage 4

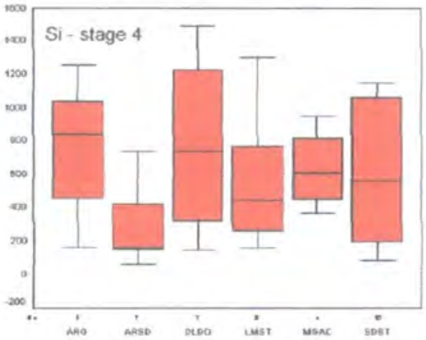


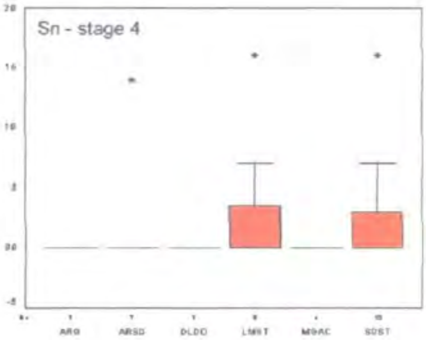

Mn - stage 4
200
100
0
-100
ARG
ARSD
DLDO
LMST
MGAC
SDST

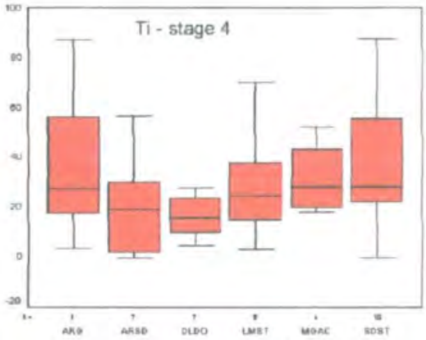

Ni - stage 4
7
6
5
4
3
2
1
0
-1
ARG
ARSD
DLDO
LMST
MGAC
SDST

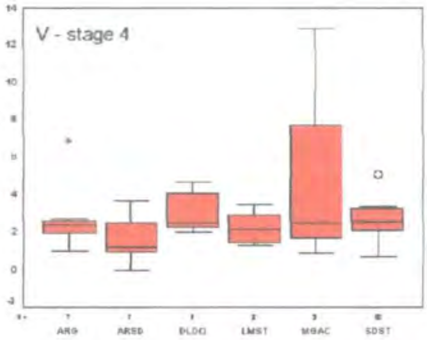

P - stage 4
1200
1000
800
600
400
200
0
-200
ARG
ARSD
DLDO
LMST
MGAC
SDST


Sc - stage 4
ARG
ARSD
DLDO
LMST
MGAC
SDST


Si - stage 4
1600
1400
1200
1000
800
600
400
200
0
-200
ARG
ARSD
DLDO
LMST
MGAC
SDST


Sn - stage 4
20
15
10
5
0.0
-5
ARG
ARSD
DLDO
LMST
MGAC
SDST


Ti - stage 4
100
80
60
40
20
0
-20
ARG
ARSD
DLDO
LMST
MGAC
SDST


V - stage 4
14
12
10
8
6
4
2
0
-2
ARG
ARSD
DLDO
LMST
MGAC
SDST

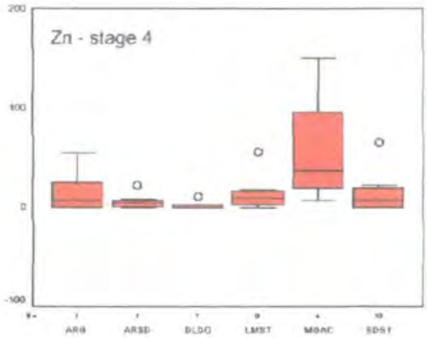
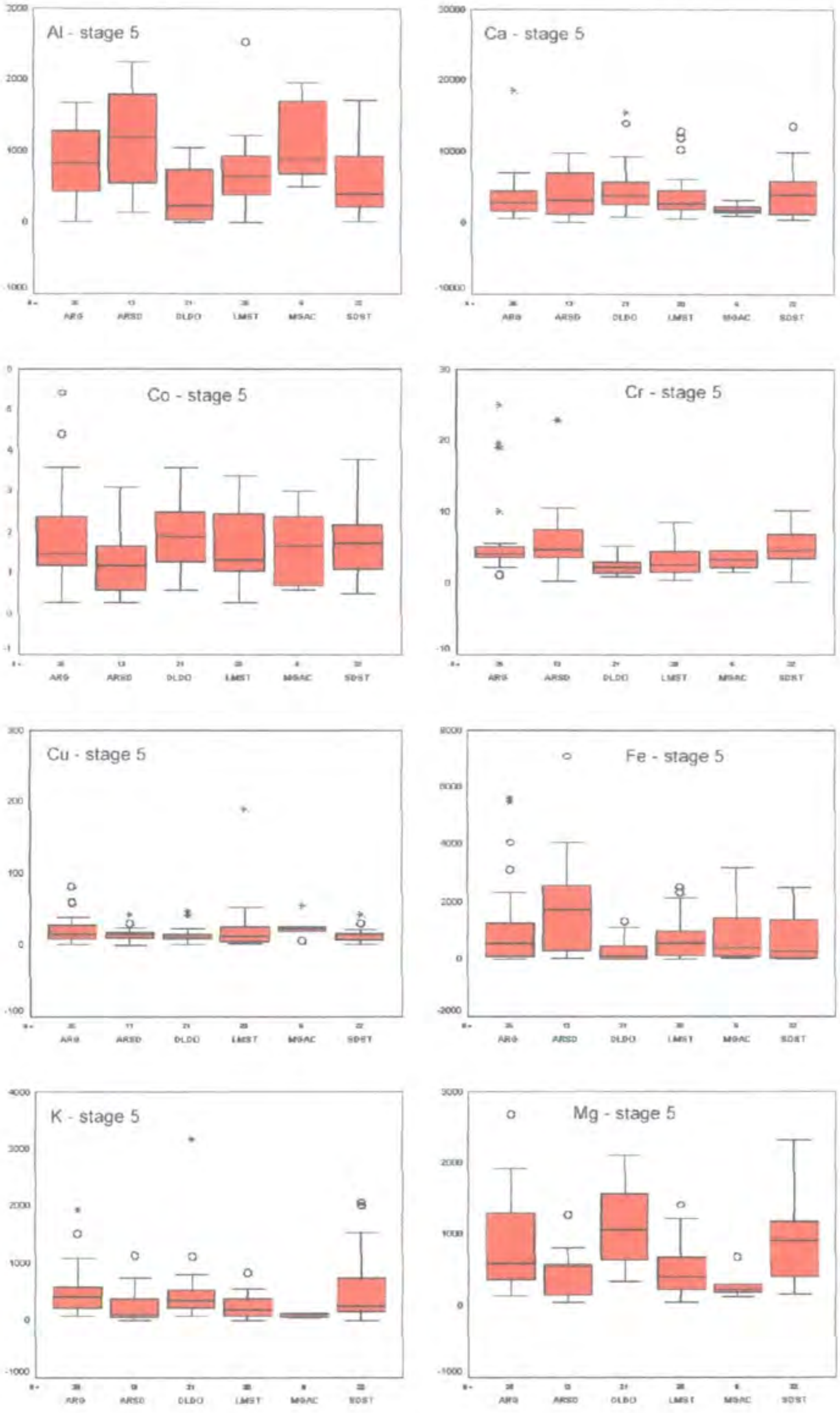
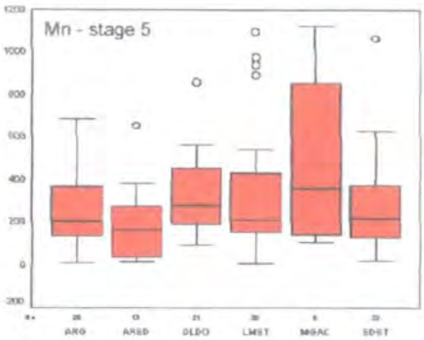
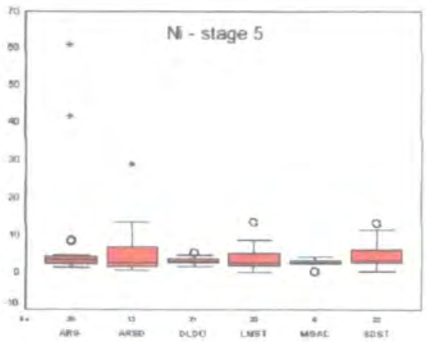
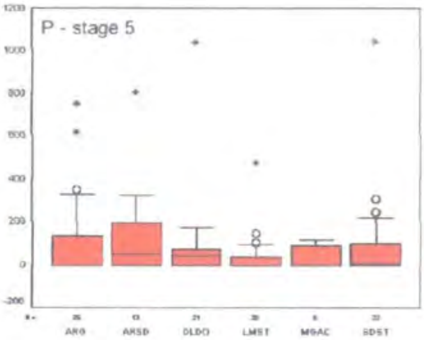

Zn - stage 4
200
100
0
-100
ARG
ARSD
DLDO
LMST
MGAC
SDST

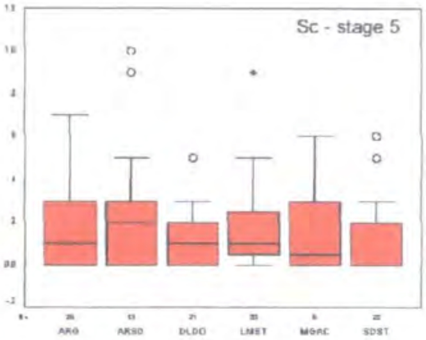
Figure H.10 Boxplots geology stage 5

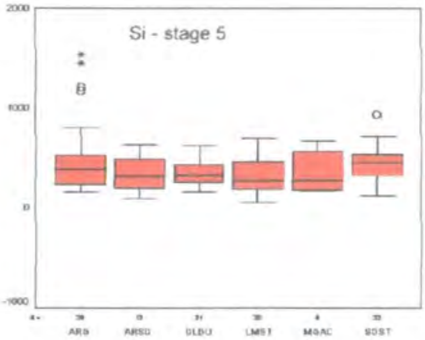


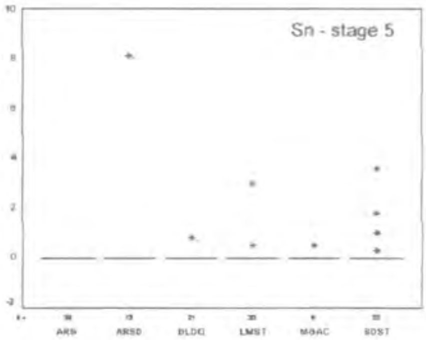

Mn - stage 5
1200
1000
800
600
400
200
0
-200
ARG
ARSD
DLDO
LMST
MGAC
SDST

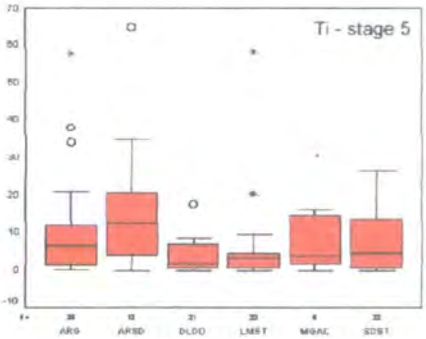

Ni - stage 5
70
60
50
40
30
20
10
0
-10
ARG
ARSD
DLDO
LMST
MGAC
SDST

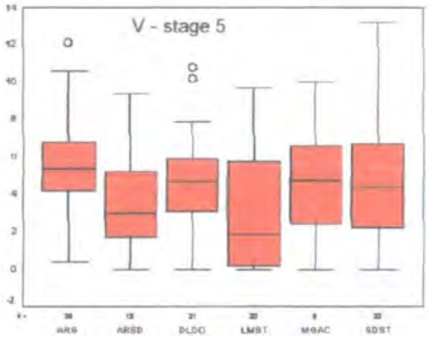

P - stage 5
1200
1000
800
600
400
200
0
-200
ARG
ARSD
DLDO
LMST
MGAC
SDST


Sc - stage 5
ARG
ARSD
DLDO
LMST
MGAC
SDST


Si - stage 5
2000
1000
0
-1000
ARG
ARSD
DLDO
LMST
MGAC
SDST


Sn - stage 5
10
8
6
4
2
0
-2
ARG
ARSD
DLDO
LMST
MGAC
SDST


Ti - stage 5
70
60
50
40
30
20
10
0
-10
ARG
ARSD
DLDO
LMST
MGAC
SDST


V - stage 5
14
12
10
8
6
4
2
0
-2
ARG
ARSD
DLDO
LMST
MGAC
SDST

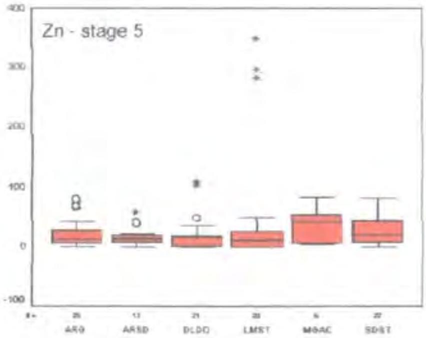
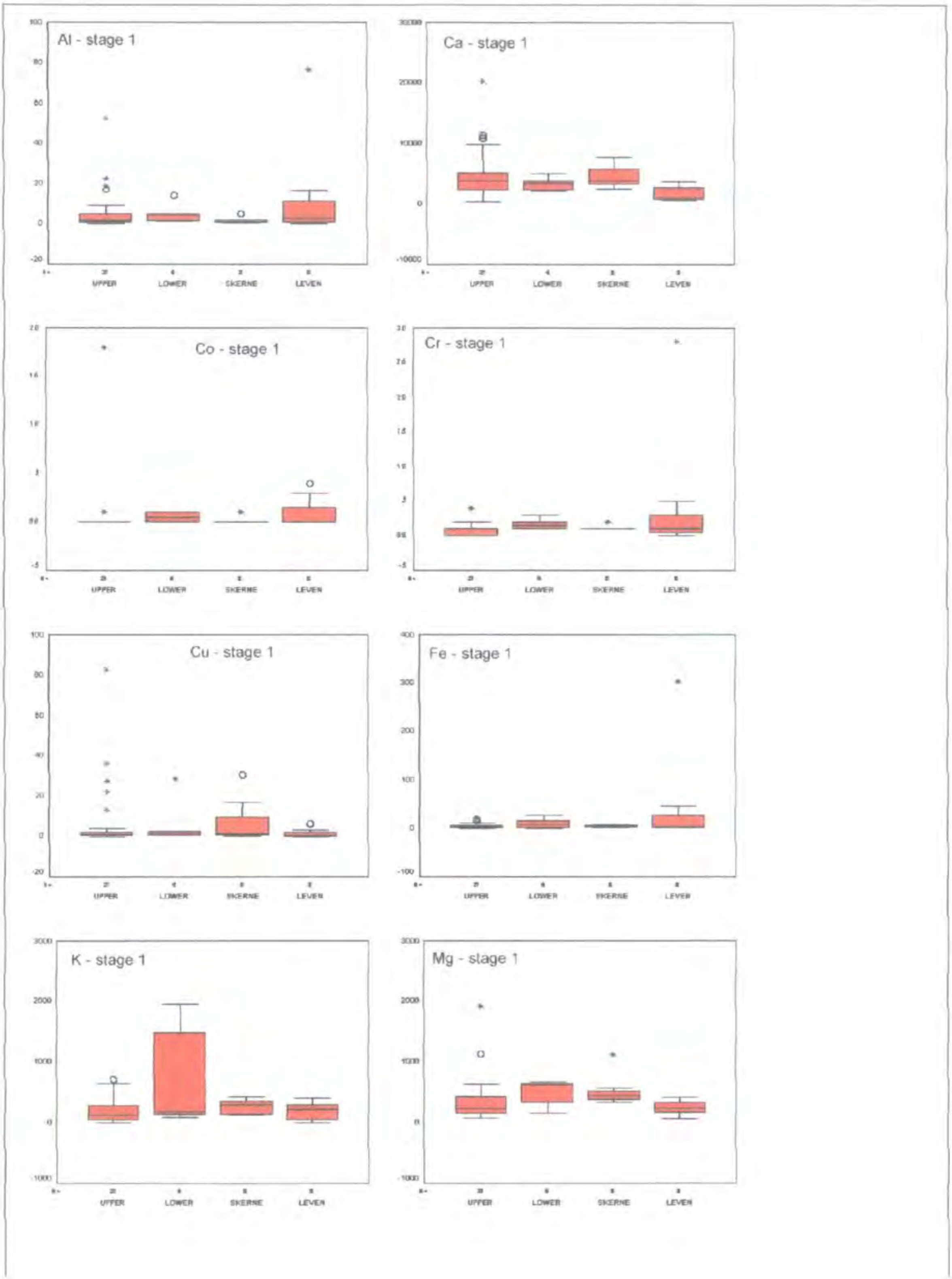

Zn - stage 5
400
300
200
100
0
-100
ARG
ARSD
DLDO
LMST
MGAC
SDST

Figure H.11 Boxplots subcatchment stage 1



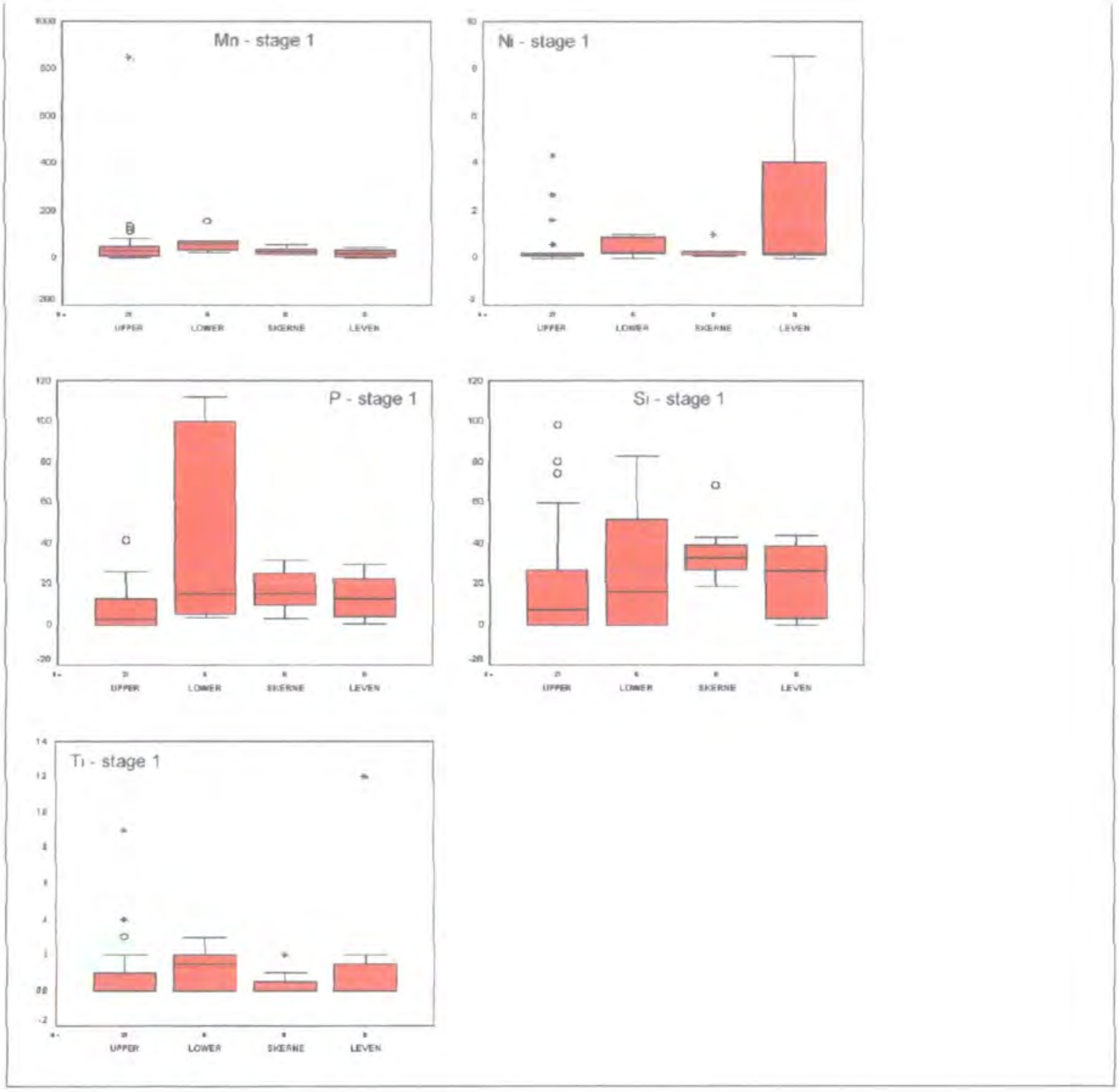
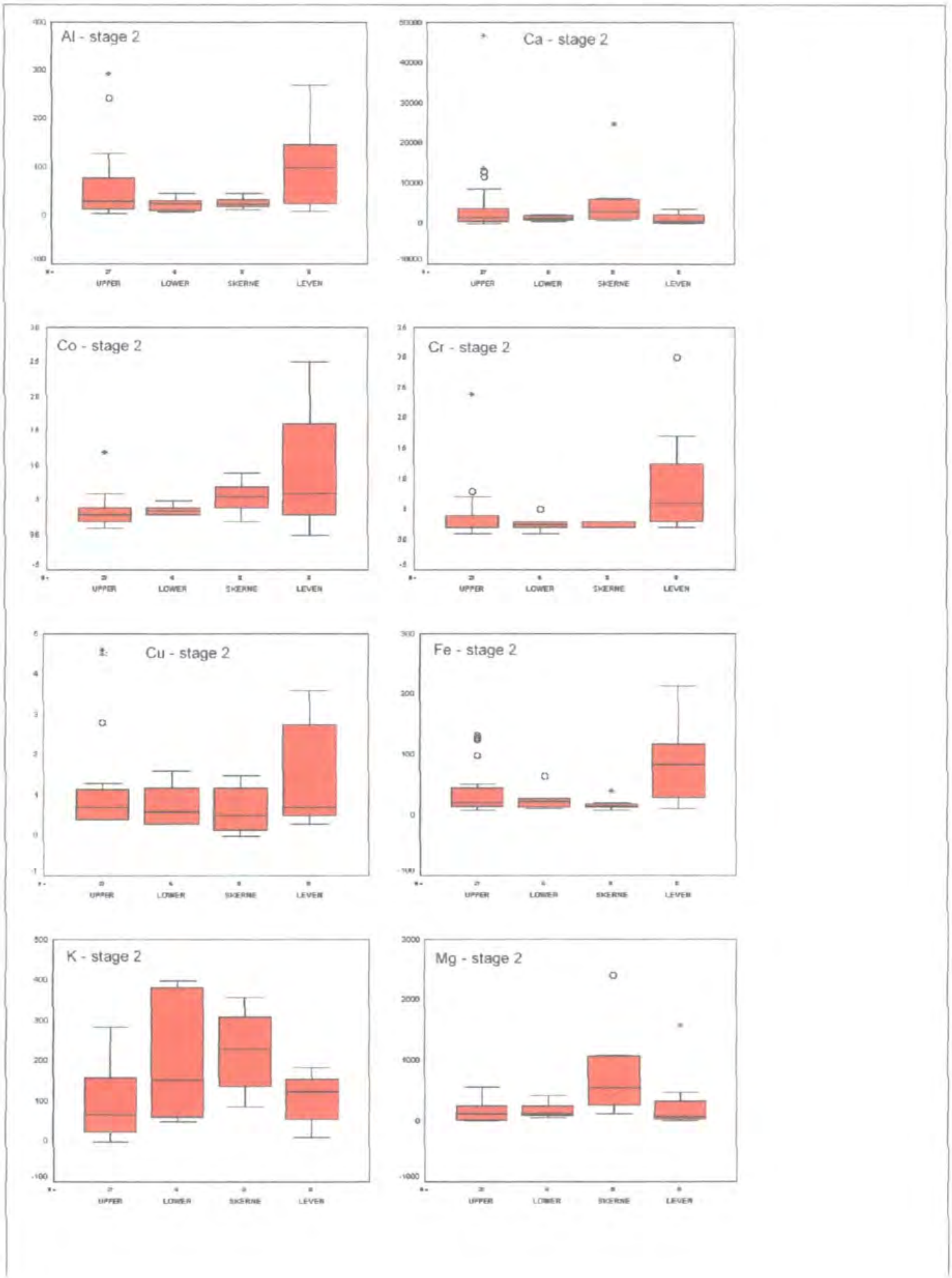

Mn - stage 1
1000
800
600
400
200
0
-200
Ni - stage 1
10
8
6
4
2
0
-2
P - stage 1
Si - stage 1
120
100
80
60
40
20
0
-20
Ti - stage 1
UPPER
LOWER
SKERNE
LEVEN

Figure H.12 Boxplots subcatchment stage 2



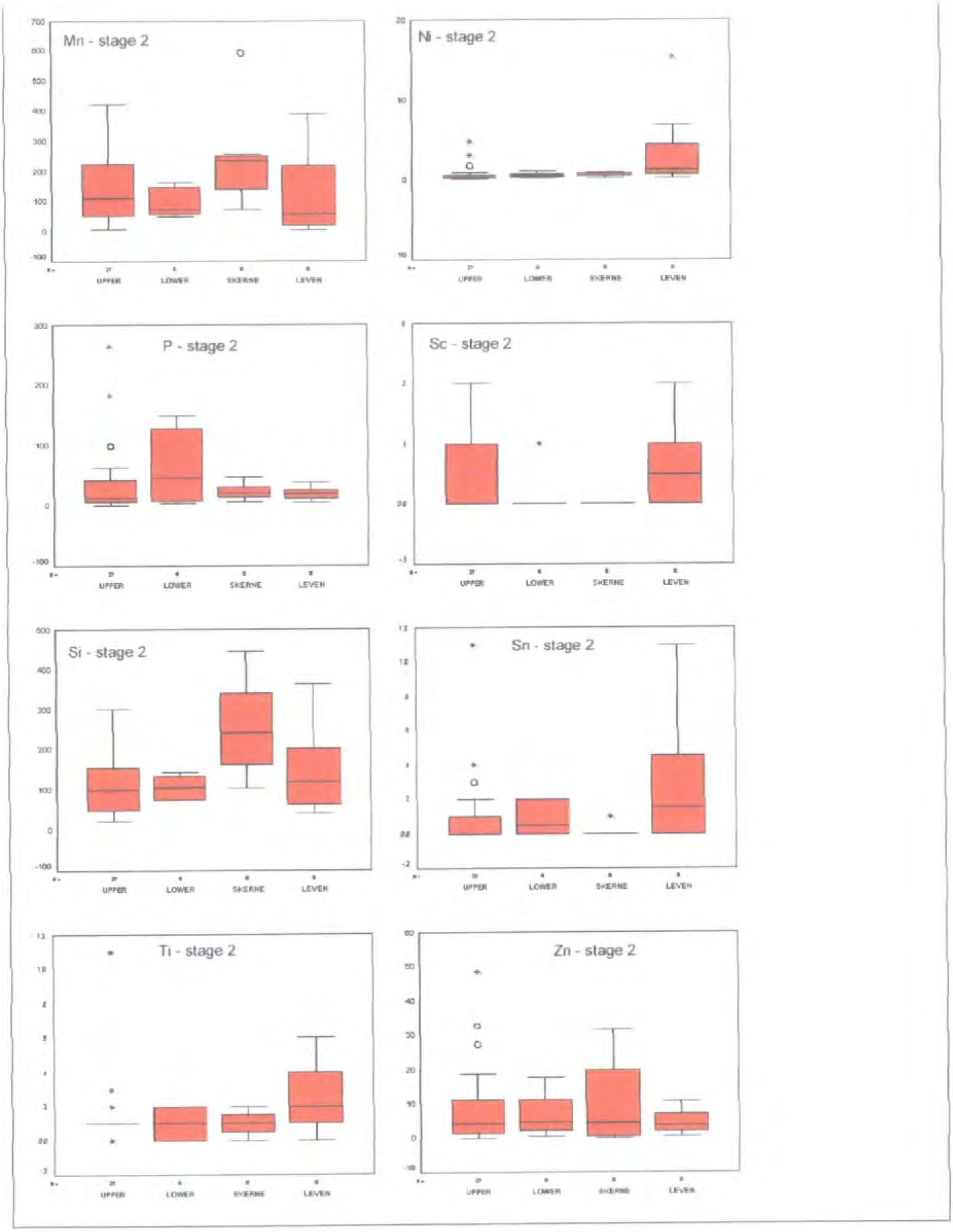
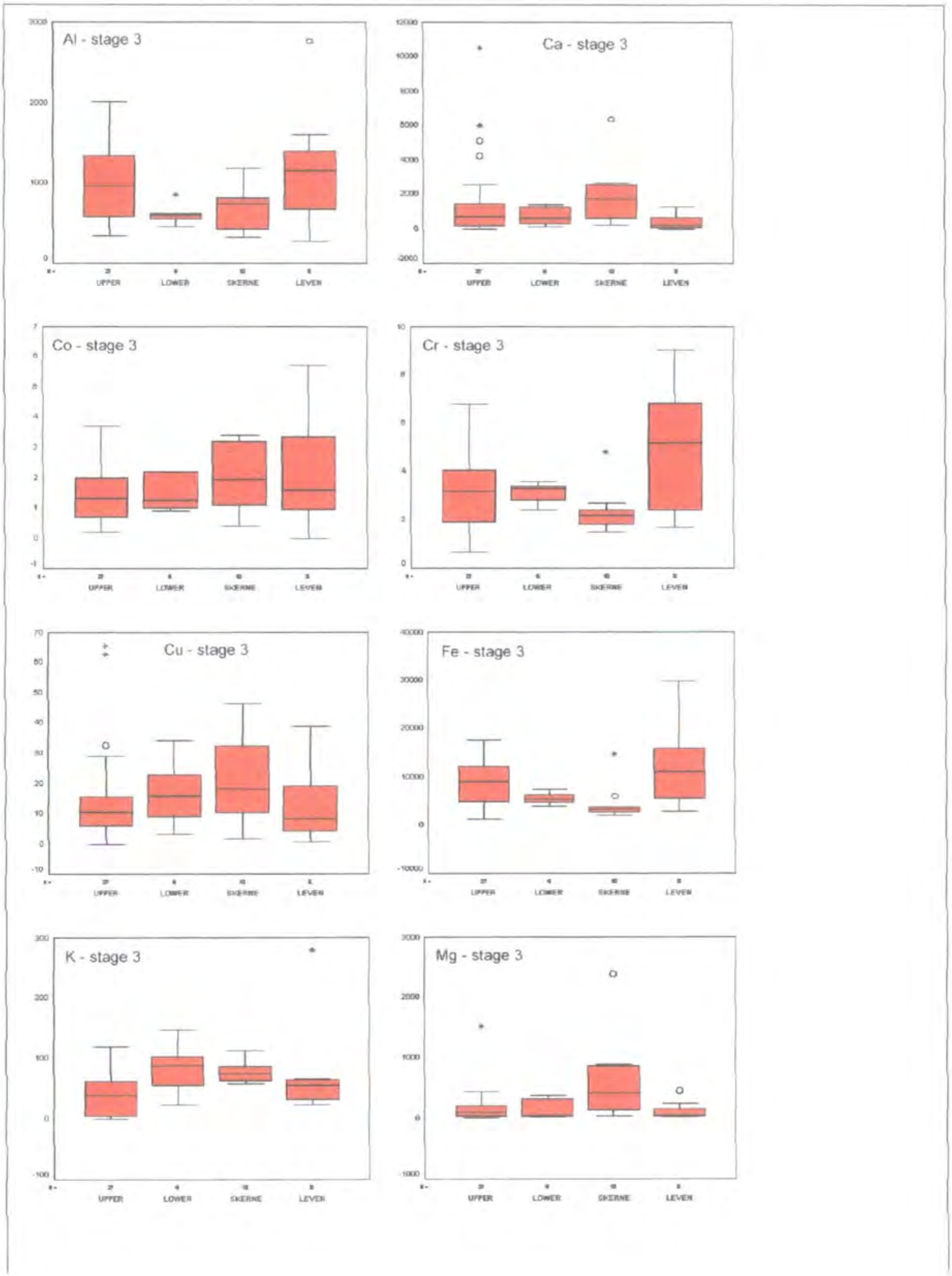

Mn - stage 2
700
600
500
400
300
200
100
0
-100
UPPER
LOWER
SKERNE
LEVEN
Ni - stage 2
20
10
0
-10
UPPER
LOWER
SKERNE
LEVEN
P - stage 2
300
200
100
0
-100
UPPER
LOWER
SKERNE
LEVEN
Sc - stage 2
UPPER
LOWER
SKERNE
LEVEN
Si - stage 2
500
400
300
200
100
0
-100
UPPER
LOWER
SKERNE
LEVEN
Sn - stage 2
-2
UPPER
LOWER
SKERNE
LEVEN
Ti - stage 2
-2
UPPER
LOWER
SKERNE
LEVEN
Zn - stage 2
60
50
40
30
20
10
0
-10
UPPER
LOWER
SKERNE
LEVEN

Figure H.13 Boxplots subcatchment stage 3



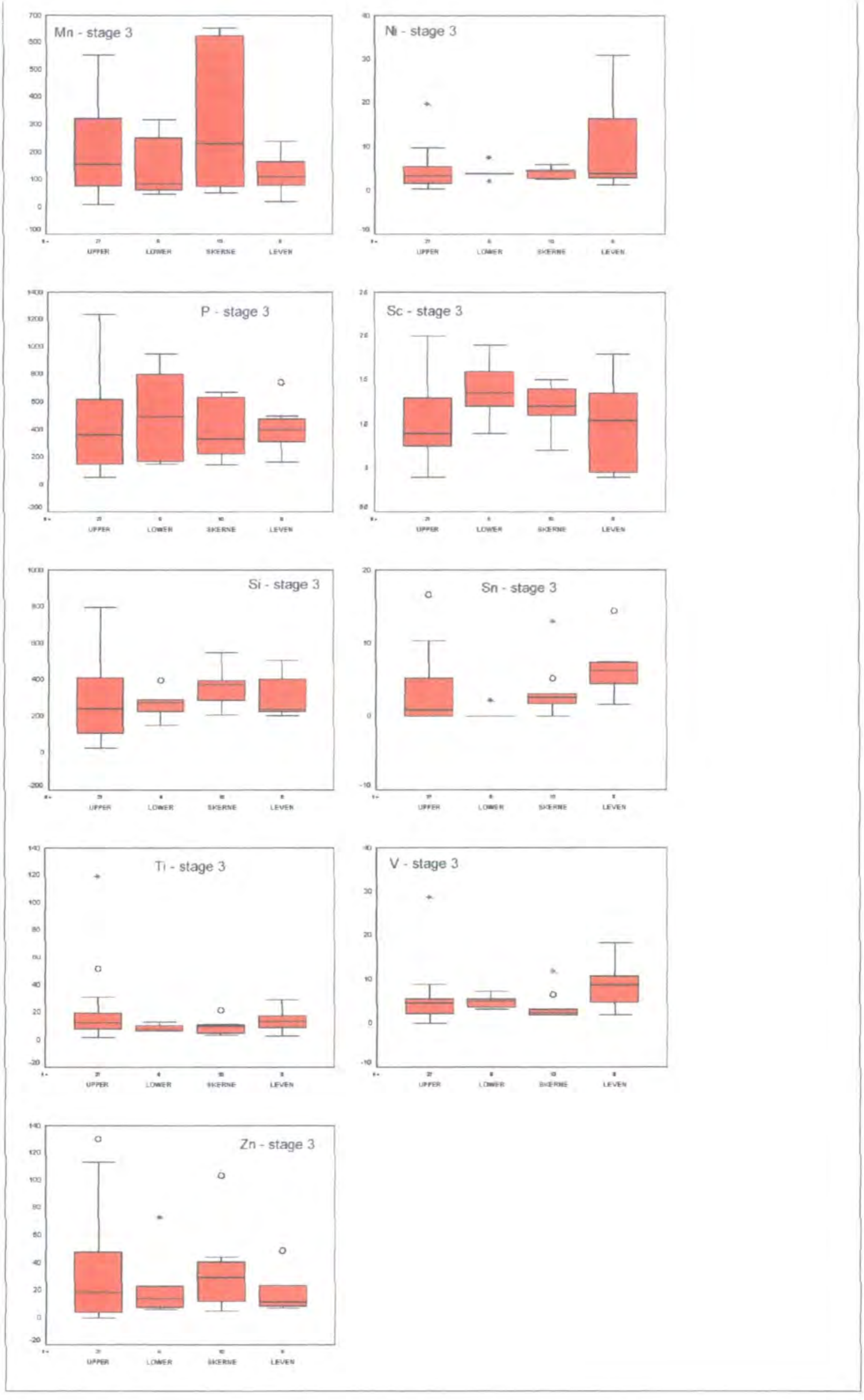
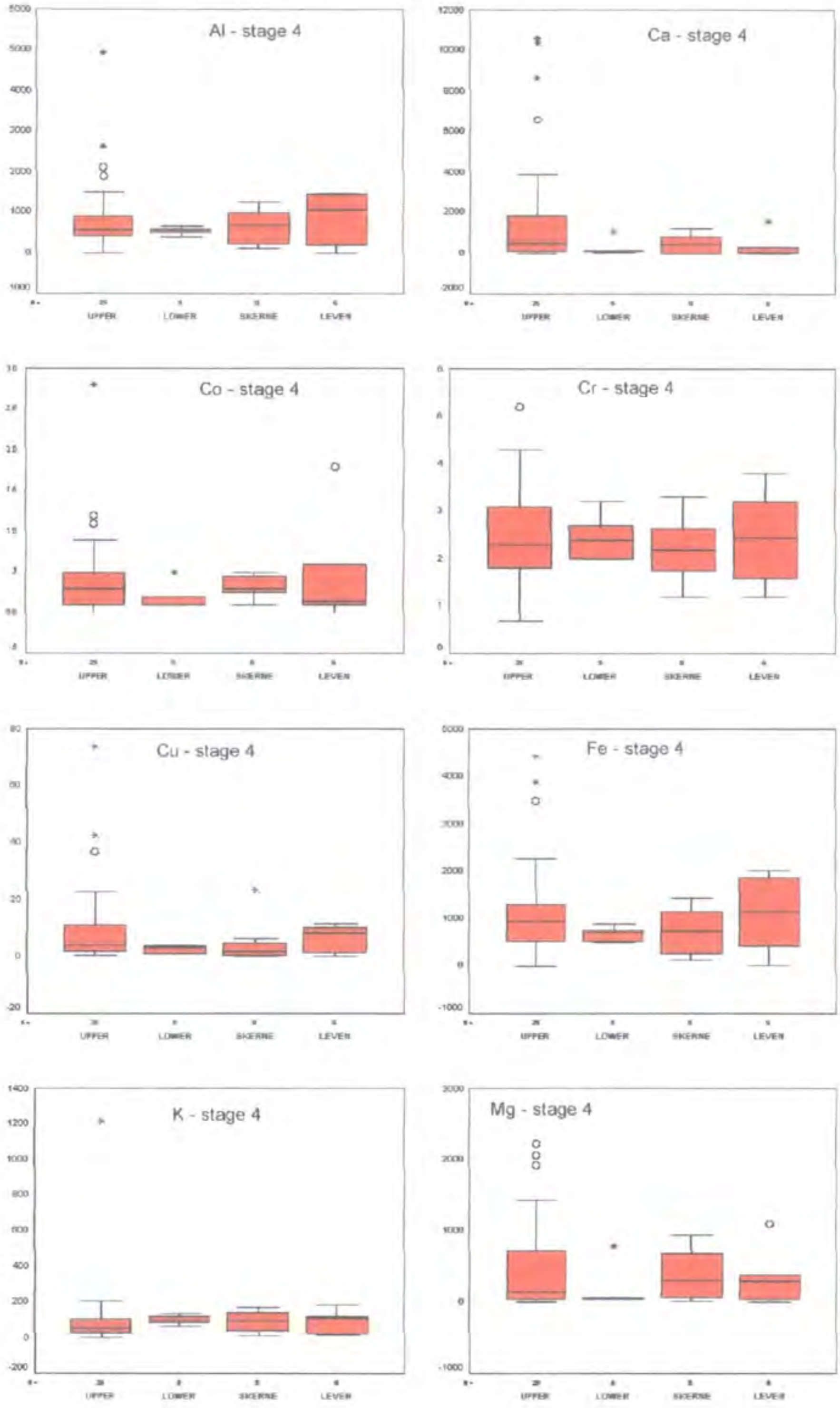
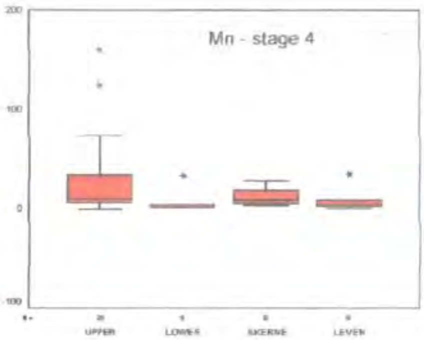
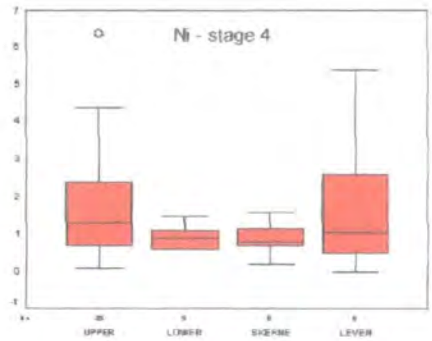
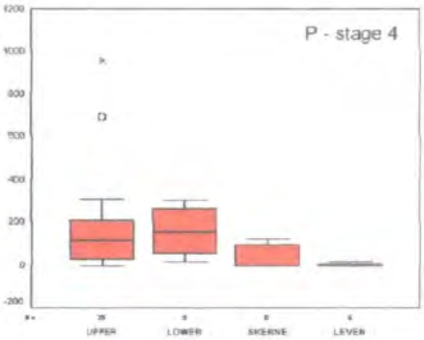

Mn - stage 3
700
600
500
400
300
200
100
0
-100
27
6
10
8
UPPER
LOWER
SKERNE
LEVEN
Ni - stage 3
40
30
20
10
0
-10
P - stage 3
1400
1200
1000
800
600
400
200
0
-200
Sc - stage 3
Si - stage 3
1000
800
600
400
200
0
-200
Sn - stage 3
20
10
0
-10
Ti - stage 3
140
120
100
80
60
40
20
0
-20
V - stage 3
40
30
20
10
0
-10
Zn - stage 3
140
120
100
80
60
40
20
0
-20

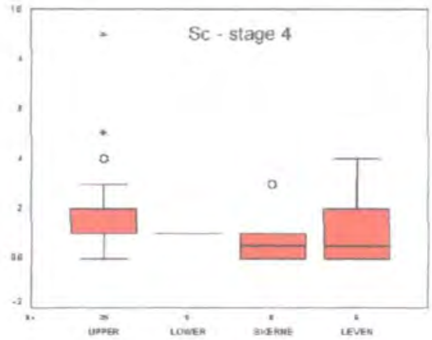
Figure H.14 Boxplots subcatchment stage 4

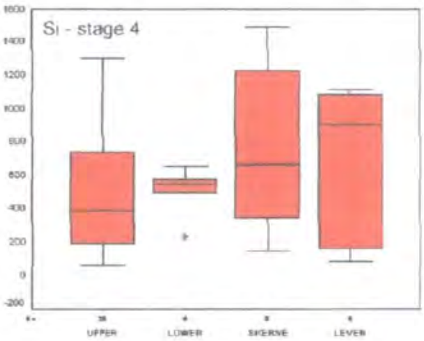


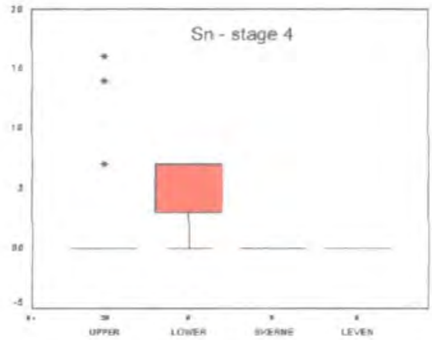

Mn - stage 4
200
100
0
-100
UPPER
LOWER
SKERNE
LEVEN

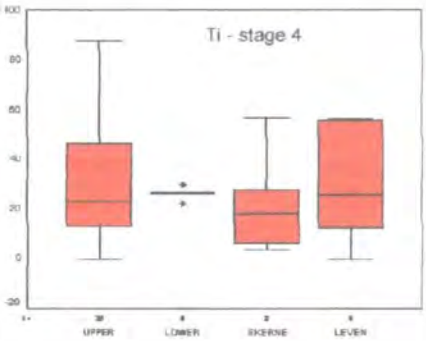

Ni - stage 4
7
6
5
4
3
2
1
0
-1
UPPER
LOWER
SKERNE
LEVEN

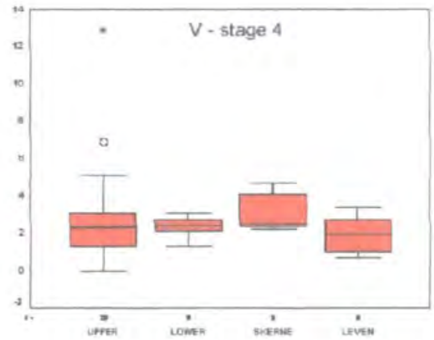

P - stage 4
1200
1000
800
600
400
200
0
-200
UPPER
LOWER
SKERNE
LEVEN


Sc - stage 4
UPPER
LOWER
SKERNE
LEVEN


Si - stage 4
1600
1400
1200
1000
800
600
400
200
0
-200
UPPER
LOWER
SKERNE
LEVEN


Sn - stage 4
UPPER
LOWER
SKERNE
LEVEN


Ti - stage 4
100
80
60
40
20
0
-20
UPPER
LOWER
SKERNE
LEVEN


V - stage 4
14
12
10
8
6
4
2
0
-2
UPPER
LOWER
SKERNE
LEVEN

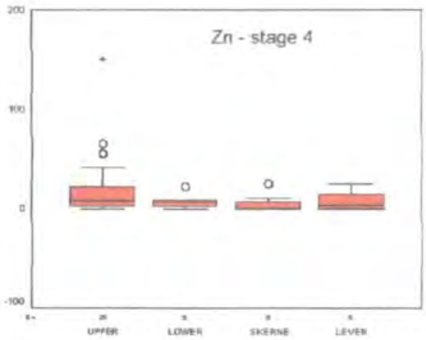
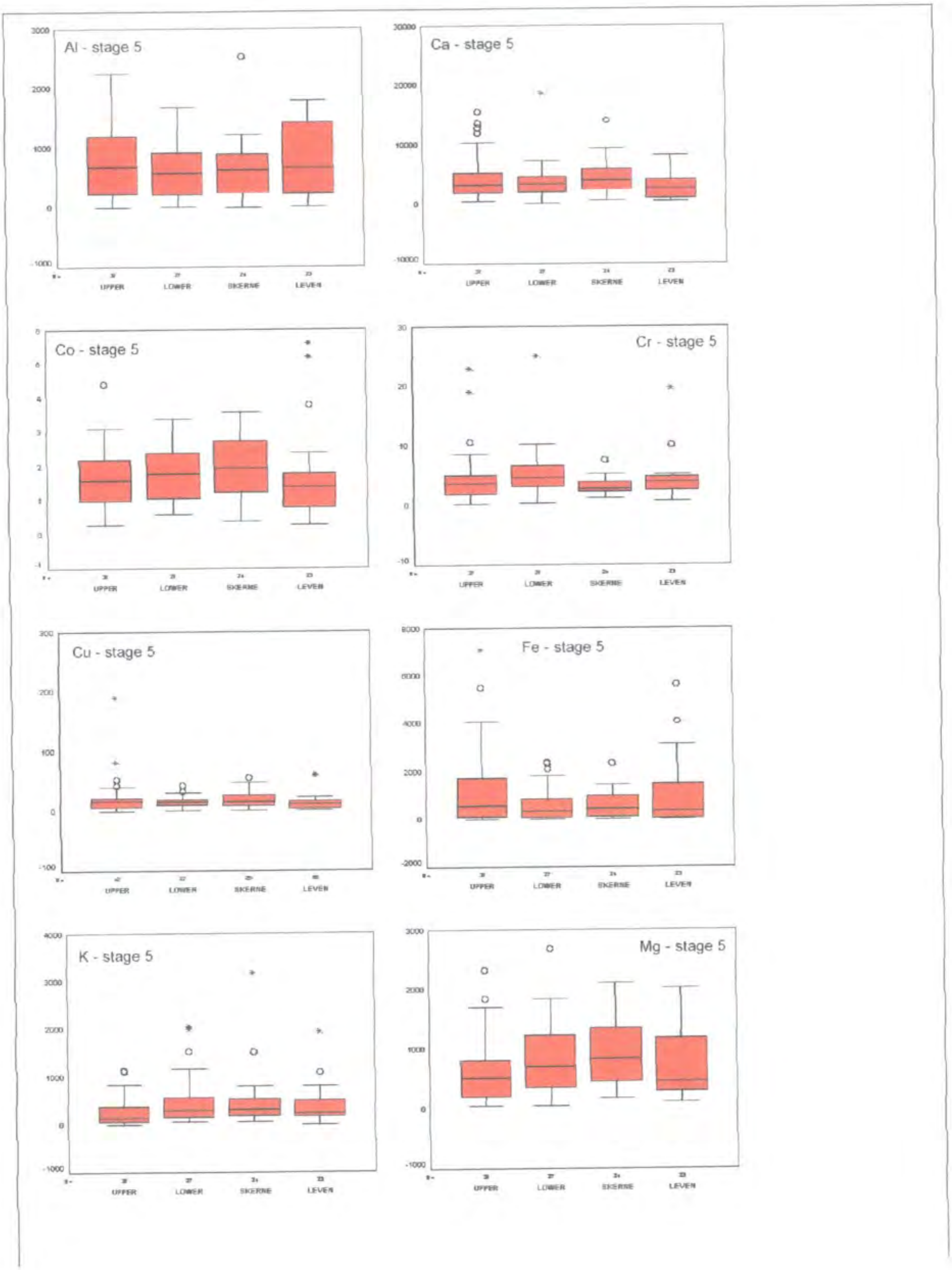
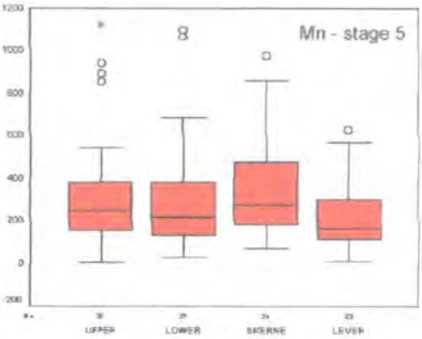
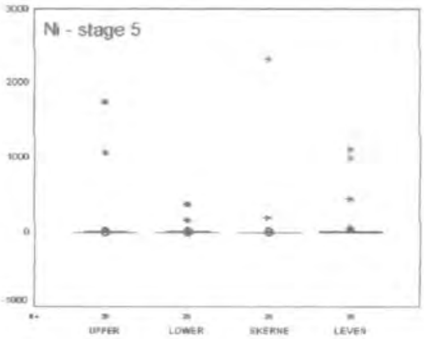
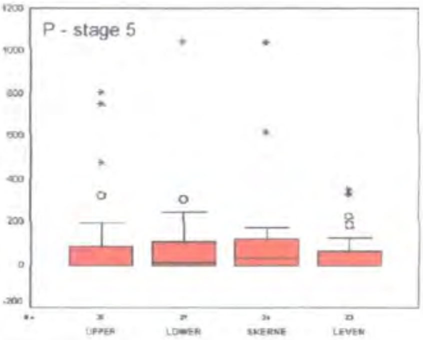

Zn - stage 4
200
100
0
-100
UPPER
LOWER
SKERNE
LEVEN

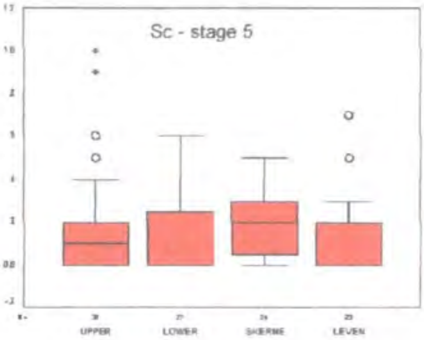
Figure H.15 Boxplots subcatchment stage 5

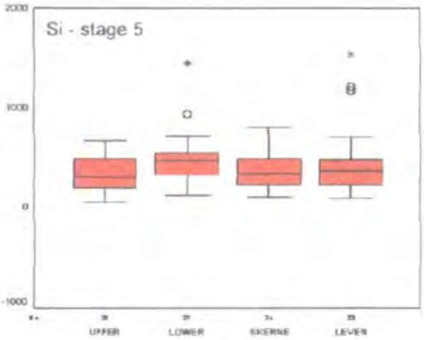


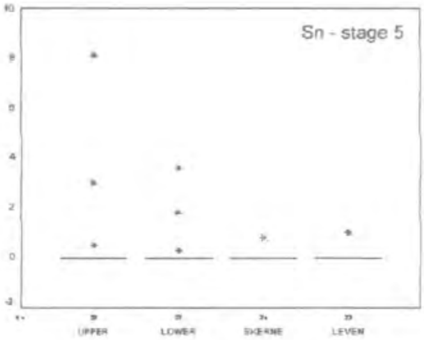

Mn - stage 5
1200
1000
800
600
400
200
0
-200
UPPER
LOWER
SKERNE
LEVEN


Ni - stage 5
3000
2000
1000
0
-1000
UPPER
LOWER
SKERNE
LEVEN


P - stage 5
1200
1000
800
600
400
200
0
-200
UPPER
LOWER
SKERNE
LEVEN


Sc - stage 5
UPPER
LOWER
SKERNE
LEVEN


Si - stage 5
2000
1000
0
-1000
UPPER
LOWER
SKERNE
LEVEN


Sn - stage 5
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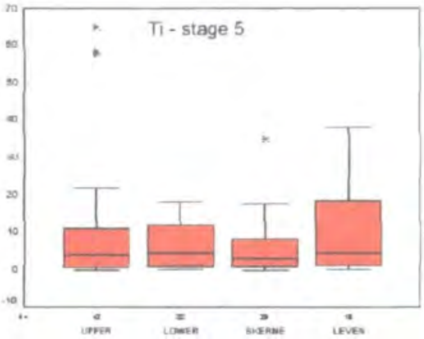
8
6
4
2
0
-2
UPPER
LOWER
SKERNE
LEVEN


Ti - stage 5
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40
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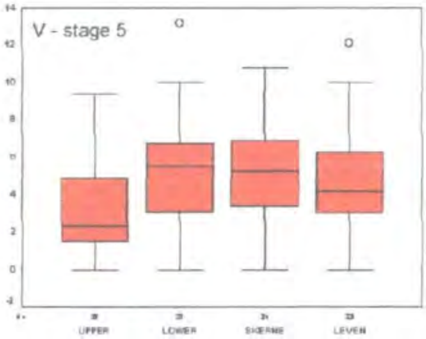
UPPER
LOWER
SKERNE
LEVEN


V - stage 5
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12
10
8
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4
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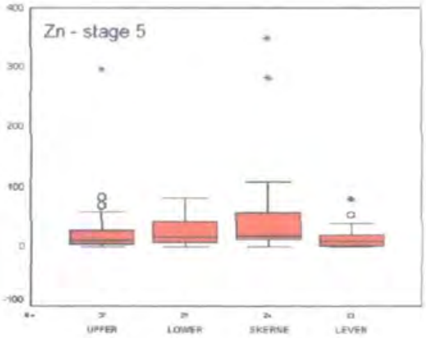
LOWER
SKERNE
LEVEN


Zn - stage 5
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300
200
100
0
-100
UPPER
LOWER
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LEVEN

Appendix I

Figure I.1 PCA results for water data

Eigenanalysis of the correlation matrix			
	CF1	**CF2**	**CF3**
Eigenvalue	5.3807	2.8801	1.0931
Proportion	0.489	0.262	0.099
Cumulative %	0.489	0.751	0.85
Variable	**CF1**	**CF2**	**CF3**
Al	-0.347	-0.332	*0.01*
Ca	-0.27	0.422	-0.206
Cu	*-0.089*	-0.237	-0.516
Fe	-0.337	-0.34	*0.061*
K	-0.37	0.236	*-0.075*
Mg	-0.296	0.409	*-0.124*
Mn	-0.285	-0.305	0.197
P	-0.284	0.367	*0.119*
Si	-0.419	*-0.011*	*-0.084*
Ti	-0.324	-0.29	*-0.05*
Zn	*0.133*	*-0.075*	-0.777

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