Accumulation of metals by aquatic plants in the river wear system

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ACCUMULATION OF METALS BY AQUATIC PLANTS IN THE RIVER WEAR SYSTEM

by

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This thesis which is entirely the result of my own work has not been accepted for any degree and is not being submitted concurrently in candidature for any other degree.

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ABSTRACT

A study was made of a range of aquatic plants from various parts of the River Wear system, for 13 metal elements. The heavy metal content of the plants was related to the chemistry of the water using the enrichment ratio.

Different chemical environments were studied in an attempt to establish factors affecting the accumulation of heavy metals.

Marked increases were found in Zn, Pb and Cd in *Cladophora glomerata* and *Fontinalis antipyretica* sampled downstream of the entry of an industrial effluent as compared to a site upstream of this effluent. A clear linear relationship was established for Zn and Pb between the concentration in the plant and that in the water for *Cladophora glomerata*, in strictly comparable situations at sites above and below the effluent. Divided samples of *Fontinalis antipyretica* showed marked increases in many heavy metals in the older material as compared to the younger tips. It is suggested that bryophyte tips could reliably indicate the heavy metal concentration of river water. It is also suggested that leaves of *Ranunculus penicillatus* var. *calcareus* might be useful in indicating heavy metals.

Plants from a Zn and Pb polluted tributary (Rookhope Burn) showed marked accumulation of Zn and Pb compared to similar plants from waters with low concentrations of these heavy metals.

In Brandon Pithouse acid streams enrichment ratios were encountered, at pH <3, several orders of magnitude lower than sites of pH 6-8. It is suggested that pH might have a direct or indirect influence in reducing this ratio.

It is also suggested that both physiological and environmental parameters, notably chemical speciation, are important factors affecting enrichment ratios. Importance was attached to defining limits to enrichment ratios so that aquatic plants could be used to indicate heavy metal concentrations in a wide range of flowing waters.

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CHAPTER ONE

1. INTRODUCTION

1.1 Aims

Many attempts have been made to use aquatic organisms as 'indicators' of their environment. Most of these studies have been based on the use of different community structures to indicate certain types of pollution. The classic studies of indicator communities have been concerned mainly with identifying the effects of organic pollution (Kolkwitz and Marsson, 1908; Butcher, 1947, 1955; Fjerdingstad, 1950; and Sladeček, 1958). Hynes (1960) pointed out that these zonal systems can become unwieldy and tend to break down where the pollution is not organic. Toxic substances in the aquatic environment present a different problem as far as biological indicators are concerned.

Pollution of flowing waters by dissolved metals (notably Zn, Cu and Pb) has been thoroughly studied by a number of authors (Carpenter, 1924, 1925, 1928; Pentelow and Butcher, 1938; Jones, 1940, 1940b, 1938). Reviews of works concerned with the effects of heavy metals on the flora and fauna of rivers have been given by Hynes (1960) and most recently by Whitton and Say (1975).

There has been less research into the use of aquatic organisms as quantitative indicators of metal pollution. It has therefore been the aim of the present study to investigate the composition of a range of aquatic plants from diverse riverain environments for 13 metal elements. An attempt has been made to establish relationships between the heavy metal content of the plants and that of the water. If the limits of variation for this relationship can be clearly defined then selected species would be suitable as quantitative indicators of heavy metals in flowing waters. It is therefore possible to devise an efficient monitoring system which could have a number of advantages over others.

(i) The ability of aquatic plants to concentrate trace elements has been noted (Bowen, 1966). Therefore, elements which are not easily detectable in the water might become obvious in plant tissue.

(ii) Increases in metals known to be toxic could be determined at the producer level. Such fundamental information would be useful in tracing the effects of these metals up the food chain.

(iii) A reliable and economic monitoring system would be of great value in safeguarding water supply. This is especially relevant with the increase in lowland abstraction of water from rivers. Furthermore, changes in heavy metal concentration resulting from the transfer of river water could be simply monitored. One illustration of this is the proposed transfer of water from the River Tyne to the River Wear in part of the 'Kielder' scheme.

(iv) Particular plants might be used in monitoring long term changes in the heavy metal status of rivers, allowing comparisons from year to year.

(v) There is the possibility of detecting a 'flush' of heavy metals which might otherwise escape notice.

(vi) In general, analysis of selected plants could act as a supplement to routine chemical analysis and in some instances act as a suitable replacement.

With these factors in mind a survey was carried out in order to determine the composition of some larger aquatic plants in parts of the River Wear system affected by different types of metal pollution. It was hoped that some of the factors affecting the accumulation of metals could be determined in order to select possible indicator species.

Some clarification was needed of the physical and chemical parameters affecting the water so that relationships with the plants could be better understood.

Three distinct environments were chosen from within the River Wear system to establish the variation in accumulation under different conditions.

(a) The lower reaches of the River Wear in the region of an industrial effluent.

An attempt was made to monitor the effluent, known to contain heavy metals, both by analysis of the water and macrophytic vegetation above and below its outfall.

(b) Rookhope Burn, an upland tributary of the River Wear.

This was chosen in order to study the effects of heavy metals in much higher concentrations. The past and present mining activity in the area has given rise to high concentrations of Zn and Pb.

(c) Brandon Pithouse Acid Stream.

This minor tributory of the River Deerness exemplifies an extreme environment with high heavy metal content caused by low pH.

1.2 Literature referring to the chemistry and accumulation of metals in the aquatic environment

1.2.1 Introduction

According to Hynes (1960), 'rivers are strict individualists, each of which varies in its own way'.

A vast array of chemical, geological and hydrological features are present and always changing in river systems. Bowen (1966) has stated that the main ions present in river water vary with climate and local geology. In temperate regions it is the latter which is of fundamental importance. Livingstone (1963) regards rivers as representing the average soil solution in the region which they drain. It is therefore clear that there is an inherent variation in the chemistry of river water before taking into account biological factors or the effects of civilisation.

A number of authors have concluded that rivers are best studied by defining reaches (Carpenter, 1928; Butcher, 1933; Huet, 1954). In this context, Hynes (1960) states that one of the fundamental factors affecting any given reach is its ionic composition. The concentrations of K, NO_3-N and PO_4-P are of particular importance to aquatic plants, as key nutrients.

Other 'essential elements' for green algae and angiosperms are: Na, Ca, Mg, Zn, Cu, Mn and Fe, according to Bowen (1966). In addition, Co is quoted by Round, (1965) as essential for algae. Essentiality however, has not been shown for some heavy metals, notably Pb and Cd.

It is when natural waters contain an excess of any particular element that inorganic pollution problems arise. The present study is concerned with excesses or potential excesses of particular cations and the possibility of using aquatic plants to monitor them.

1.2.2 Heavy metals in fresh water

The term heavy metal has been defined in a number of ways (Whitton and Say, 1975). However, Passow et al.'s (1961) definition referred to 40 or so metals having a density of greater than five. In the present study the following are defined in this way: Zn, Cu, Mn, Fe, Al, Pb, Cd, Co and Ni.

Heavy metals originate from a wide range of sources. Two of the most important are mining activities and industrial effluents, according to Hynes (1960) and Bowen (1966). Whitton and Say (1975) are more specific concerning industrial sources of heavy metals and include the manufacture of paints, batteries and television tubes. A certain amount of heavy metal in river water is 'natural', in as far as rivers reflect the areas which they drain (Bowen, 1966). This 'background' concentration is often increased considerably by mining activities of various types. This is illustrated by lead mining in the Rheidol Valley, Cardiganshire which resulted in heavy metal pollution by mine effluents and tip drainage (Carpenter, 1924). The slow recovery of rivers from such pollution has been demonstrated by a series of studies over many years, (Reese, 1937; Newton, 1944; Jones, 1940b; Fuge, 1972).

In the River Wear system some data have been presented by Snow and Whitton (1971) from the chief lead mining area in the region of Rookhope Burn. Leeder (1972) also investigated concentrations of dissolved Zn and Pb in the same river. The most detailed work concerning mining and heavy metals in the area has been carried out by Say (1977). He studied mainly Zn pollution in the Alston mineralised block, which includes part of the River Wear catchment.

Streams of low pH (less than three) are also associated with high concentrations of heavy metals (Hargreaves *et al.*, 1975). On the whole, these streams are connected with coal mining wastes. A survey of the chemistry and flora of acid streams throughout Britain is given by Hargreaves *et al.* (1975).

It has frequently been noted that the discharge of a river markedly affects the concentrations of heavy metals (Carpenter, 1928; Hynes, 1960); although no consistent pattern has emerged (Wilson, 1976). Information from Hellmann (1970) has been quoted by Wilson (1976) in an explanation of the effects of discharge. Simply, heavy metal concentration relies on the balance between the increasing 'suspended' or non-filtrable fraction, with the decreasing 'soluble' or filtrable fraction, with dilution. It is therefore impossible to generalise concerning this effect.

In a consideration of the chemical state of heavy metals in fresh water three problems arise.

(i) Collection and storage

Robertson (1969) has discussed the problems encountered with the contamination of laboratory apparatus.

Methods of preservation and adsorption of heavy metals have been discussed by Smith (1973a, 1973b). He concluded that a pH of 1.5 or less is required to preserve most metals in true solution. Allen *et al.* (1974) have suggested criteria for the collection of water samples.

(ii) Analytical error

The accuracy of many analytical techniques has been presented by A.P.H.A. (1971) and Allen *et al.* (1974). Reviews of atomic absorption spectrophotometry, in the analysis of natural waters, have been given by Platte and Marcy, (1965) and Fishman (1966).

(iii) Speciation

The speciation of heavy metals in natural waters has received growing attention, especially in relation to the availability of metals to aquatic organisms. Several authors have pointed out the inadequacy of knowledge in this field (Stumm and Morgan, 1970; Stumm and Bilinski, 1972; Whitton, 1972; Perhac, 1972; Whitton and Say, 1975; Wilson, 1976).

Theoretical classifications of metal ions and complexes in natural waters have been given by Stumm and Morgan (1970) and Stumm and Bilinski (1972). These define metals in aqueous solution as free ions and inorganic complexes ($<$10 nm), chelates and colloids (10-100 nm) and large colloids and precipitates ($>$100 nm). Stumm and Morgan (1970) further subdivide truly dissolved metals into 'aquo metal ions' i.e. a metal ion co-ordinated with water and inorganic hydroxo and poly hydroxo complexes. This speciation was suggested as pH dependent and could affect the adsorption of cations onto solids including aquatic organisms.

Perhac, (1972) has devised a method for separating solid and dissolved heavy metal particles, using continuous flow ultra centrifugation. He has classified metals into the following categories: true solution (<100 nm), colloidal particles (100 nm to 1500 nm), coarse particles (>1500 nm). These correspond to some extent with the hypothetical divisions noted above. Perhac's data for river water showed 90% of metals in true solution, 10% in coarse particles and colloids less than 1%. However, he noted a considerable potential for flowing waters to carry large amounts of heavy metals in colloidal form. Kennedy *et al*. (1974) have separated colloidal clay particles from 'truly dissolved' species using 0.1μ membrane filters.

The speciation of anions in natural waters must not be overlooked. Compounds of P, in particular, have a marked effect on the complexing of heavy metals. Dissolved forms of P in natural water fall into three categories: orthophosphates, inorganic condensed phosphates, organic phosphates (both dissolved and colloidal). Many of these forms affect the distribution and availability of cations, depending on pH, concentration of metal ion and other ligands (Stumm and Morgan, 1970).

Chemically, many heavy metals are found 'dissolved' in natural waters to a far greater degree than their theoretical solubility products allow (Stumm and Morgan, 1970). Chelation with organic complexes has been given as an explanation of this phenomenon (Fogg and Westlake, 1955;

Shapiro, 1957; Sculthorpe, 1967). More recently it has been suggested that chelation plays only a minor role in heavy metal solubilisation and that many metals are held in colloidal dispersions, particularly Mn, Fe, Zn and Co (Shapiro, 1964; Stumm and Morgan, 1970; Perhac, 1972; Rashid, 1974). Such colloids are often associated with brown organic acids (fulvic/humic complexes) found in lake waters (Shapiro, 1964). However such complexes are not restricted to standing waters. Brown organic material has been noted in the River Wear system, associated with wash out from peaty moorland (M. Snow, pers. comm.) and in waters of the River South Tyne Catchment (Say, 1977). Wilson (1976), in a critical review of trace metals in river water, concluded that fulvic/humic acids often represent an important fraction of the filtrable heavy metal.

It is fundamental in an understanding of the availability of metal ions to aquatic organisms that inorganic and organic complexes and colloids are able to hold a variety of heavy metals. These are, in many cases, held in a readily exchangeable form. However, Elder (1975) has stated that 'few generalisations can be made about trace metal complexation because they are so highly dependent on pH and anionic concentrations'.

The need for a practical and easily applicable method of metal speciation has been acknowledged by Wilson (1976) and has particular relevance to the uptake of metals by aquatic organisms.

1.2.3 Accumulation by aquatic organisms

The use of any aquatic organism as a quantitative indicator of the surrounding water relies on the ability of living cells to take up elements against a concentration gradient, such that the internal concentration is higher than the external (Bowen, 1966). One approach is to investigate the elemental composition of organisms. Early work by Hoagland and Davis (1923) suggested that the element content of cells was much higher than the surrounding medium. There is a good deal of such information available but rarely is it directly concerned with the monitoring of the environment.

Many of the early works in freshwater are limited to a few macro-elements (Schuette and Hoffman, 1921; Birge and Juday, 1922; Harper and Daniel, 1934) and analytical methods are questionable, by recent standards (Boyd and Lawrence, 1967). There has been a considerable increase in available information with the introduction of modern analytical techniques such as atomic absorption spectrophotometry, anode stripping voltametry, neutron activation analysis. Bowen (1966) has reviewed both the composition and the accumulation of elements by living organisms. He concluded that all metals studied are more or less concentrated, except for Na which is weakly rejected. He goes on to point out that the concept of accumulator organisms arises when large amounts of particular elements are retained.

A large proportion of data from elemental composition studies in freshwaters, is concerned with the use of plant material for forage (Anderson *et al.*, 1965; Boyd, 1968, 1969, 1971; Sandholm *et al.*, 1973).

Other authors, have made attempts to relate their composition data to the chemistry of the water. Riemer and Toth (1969) analysed 11 elements including Zn, Cu, Mn and Fe. They found certain relationships, between *Potamogeton* spp. and the surrounding water notably for Mg and Fe although these were not directly proportional. Adams *et al.* (1971) found that the elemental composition of *Elodea canadensis* increased as concentrations of K, Mg, Ca, Zn, Cu and Mn in the environment, became higher.

Mayer and Gorham (1951) analysed Mn and Fe contents of some aquatic angiosperms in the English Lake District; they found large quantities of the former element, present in the tissues. However their data were more concerned with the distribution of aquatic plants than relationships with the aquatic environment.

Quantitative studies of the accumulation of heavy metals by aquatic organisms have been carried out in two ways.

(i) <u>Direct analysis</u>

This involves analysing both the organism and surrounding water.

Scott (1943) first suggested the dependence of the internal concentration upon the ionic concentration of the surrounding medium. Brooks and Rumsby (1965) quantified this relationship by proposing the term 'enrichment ratio' in their studies of New Zealand bivalves. They calculated the ratio as:

$$\frac{\text{concentration in the organism (dry weight)}}{\text{concentration in the surrounding medium}}$$

This mode of approach has been used subsequently by a number of authors in both marine and freshwater environments (Pringle *et al.*, 1968; Boyd and Lawrence, 1967; Bertine and Goldberg, 1972).

(ii) The use of radio-active isotopes

This technique can be used to establish the same ratio, usually under experimental conditions (Timofeeva-Resovskaya *et al.*, 1961; Gileva, 1964; Harvey and Patrick, 1967; Cushing and Rose, 1970).

As Bowen (1966) pointed out, different authors have adopted various ways of expressing this ratio. The majority have quoted ratios as a fraction of dry weight although fresh weight may have more physiological significance. There are several expressions for the enrichment ratio, which include, 'concentration factor' (Bowen, 1966), used by the majority of authors, 'coefficient of accumulation' (Timofeeva-Resovskaya, 1961), 'accumulation factor' (Gileva, 1964) and 'enrichment factor' (Dietz, 1973). However, the term 'enrichment ratio' as defined above, and adopted by Whitton and Say (1975), will be used throughout this work.

Enrichment ratios have been calculated for two species of seaweed (*Fucus* sp. and *Porphyra* sp.) and for the soft parts of limpets in British Isles coastal waters (Preston *et al.*, 1972). These authors concluded that *Fucus* sp. would be a good quantitative indicator for Zn, Mn, Fe and Ag.

Boyd and Lawrence (1967) analysed 14 genera of freshwater algae, including *Cladophora* sp., for a large number of macro- and micro-elements. The composition of these was related to the water using enrichment ratios. These ranged from 3000 to 12000 for most elements. They concluded that "elevated accumulation of most elements occurred when samples of algae from waters of high concentration were compared to samples from water of low content but the relationship did not hold for waters of intermediate level." Marked enrichment of Zn, Cu, Mn, Fe was found in all genera. However, few if any of their samples were taken from flowing waters.

Neutron activation analysis has been used by Fjerdingstad (1974) to calculate enrichment ratios for a very large number of trace elements in *Chlamydomonas nivalis*, from the snows of Greenland. The ratios for Zn, Cu, Mn and Fe, were much lower than those quoted by other authors for more complex plants.

A considerable accumulation of metals by filamentous algae has been noted by several authors (Davis *et al.*, 1958; Timofeeva-Resovskaya *et al.*, 1961; Gileva, 1964). Until recently the potential use of these organisms had not been exploited. However, Keeney *et al.* (1976) used *Cladophora glomerata* as a space/time indicator of heavy metals in the Lake Ontario catchment. They found a narrow range of enrichment ratios: Zn, 1000 to 2900; Cu, 1900 to 2200; Pb, 16000 to 20000. The ratios, particularly for Cu, were found to be comparable with those found in the mining area of the Upper Spokane River.

Dietz, (1973) has investigated two species of aquatic moss and four species of aquatic angiosperm from the River Ruhr. He found surprisingly little variation in enrichment ratios for trace elements. The heavy metals studied included Zn, Cu, Mn, Fe, Pb, Ni, and Hg. Enrichment ratios were calculated using wet weight but a correction for dry weight was given.

Adams *et al.* (1973) have analysed 30 species of aquatic vascular plant for 11 elements including Na, K, Mg, Ca, Zn, Cu, Mn, Fe and Al. They suggested that a number of these species could be used as suitable quantitative monitors on the basis of the variation in element composition but they did not give any enrichment ratios.

Data for the River Wear system concerning the enrichment of plants are scarce. Leeder (1972) has studied the lower reaches of Rookhope Burn. He investigated the composition of *Lemanea fluviatilis, Hygrohypnum ochraceum* and *Mimulus guttatus,* using enrichment ratios to relate the composition of Zn and Pb to the water chemistry. Although these ratios were by no means constant, he found that an overall increase in Zn and Pb concentrations in the water corresponded with overall increases for these elements in the plant.

Some composition data have been given by Patrick (1973) for a moss found at pH 2.6 in Brandon Pithouse Acid Stream. These data were compared with data from a stream in the Nenthead region of the River South Tyne Catchment containing in excess of 9 mg l^{-1} Zn.

The study of metal uptake and accumulation, using ratioactive isotopes, has rarely been used in conjunction with mineral composition studies (Whitton and Say, 1975). Cross *et al.* (1971) have pointed out some differences in the availability of Zn^{65} and total Zn to aquatic organisms in relation to the chemical speciation of this metal, in an experimental marine ecosystem. Enrichment ratios were in the region of 4900 for Zn^{65} and 7200 for total Zn (dry weight), in a mixed phytoplankton community (mainly *Chlorella* sp., *Nitzschia closterium* and bacteria). These authors suggested that the difference in concentration factors might be caused by the presence of a non exchangeable 'pool' of organically complexed Zn available to the phytoplankton but not available for exchange with Zn^{65}. They went on to point out the need to study both stable and radioactive isotopes in tracer experiments. The possible effects of chemical speciation on the biological availability of cations have already been mentioned in 1.2.2.

The ability of aquatic organisms to concentrate radio-active isotopes has been used as a guide to their concentration in the environment. For example, stream bryophytes have been used to indicate the presence of U^{235} in the bed-rock (Whitehead and Brooks, 1969).

Several experimental studies using radioactive isotopes have shown that within limited ranges of micro-concentrations, enrichment ratios remain stable. The enrichment of these isotopes is therefore proportional to their concentration in the surrounding medium. Timofeeva-Resovskaya *et al.* (1961) found constant enrichment ratios over a wide range of micro-concentrations for many elements including Zn^{65} in their investigation of 32 species of fresh water plants. Gileva (1964) found similar stability for enrichment ratios of many radio-active isotopes in *Cladophora fracta*. However, proportionality was not found for Zn^{65} because of the high minimum concentration used (10^{-4}M, 6.5 mg l^{-1}). The enrichment ratios for Zn^{65} in *Fontinalis antipyretica* have been found constant over a range of 10^{-4} to 10^{-2} mM Zn (0.007 to 0.5 mg l^{-1}), in experiments carried out by Pickering and Puia (1969).

A number of similar experimental enrichment ratios, however, have to be treated with some caution as the data have not been obtained at equilibrium conditions (Cushing and Rose, 1970).

Much of the cultural work with radio-active isotopes has been concerned with the mechanism of uptake of metal ions rather than the overall accumulation. Some early studies stated an apparent relationship between Zn^{65} uptake and photosynthesis (Bachmann and Odum, 1960; Gutknecht, 1963), implying some form of obvious active uptake. It has been pointed out that this may well have been an artefact, caused by pH changes during the experiments (Bryan, 1969; Cushing and Rose, 1970).

The concensus of opinion now seems to indicate that the initial means of uptake of divalent heavy metal ions, particularly Zn^{65}, is actually a very fast physico-chemical phenomenon of some kind, independent of cell energy (Gutknecht, 1963; Broda, 1965, 1972; Pickering and Puia, 1969). This is followed by a slower binding process into the cells (Cushing and Rose, 1970; Faill*et al.* 1976).

Some authors have found that the initial uptake corresponds with physical surface equations, e.g. the

Freundlich equation (Gutknecht, 1963) or the Langmuir adsorption equation (Gileva, 1964), and is therefore proportional to the concentration of elements in solution. The constancy of the enrichment ratio under equilibrium conditions (Gileva, 1964; Pickering and Puia, 1969) implies that subsequent accumulation is also proportional to the concentration in solution.

The literature supplies some evidence for the practical use of certain aquatic organisms as potential indicators of heavy metals. There is also sufficient experimental evidence, concerning the mechanism of uptake, to warrant further investigation into the use of aquatic plants as quantitative indicators of heavy metals in river water.

1.3 Environmental Background of River Wear system

1.3.1 Introduction

Basic information is available concerning the biology and chemistry of the River Wear system from the annual reports of the Northumbrian Water Authority and the former Northumbrian River Authority (1967 to 1976).

A general account of the River Wear has been given by Whitton and Buckmaster (1970) together with a survey of the macrophytes throughout the freshwater reaches. According to these authors, two of the main influences in the system prior to 1967 were pumped mine water and sewage effluents.

In a survey of the chemistry of the river and some of its main tributaries, Snow and Whitton (1971) pointed out an overall increase in key plant nutrients from source to mouth. They also noted the presence of Zn and Pb in some upland tributaries (1.2.3) but found only small concentrations of these metals in the main river. Detailed chemical information concerning the reaches of the river below Durham has been presented by Sunderland and South Shields Water Company; records of which are held in the Botany Department, Durham University.

In 1972 a new effluent entered the River Wear below Durham. This was of particular interest as it was known to contain heavy metals.

There have been some marked changes in the flora of the river over the last ten years. One of the most important has been the spread of *Ranunculus penicillatus* var. *calcareus* in the lower reaches of the River Wear, recorded by Holmes *et al.* (1972). In their recent re-survey of the River Wear, Holmes and Whitton (1977) suggested that the spread of this plant and other species has been brought about by the improvement in environmental conditions, particularly the reduction of suspended solids and pumped mine water.

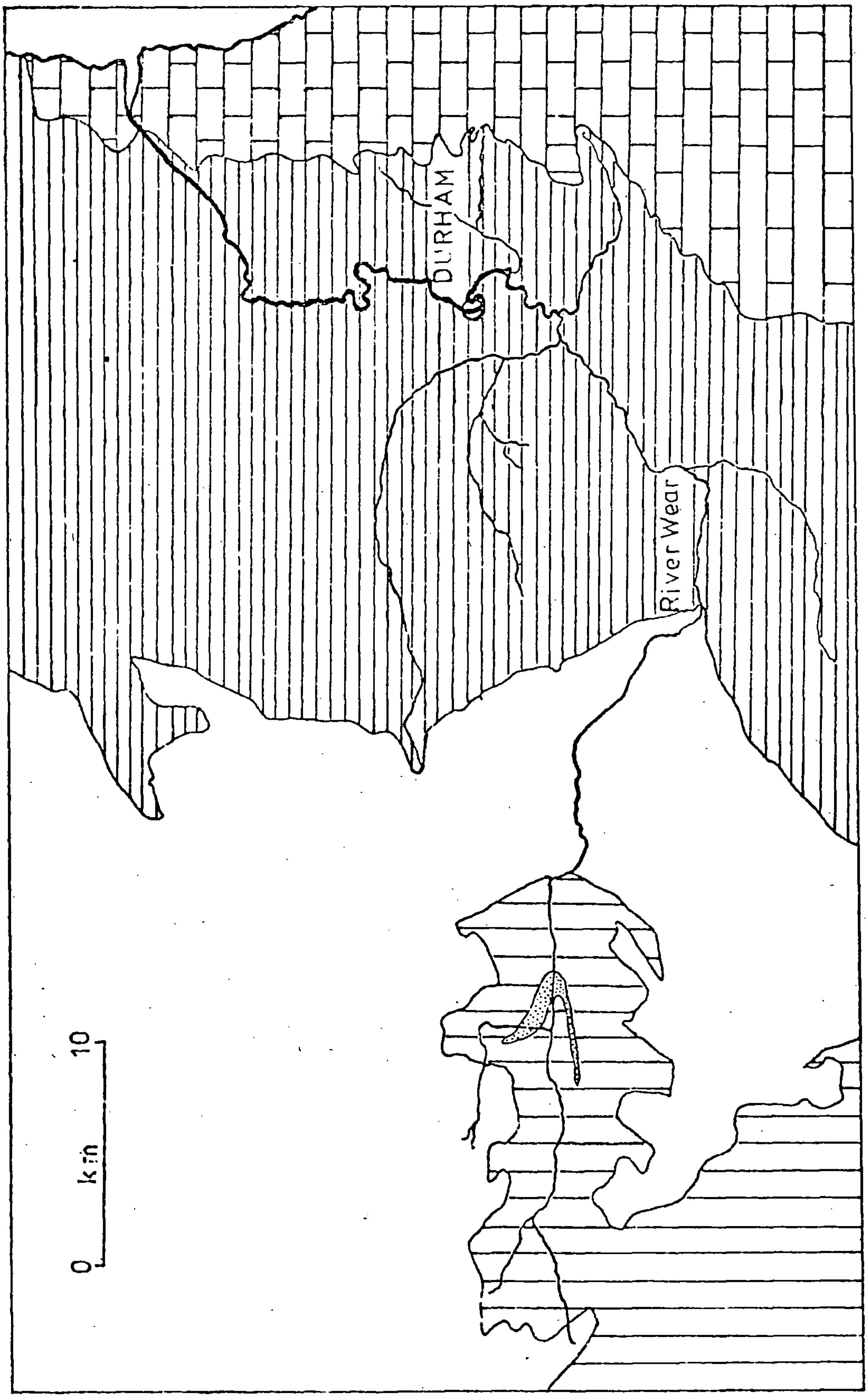
The pollution by heavy metals of the main upland tributary, Rookhope Burn, has received some attention. As mentioned in 1.2.3, Leeder (1972) studied Zn and Pb concentrations in both the water and aquatic plants of the river. Say (1977) has given further information concerning Zn-rich tributaries and adits of Rookhope Burn. The possibility of increased heavy metal pollution in the River Wear, from both mining and industrial activities, has been pointed out by Holmes and Whitton (1977).

There have been several studies concerning the biology and chemistry of Pithouse Acid Stream, which enters the River Deerness in the north-western part of the catchment. Robinson (1971) has given a general account of the stream, noting high concentrations of heavy metals and a very low pH. Pomfret (1973) has discussed aspects of the acid tolerance of algae in and around this stream. The most detailed study has been carried out by Hargreaves (1977), who discussed the effects of pH, acidity and heavy metals on the flora of the stream.

1.3.2 Geology

The geology of the River Wear catchment is illustrated in Fig. 1.1. The system drains off the uplifted and mineralised Alston block and over the gently eastward dipping Carboniferous series (Johnson, 1970). The rivers and streams of Weardale have cut down through the Millstone Grit to the underlying Carboniferous Limestone series (Cairney and Storey, 1970). The latter comprises the cyclic limestones, shales, sandstones and coal of the Yoredale series (Johnson, 1970).

A number of commercially important ores have been mined from the mineralised Alston block. In the Weardale region the most intense activity occurred intermittently in the eighteenth and nineteenth centuries (Dunham, 1948). According to Johnson (1970) the ores include sphalerite (ZnS), limonite ($2Fe_2O_3.3H_2O$), galena (PbS), barytes ($BaSO_4$), witherite ($BaCO_3$) and fluorite (CaF_2). Most of the upper tributaries show evidence of the old mine workings. The most significant of the mining areas lies in the region of Rookhope.


DURHAM
River Wear
0
km
10

From Stanhope to Wolsingham the River Wear flows over the alternating bands of limestone, shale and sandstone of the Millstone Grit.

In its lower reaches, the river, together with its major tributaries, drains the strata of the Coal Measures (Cairney and Storey, 1970). One important exception to this is the River Gaunless which originates in the Magnesian Limestone prominent in the south and south-east of Co. Durham. In the lower part of the catchment the river is hardly affected by the underlying geology. It meanders, across the thick alluvial deposits of the flood plain (Cairney and Storey, 1970), to its mouth at Sunderland. Fuller accounts of the geology of the area are given by Hickling *et al.* (1931) and Dunham (1948).

1.3.3 Hydrology and Geography

In order to locate accurately the features of interest, the River Wear and its tributaries have been marked in km.

On the main river these km marks increase from 0.0 at the headwaters to 106.9 at the mouth (Whitton and Buckmaster, 1970). The point of entry of any tributary into the river is also given as 0.0. In this case, km marks increase upstream and tributary marks are prefixed with a minus sign, e.g. the gauging station on the River Rookhope Burn is at - km 0.6 from the point of entry of the tributary into the River Wear. This system has been used to locate sites in the River Tweed system (Holmes, 1975) and the River Tyne (Holmes *et al.*, 1972). Further identification of individual sites is given by a numerical system of stream and reach numbers, fully described in 2.3.1.

The hydrology of the system is closely related to the geology. In the upper part of the catchment area the River Wear and its tributaries flow quickly down steep but uniform gradients. On the whole, the flow rate decreases towards the lower part of the system where the river reaches the gentle gradient of its flood plain.

The source of the River Wear is at the junction of two fast flowing tributaries, Kilhope Burn and Burnhope Burn (Wearhead, km 0.0). The river is typically fast flowing to km 12.6 where Rookhope Burn enters at Eastgate. The substratum comprises large amounts of sheet rock and boulders in this stretch.

The river continues in a generally east to south easterly direction. The gradient becomes shallower and the substratum changes to small boulders and cobbles, until it crosses onto the Coal Measures of the Durham plain. Here it begins to veer northeastwards and deeper silty reaches occur. These are interspersed by riffles of faster flowing water, often containing large sandstone boulders and some sheet rock (Whitton and Buckmaster, 1970). The River Gaunless, a major tributary, enters the River Wear at km 44.1, downstream of Bishop Auckland.

In the middle stretches the river becomes slower and begins to flow in deep silty meanders with only occasional faster stretches of water. As it progresses towards the tidal limit at km 91 it becomes much deeper and riffles no longer occur. Beyond this point the river becomes estuarine before reaching the mouth at Sunderland.

The total length is 106.9 km from Wearhead to Wearmouth Bridge (Whitton and Buckmaster, 1970).

The Rivers Browney and Deerness rise in the higher parts of the Coal Measures and both flow down a fairly uniform gradient before the latter joins the former at - km 6.0. The confluence with the main river occurs at km 58.5.

The whole river system is subject to quite marked changes in discharge, particularly in its upper catchment where the rainfall is considerably higher, 800 to 1800 mm per year, according to location (Smith, 1970; Snow and Whitton, 1971). Northumbrian Water Authority data (1973), at Sunderland Bridge gauging station (km 58.3), show a range of flows from 1.5 to 141 $m^3\ s^{-1}$ for the period March to October 1973 with a mean value of 5.8 $m^3\ s^{-1}$.

Major flooding was rare during the period of study, (March, 1972 to January, 1974) although minor floods have occurred intermittently at various seasons. The flows were much higher in winter than in summer. At times the river was subject to exceptionally low flows during the summer months, e.g. during the period March to October 1973 the flow remained almost continually low and recordings less than 2.0 $m^3\ s^{-1}$ were frequent at Sunderland Bridge gauging station (Northumbrian Water Authority, 1973).

Table 1.1 summarises hydrological data at three of the gauging stations in the River Wear system during the period March to October 1973. Further hydrological information is given by Cairney and Storey (1970) and details

TABLE 1.1 Hydrology of the River Wear system, March to October 1973

Data abstracted from Northumbrian Water Authority

gauging station (N.W.A.)	river	km	catchment km^2	flow ($m^3 s^{-1}$) mean	max	min
Stanhope	Wear	14.8	171.9	1.97	54.34	0.48
Sunderland Bridge	Wear	58.3	657.8	5.82	141.3	1.52
* Eastgate	Rookhope Burn	-0.6	36.4	0.45	12.08	0.09

* records calculated without August 1973 figures

of climate in the region by Smith (1970).

1.3.4 Rookhope Burn

1.3.4 (a) Geography

The stream rises at Rookhope Burn Head from the junction of several minor tributaries. It flows eastward for 7 km before turning south for 6 km, to join the main river at km 12.6. This tributary drains an area of open moorland and rough pasture, in common with other Weardale streams (Snow and Whitton, 1971). The lower reaches have steep banks and are well shaded by woodland. The area receives high and localised rainfall often giving rise to small floods. The hydrology of the river is dealt with in 1.3.2 and Table 1.1. The headwaters rise from peat bogland and the river flows down an uneven gradient of alternating Carboniferous shales and sandstones. Above Rookhope Village the stream flows in long shallow stretches down a gentle slope. The bed comprises mainly boulders and pebbles. After turning south at Rookhope Village it flows steeply down over bands of limestone and igneous rock, which give rise to a series of fast flowing stretches and occasional waterfalls.

1.3.4 (b) History of lead mining

Lead mining in the Rookhope area is thought to have begun in Roman times. It did not reach its heyday until the eighteenth and nineteenth centuries, mainly under the auspices of the London Lead Co. and the Beaumont family (Johnson, 1970). Output reached its peak between 1815 to 1880; most of the derelict mine workings and spoil heaps originate from this period. In the later part of the nineteenth and early twentieth centuries the lead mining industry declined and most of the workings were taken over by the Weardale Lead Co. (Dunham, 1969). The ores mined were chiefly sphalerite (ZnS) and galena (PbS) mentioned in 1.2.2; sufficient silver (Ag) was present in these to make it worthwhile re-extracting (Johnson, 1970). The silver was removed from the inside of the flues of the lead smelter. The last vestiges of the latter lie upstream of Rookhope Village and have only recently been dismantled. The other main ore of interest was chalcopyrite ($CuFeS_2$), a copper ore, which was worked at Groverake in the upper Rookhope Valley.

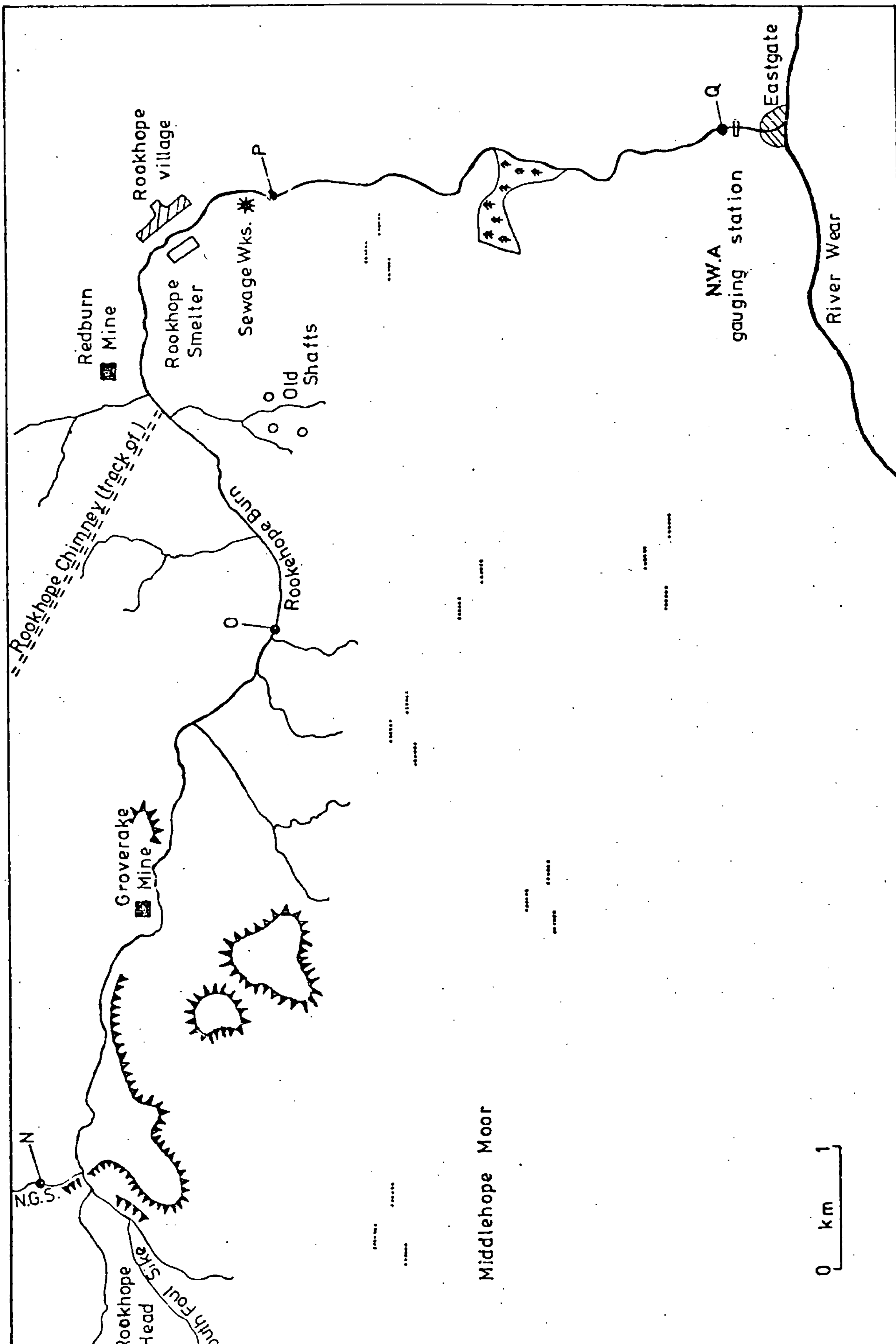
The development of the non-metallic mining industry has brought about renewed activity in the area; large deposits of fluorite (CaF_2) have been found in the vicinity of Rookhope. The Weardale Lead Co., a former subsidiary of I.C.I. Ltd, carried out most of the operations in the Rookhope valley at the time of the study. A brief description of the individual mines is given by Leeder (1972) and more details of the economic geology of the region have been given by Dunham (1948, 1959).

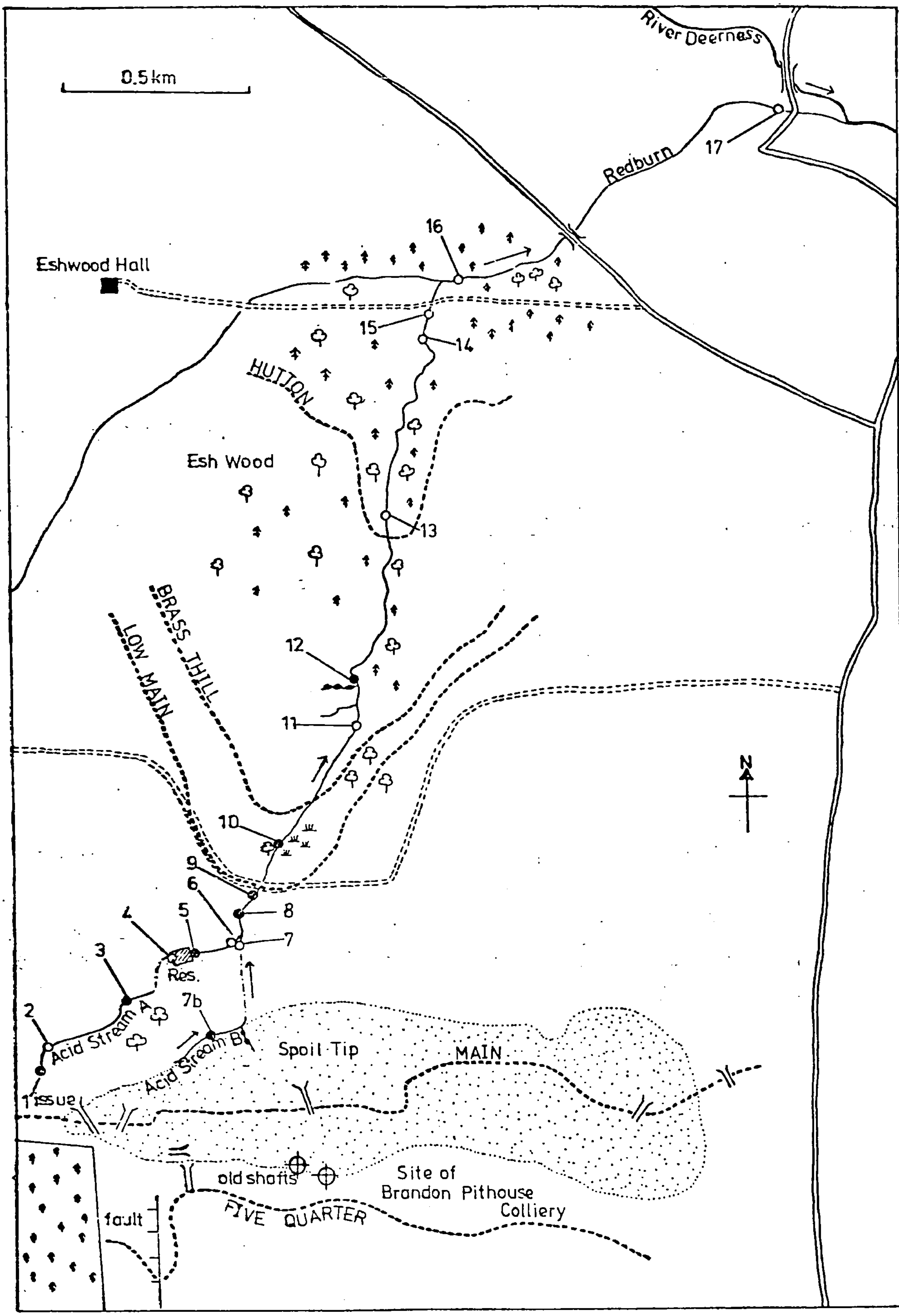
High concentrations of Zn and Pb in the river are the result of run-off from the old spoil heaps and adits. Fig. 1.2 summarises the course of the river and features of interest concerning the mine workings in the area.

1.3.5 Brandon Pithouse acid streams

1.3.5 (a) Geography

The location of the streams, together with some of the more important features, is illustrated in Fig. 1.3. The main stream flows in a north to north-


Rookhope village
P
Redburn Mine
Rookhope Smelter
Sewage Wks.
Old Shafts
Q
Eastgate
N.W.A gauging station
River Wear
Rookhope Chimney (track of)
Rookhope Burn
O
Groverake Mine
N
N.G.S.
Rookhope Head
South Foul Sike
Middlehope Moor
0 km 1



River Deerness
0.5 km
17
Redburn
16
Eshwood Hall
15
14
HUTTON
Esh Wood
13
BRASS THILL
LOW MAIN
12
11
N
10
9
6
8
5
7
4
3
Res.
7b
2
Acid Stream A
Acid Stream B
Spoil Tip
MAIN
1 issue
old shafts
Site of
Brandon Pithouse
Colliery
fault
FIVE QUARTER

easterly direction for 3.6 km before joining Red Burn at - km 1.0. This stream meets the River Deerness at - km 3.7.

The acid waters issue at two points below the spoil heap. Acid Stream A springs from an earthenware pipe near the site of old drifts. Stream B has a diffuse source, seeping from the base of the tip into a deep channel of clay and silt. It is possible that this stream originates from old drifts now covered by the tip (Pomfret, 1975; Hargreaves, 1977). It then disappears underground, re-emerging a few metres before the junction with the main stream (- km 3.0). For the first 200 m Stream A flows over a substratum composed of clay with occasional shalely reaches. In 1970, part of the drainage channel was re-excavated to prevent the flooding of farm land (Robinson, 1971). The stream passes underground for a few metres before entering a small reservoir; the purpose of which is not clear. From the reservoir, the stream flows down a steeper gradient over a mixed substratum of pebbles and sand to the entry point of Stream B. After the confluence, the stream flows steeply down over heavy precipitates of Iron oxides and receives drainage from arable land before entering Esh Wood. The lower parts of the stream were heavily shaded during the period of study. In general the substratum is more silty and the presence of Iron oxides diminishes.

The discharge of Stream A remained remarkably constant, at its source, throughout the period of study. The mean value was 0.3 l s^{-1}. However, both streams were subject to spectacular 'flash' flooding caused by run-off from the tip. This tended to scour the stream bed and intermittently removed most of the vegetation, apart from that near the source of Stream A.

On occasions in winter the middle reaches of the stream froze over and at times in summer parts of the stream dried out completely. The biological implications of these extremes have been discussed by Hargreaves (1977) who has also given more detailed accounts of the environmental background of the stream.

1.3.5 (b) History of coalmining

The area has been mined on a small scale for many centuries. Shaft mining was first recorded in 1838. The main shaft was sunk in 1926 and the modern workings interconnect with the old drifts in the Five Quarter and Main seams (Pomfret, 1973). The colliery was closed in 1966 leaving a spoil heap 800 m across (Robinson, 1971). In recent years the heap has been considerably altered in order to lower and stabilise it. This had little effect on the streams during the period of study (Hargreaves, 1977).

CHAPTER TWO

2. METHODS

2.1 Water Samples

2.1.1 Collection and storage

Samples were taken from the main current of the river or stream immediately below the surface. On several occasions four replicate samples were taken to illustrate the limits of variation. All containers to be used for sampling were soaked in 5% HCl for 24 hours and rinsed six times in glass distilled water before use. This procedure was carried out to ensure freedom from contamination. The samples were filtered through an acid washed No. 2 'Sinta' glass funnel to remove larger suspended matter and most algae.

Samples for cation analysis were collected in 100 ml 'Pyrex' bottles. These were chosen as being the least likely to cause trace contamination. Tests showed that certain polythene containers leached large quantities of Zn and Fe in particular (Test A). No measurable contamination of any Zn, Cu, Pb or Cd was encountered with 'Pyrex' (Test B).

Test A

Four acid washed polyethylene containers were filled with glass distilled water and analysed after 7 days. Glass distilled water was kept in an acid washed 'Pyrex' container and analysed along with the samples (e). Contamination is obvious.

	Zn	Cu	Fe	Pb
(a)	0.015	0.015	0.84	0.018
(b)	0.098	0.023	0.47	0.010
(c)	0.020	0.009	0.76	0.024
(d)	0.008	0.007	0.33	0.006
(e)	<0.002	<0.002	<0.01	<0.001

Test B

Four acid washed 'Pyrex' bottles (ground glass stoppers) were filled with glass distilled water and acidified with 0.5 ml 'Aristar' HCl. The samples were analysed immediately and at 7 day intervals subsequently. The data presented below applies to all four samples.

	Zn	Cu	Pb	Cd
initial	<0.002	<0.002	<0.001	<0.0001
after 7 days	<0.002	<0.002	<0.001	<0.0001
after 14 days	<0.002	<0.002	<0.001	<0.0001
after 21 days	<0.002	<0.002	<0.001	<0.0001

It is clear that none of the heavy metals analysed showed any signs of increase from leaching. In both cases, analysis was carried out as described in 2.12.

Samples for the analysis of anions and pH were collected in 300 ml heavy duty polythene containers, in the same manner as the cation samples.

On return to the laboratory all samples were stored in the dark in a refrigerator at 4°C until analysis was carried out. Trace element analysis was carried out as soon as possible after collection, before loss could occur, through precipitation. Heavy brown flocs of humic material tended to form in samples from the River Wear if these were left standing (1.2.2). PO_4-P, NH_3-N, NO_2-N and NO_3-N were determined on return to the laboratory. When this was not possible analysis was completed within 48 hours.

2.1.2 Analysis of cations

Cation analysis was carried out using a Perkin-Elmer model 403 Atomic Absorption Spectrophotometer. The elements analysed included Na, K, Mg, Ca, Zn, Cu, Mn, Fe, Al, Pb, Cd, Co and Ni. In most cases the standard conditions were used (Perkin - Elmer manual). Pb and Cd were analysed using the Tm sampling boat procedure (Kahn *et al.*,1968).

2.1.3 Analysis of anions

The analysis of anions included the regular analysis of Cl, Si, PO_4-P, NH_3-N, NO_2-N and NO_3-N. Other analyses included pH, conductivity and optical density. All optical density measurements of the colourimetric procedures were performed on a Uvispek (Hilger & Watts).

Cl. Analysis of Cl was made by argentometric titration (A.P.H.A., 1971).

Si. The determination of Si was carried out by the heteropoly blue method (A.P.H.A., 1971).

PO_4-P. For normal river waters, the stannous chloride procedure was adopted (A.P.H.A., 1971) without any pre-treatment of the samples. The detection limit for this technique using 400 mm silica cells was 0.01 mg l^{-1} PO_4-P. Where interference was encountered, an extraction procedure using n-hexanol was used (Mackereth, 1963). Not only is interference reduced or eliminated but the sample is also concentrated. Reduction of ammonium molybdate to a complex blue colour with stannous chloride was carried out in a similar manner to the standard method. A detection limit of 0.001 mg l^{-1} PO_4-P could be attained by this method.

NH_3-N. The recommended procedure for the analysis of NH_3-N is distillation followed by nesslerization (A.P.H.A., 1971). This procedure was used for some determinations but the time taken for each sample was too long for use in regular analysis. The simpler procedure of direct nesslerization of the sample was therefore adopted for the bulk of analysis (A.P.H.A., 1971). Clarification of the sample was carried out by the addition of 0.5 ml of $ZnSO_4$ (1000 mg l^{-1}) to 40 ml sample. 0.1 N NaOH was then added dropwise to a pH of 10.5. The flocculent precipitate which appeared was centrifuged down at 3000 r.p.m. for 2 min. A 25 ml aliquot of the supernatant was taken for nesslerization. The yellow colour was measured at 420 nm in 400 mm silica cells. Optimum colour development occurred between 35 and 45 minutes. A detection limit of 0.01 mg l^{-1} NH_3-N was found possible using this method.

NO_2-N. The procedure adopted was that of Crosby (1967). An initial measurement of the sample was carried out at 520 nm to allow a correction for the natural colour of the water. This value was subtracted from the final colour reading to obtain the true optical density. Use of 400 mm cells gave a detection limit of 0.002 mg l^{-1} NO_2-N.

NO_3-N. The procedure of Hammond (1959) was used for the majority of samples. This is a single step, rapid, procedure involving 3:3'-dimethylnapthidine. There were two major disadvantages in the use of this technique. Firstly, occasional colour instability was encountered. This was improved by diluting the purple reaction product with 25% H_2SO_4 in place of distilled water. Secondly, a highly coloured blank occurred which absorbed, to some extent, at 570 nm (the wavelength of colour measurement). This allowed a detection limit of only 0.5 mg l^{-1} using 100 mm cells. Maximum colour development occurred after 20 minutes and remained stable for only 10 minutes.

The procedure of Montgomery and Dymock (1962) was adopted for certain samples. The reaction was carried out in a constant room temperature at 5°C to minimise the temperature dependence of the reaction. Using 400 mm cells a detection limit of 0.05 mg l^{-1} was found (0.2 mg l^{-1} NO_3-N, using 100 mm cells).

Other analyses. pH was determined in the laboratory using an E.I.L. pH meter. Conductivity was measured with a Lock Conductivity Bridge. Optical density was measured directly on a Uvispek spectrophotometer at 420 nm in 400 mm silica cells.

2.1.4 Analysis of water from acid mine drainage

Waters from acid mine drainages presented certain analytical problems. Several modifications to the above procedures were made.

Cl. The normal argentometric titration did not give any end point with acid water because of interference. The sample was therefore clarified by adjusting the pH to 10.5 with 1N NaOH and centrifuging down the heavy precipitate. The supernatant was then re-adjusted to pH 7. A 25 ml portion of this was taken for titration in the usual way.

PO_4-P. All analysis for orthophosphate was carried out by extraction into n-hexanol (Mackereth, 1963). The normal phosphate procedure gave a low recovery.

NO_2-N and NO_3-N. The high concentrations of Fe found in acid waters (>80 mg l^{-1}) caused considerable interference in the colourimetric determination of NO_2-N and NO_3-N. The interference was in the form of colour enhancement. Removal of the Fe present was therefore necessary. The samples were passed through a column of cation exchange resin (Amberlite IR 120 H form). Analysis for NO_3-N was then carried out by the method of Montgomery and Dymock (1962). No readings could be obtained for NO_2-N after this pre-treatment. It is felt that any trace quantities present would be lost on a cation exchange column. NO_2-N results are therefore not presented for acid waters.

SO_4-S. The procedure used was than of Colson (1963). Samples were diluted by a factor of 10 after ion exchange (through Amberlite IR 120 H-form) before titration against $Ba(ClO_4)_2$.

Acidity. The determination of acidity was carried out by hot titration to pH 8.3 using phenolphthalein indicator (A.P.H.A., 1971).

2.2 Plant samples

2.2.1 Collection

For several reasons, plants were always collected at low flow.

(i) Only at these times could samples be collected across the rivers.

(ii) The plants were less silted up and therefore easier to clean.

(iii) Periods of low flow were expected to give the most stable water chemistry.

Plants from the River Wear were collected over 20 m stretches, in the main current, away from the banks. An experiment was conducted using the alga *Cladophora glomerata* to establish the variation in composition within a sampling site. This test confirmed the use of the above criteria (5.2.1).

Plants from Rookhope Burn were also collected from 20 m stretches of river. Where it was possible, the same sampling criteria were used. However application of these criteria was not always possible. *Mimulus guttatus* tended to occupy habitats not in the main stream. *Hygrohypnum ochraceum* usually occurred towards the river bank.

Brandon Pithouse stream presented different sampling problems because of its small size. In this case 10 m reaches were chosen. The same sampling criteria were used i.e. the plants collected were submerged in the main flow of the stream except for the emergent *Juncus effusus*.

Samples of this species were taken from plants whose roots stood permanently in acid water.

Visually mature healthy plants were always selected, avoiding obviously very young or very old material.

Plant material was always collected from four suitable areas within the site to ensure representative replicate samples.

2.2.2 Washing

As a general procedure, all plants were washed thoroughly in river water at the time of collection to remove as much silt as possible. Excess water was removed by squeezing. The samples were then transferred to polythene bags and stored until return to the laboratory. Further washing procedures were carried out immediately on return to the laboratory. The aim of this was to remove all grit and other debris such as invertebrates. Presence of foreign matter could affect the dry weight of the sample and might also lead to contamination. All washing in the laboratory was carried out with distilled water. Care was taken to avoid over washing because of the risk of leaching.

Healthy *Cladophora glomerata* growing in a fast current was usually fairly grit free but thorough inspection was required to ensure removal of larvae.

A matted growth habit of *Vaucheria sessilis* made removal of all silty material practically impossible.

Algae such as *Stigeoclonium tenue* from Rookhope Burn or *Hormidium rivulare* from Brandon Pithouse stream tended to retain particles of inorganic and organic debris. These were removed as far as possible during the standard washing procedure.

The filaments of *Lemanea fluviatilis* were almost always grit free. The attachment organs of the alga were so intimately mixed with the substratum that removal of debris was not possible. These parts were therefore removed altogether during washing.

Euglena mutabilis from Brandon Pithouse stream, presented special problems in its collection and washing. The alga grew in a thick film on top of a muddy substratum. Field washing was therefore not possible. All samples of the alga and sediment were scraped into a jar. In the laboratory this mixture was shaken and then allowed to settle. The *Euglena* could then be poured away from the sediment. Centrifuging and washing several times ensured the removal of all the stream water and most of the sediment.

Those mosses which grew away from the stream bed and were washing in the current were relatively easy to clean e.g. *Fontinalis antipyretica* and *Drepanocladus fluitans*. Those which were closely appressed to their substratum tended to hold large quantities of debris in the thallus. *Eurhynchium ripparioides* and *Fissidens crassipes* were virtually impossible to clean thoroughly.

If the mosses were to be divided this procedure was carried out at the washing stage. Individual filaments were taken, measured and cut at 30 mm intervals from the tip.

The higher plants presented few problems in washing. Special care was required when cleaning the roots to ensure all grit was removed. Division of higher plants into root stem and leaf was carried out during washing.

2.2.3 Microscopic examination

A detailed survey of the microflora associated with each plant was not attempted. Certain microscopic examinations were undertaken to ensure biological contamination was kept to a minimum.

2.2.4 Storage

After washing, the samples were transferred to acid washed petri dishes and dried in an oven at 105°C for 48 h. Baker *et al.* (1964) noted that samples should be dried as quickly as possible to prevent loss in dry matter caused by continuing respiration. Precautions were also taken to reduce the possibility of contamination from dust in the oven.

The dried samples were ground by hand in a porcelain mortar and pestle, rather than with an automatic grinder. Hood *et al.* (1944) have stated that many grinders are sources of metal contamination.

The powdered samples were transferred to plastic sample tubes and desiccated for 24 h. The tubes were then stoppered with a polythene cap and stored until analysis. The samples were re-desiccated for 24 h prior to weighing out.

2.2.5 Digestion

2.2.5 (a) Sample size

Roughly equal amounts of the four replicate samples were taken for analysis. The sample size varied according to the amount of material available. The minimum and maximum quantities used were 0.1 g and 0.3 g (dry weight), respectively. Test (C) shows no significant difference between results using the maximum and minimum sample size.

Test C

Three approximately equal replicates of dried *Cladophora glomerata* were weighed out accurately for each sample size (0.1 g, 0.2 g and 0.3 g). These were digested and analysed for Zn as recorded in 2.2.5 (b) and 2.2.6.

size	weight	mean Zn $\mu g\ g^{-1}$
0.1	0.1201	63.5 ± 4.6
0.2	0.2018	61.3 ± 5.8
0.3	0.3193	61.2 ± 3.9

Samples were weighed out in 100 ml polypropylene digestion bottles. The bottle was weighed to 4 decimal places. The approximate weight of samples was added using a 2 figure balance. The bottle plus sample was then weighed accurately to 4 decimal places and the dry weight calculated by difference.

2.2.5 (b) Wet pressure digestion

The samples were digested using a modification of the wet pressure digestion described by Adrian (1973). The digestion does not carry to completion but is sufficient to release all the cations into solution.

2 ml 'Aristar' grade HNO_3 were added to each sample, the caps were screwed down and the samples left overnight to pre-digest. 1 ml 7 + 1 H_2O_2 (Analar 100 vol.) + H_2SO_4 (Aristar) was added and the caps re-tightened. The bottles were placed in a polythene bowl and hot water was circulated (70-80^{o}C) for three hours. The gases build up a pressure as the digestion proceeds. At the end of the digestion period the caps were loosened and the excess gases allowed to escape for one hour. 20 ml double distilled water was then added to each digest. The samples with washings were transferred to centrifuge tubes and centrifuged for 5 min. at 3500 r.p.m. The yellow supernatant was poured off and retained. The precipitate was washed with a 10 ml aliquot of double distilled water and re-centrifuged. The second supernatant was added to the first and the volume made up to 50 ml in a volumetric flask. The solutions were stored in the digestion bottles until analysis.

2.2.5 (c) Comparison of digestion techniques

A comparison of four digestion techniques is given in Test D.

Test D

Four replicate samples (0.3 g) of dried *Ranunculus penicillatus* var. *calcareus* were weighed our accurately for each analytical technique. The four methods used were.

(a) Dry ashing (Johnson and Ulrich, 1959)

(b) Wet digestion (Johnson and Ulrich, 1959)

(c) Wet pressure digestion (Adrian, 1973)

(d) Wet pressure digestion, modified by replacing perchloric acid ($HClO_3$) with Hydrogen peroxide (H_2O_2: 100 vol) described in 2.2.5 (b).

Method (a) has been questioned by Gorsuch (1959) because of the possible loss of volatile metals. Keeney *et al.*, (1976) have since noted the conclusions of Lord (1974), who has stated that serious loss of Cd occurs above 350°C and a similar loss of Pb at temperatures above 500°C. Samples were ashed in a muffle furnace for 12 h at 450-550°C.

Methods (b) and (c) were not practical on a large scale, in the laboratory facilities available, because of the explosive nature of $HClO_3$. Method (b) was carried out on micro-kjeldahl apparatus in a fume cupboard. The fumes were ducted away and dissolved in water. Method (c) was carried out as described in 2.2.5 (b) except for the modification noted above.

Method (d) was carried out as described in 2.2.5 (b). It was particularly important that data for heavy metals were comparable with those from other digestion techniques. The comparison was designed to see if this method was feasible for digesting large numbers of samples.

The results are presented in Table 2.1. It is clear that Pb, Cd and possibly some Zn are lost in the dry ashing technique, although recoveries of major cations are higher than the other methods. The technique was therefore rejected.

TABLE 2.1 Comparison of four methods of plant analysis
Concentrations in $\mu g\ g^{-1}$ dry weight; mean and
standard deviation of four replicates of *Ranunculus pencillatus* var. *calcareus*.

Technique	Na	K	Mg	Ca	Zn	Cu	Mn	Fe	Pb	Cd
(a)	13708±148	33071±781	2789±45	8832±188	1218±34	31.5±1.0	4688±102	1712±529	52.2±2.0	5.53±0.22
(b)	13223-76	31223±76	2733±16	9112±263	1304±48	35.2±1.4	4886±150	1267±150	61.3±2.6	8.28±0.14
(c)	12957-216	28373±297	2695±7	8560±463	1291±51	29.6±0.5	5566±69	1302±93	60.3±3.2	8.54±0.41
(d)	11999-311	26791±431	2649±70	8133±118	1270±50	29.2±0.5	5512±24	1117±124	60.4±1.8	8.17±0.17

Methods (b), (c) and (d) show very similar results for the heavy metals although recovery of Na and K is lower. Method (d) was adopted for the reasons of convenience mentioned above.

2.2.6 Analysis of plant digests

All analysis was carried out on the Perkin-Elmer 403 atomic absorption spectrophotometer using an acid resistant nebulizer. The following 13 cations were measured by standard aspiration procedures (Perkin-Elmer manual): Na, K, Mg, Ca, Zn, Cu, Mn, Fe, Al, Pb, Cd, Co, Ni.

2.3 Location of sites and reaches in River Wear system

Table 2.2 is a list of all the sites sampled in the River Wear system during the course of the study. Each stream has been allotted a number and where sites have been given a reach number, this refers to a specific '10 m reach'. Further biological and chemical data for these reaches are held in the Botany Department, Durham University.

All sites have been given km marks (1.3.3) except for a number of sites in Brandon Pithouse acid streams. In this case, only the sites of major importance have been given km marks. More emphasis has been placed on the use of reaches which coincide with those used by Hargreaves (1977). Site numbers for this stream system are placed in brackets after the site description; these have been used in Fig.1.3 to identify clearly the position of the sites.

Brief descriptions of the individual sites are

TABLE 2.2 List of sites and their exact locations

stream no.	km	river name	site description	grid reference	map reference
0008	0.1	Wear	Wearhead, 20 m below confluence	NY 859394	$54^{o}45'02^{o}13$
	14.6		20 m upstream of ford at Stanhope	NY 990393	$54^{o}45'02^{o}01$
	24.3		Wolsingham Bridge, 20 m upstream	NY 073368	$54^{o}44'01^{o}53'$
	35.2		50 m upstream of bridge at Witton-le-Wear	NZ 147307	$54^{o}40'01^{o}46'$
	44.0		Bishop Auckland, 10 m above confluence with River Gaunless	NZ 214305	$54^{o}40'01^{o}40'$
	44.3		Bishop Auckland, 300 m below confluence with River Gaunless	NZ 214309	$54^{o}40'01^{o}40'$
	51.1		Willington, 20 m downstream of bridge	NZ 209344	$54^{o}42'01^{o}40'$
	58.3		Sunderland Bridge, 20 m downstream of bridge	NZ 266378	$54^{o}44'01^{o}35'$
	65.5		Shincliffe, 50 m upstream of bridge	NZ 287409	$54^{o}45'01^{o}35'$
	70.6		Durham Sands	NZ 281432	$54^{o}47'01^{o}33'$
	73.5		100 m upstream of industrial effluent	NZ 293445	$54^{o}47'01^{o}32'$
	73.9		200 m downstream of industrial effluent	NZ 292447	$54^{o}47'01^{o}32'$
	78.1		Finchale Abbey, 50 m downstream of footbridge	NZ 297472	$54^{o}49'01^{o}32'$
	80.6		Cocken Bridge	NZ 281473	$54^{o}49'01^{o}34'$
	87.9		Lumley Bridge, 100 m upstream of bridge	NZ 285509	$54^{o}51'01^{o}34'$
	90.0		Lambton Bridge, 20 m upstream of bridge	NZ 295523	$54^{o}52'01^{o}34'$

stream no.	reach	km	river name	site description	grid reference	map reference
0115		-0.5	North Grain Sike	20 m downstream of road	NZ 882450	54°48'02°11'
0012		-8.5	Rookhope Burn	10 m upstream of roadbridge	NZ 911428	54°47'02°08'
		-3.9		20 m upstream of footbridge	NZ 944416	54°46'02°05'
		-0.6		Eastgate, 20 m upstream of N.W.A. gauging station	NZ 953390	54°45'02°04'
0127	01	-3.6	Brandon Pithouse Acid Stream A	source (1)	NZ 212404	54°45'01°40'
	02			channel (2)	NZ 212406	54°45'01°40'
	03			wood (3)	NZ 215406	54°45'01°40'
	04			reservoir (4)	NZ 215406	54°45'01°40'
	05			below reservoir (5)	NZ 216406	54°45'01°40'
	06			above confluence (6)	NZ 215407	54°45'01°40'
	07	-2.9		below confluence with Stream B (8)	NZ 215407	54°45'01°40'
	08			woodland above farm track (9)	NZ 216408	54°45'01°40'
	09			bog (10)	NZ 217409	54°45'01°40'
	10	-1.6		botton of field (11)	NZ 217410	54°45'01°40'
	11			upper Esh Wood (12)	NZ 216411	54°45'01°40'
	12			middle Esh Wood (13)	NZ 218415	54°45'01°40'
	13			lower Esh Wood (14)	NZ 218416	54°45'01°40'

stream no.	reach	km	river name	site description	grid reference	map reference
0127	14	0.1		above confluence with Red Burn (15)	NZ 219417	54°45'01°40'
0125	01	-0.6	Brandon Pithouse Acid Stream B	source (7b)	NZ 215404	54°45'01°39'
	02			below pipe (7)	NZ 215406	54°45'01°40'
0022	03	-1.0	Red Burn	below confluence with Acid Stream A (16)	NZ 219417	54°46'01°40'
	06	-0.1		above Road (17)	NZ 225420	54°46'01°38'
	05			10 m above confluence with Red Burn (18)	NZ 226422	54°46'01°38'
0005	06	-3.7	Deerness	20 m below confluence with Red Burn (19)	NZ 226422	54°46'01°38'
0014		-6.1	Browney	below confluence with River Deerness	NZ 257409	54°46'01°36'

given together with the full grid reference and map reference.

2.4 Check-list of species

2.4.1 Algae

021601 *Hildenbrandia rivularis* (Liebm.) J. Ag.

021902 *Lemanea fluviatilis* (L.) Ag.

030203 *Euglena mutabilis* Schmitz

060203 *Vaucheria sessilis* de Candolle

090404 *Melosira varians* C. A. Ag.

121432 *Mougeotia* sp. (8-12 μm)

1221 *Spirogyra* spp.

122750 *Zygnema* sp.

152402 *Enteromorpha flexuosa* (Wulfen. ex Roth.) J. Ag

152902 *Hormidium rivulare* Kutz.

154532 *Stigeoclonium tenue* Kutz.

154703 *Ulothrix zonata* Kutz.

160302 *Cladophora glomerata* (L.) Kutz.

1607 *Oedogonium* sp. (9 μm)

2.4.2 Byrophytes

222102 *Scapania undulata* (L.) Dum.

232150 *Dicranella* sp.

232302 *Drepanocladus fluitans* (Dillen) Warnstorf

232501 *Eurhynchium riparioides* (Hedw.) Rich.

232602 *Fissidens crassipes* Wils. ex B.S. and G.

232701 *Fontinalis antipyretica* Hedw.

232702 *F. antipyretica* Hedw. var. *gracilis* Schp.

232801 *Grimmia alpicola* Hedw. var. *rivularis* (Brid.) Broth.

233101 *Hygroamblystegium fluviatile* (Hedw.) B.S. and G.

233202 *Hygrophypnun ochraceum* (Turn. ex Wils.) Laeske.

233401 *Leptodictyum riparium* (Hedw.)Warnst.

2.4.3 Angiosperms

260204 *Callitriche stagnalis* Scop.

260301 *Caltha palustris* L.

250801 *Elodea canadensis* Michx.

251302 *Juncus effusus* L.

260701 *Mimulus guttatus* D.C.

260902 *Myriophyllum spicatum* L.

251902 *Potamogeton crispus* L.

251906 *P. natans* L.

251910 *P. pectinatus* L.

261106 *Ranunculus fluitans* Lam.

261110 *R. penicillatus* (Dumort.) Bab. var. *calcareus* (R.W. Butcher) C.D.K. Cook

N.B. numbers refer to the file 'Specieslist', dated October 1977, held in Botany Department, Durham University.

2.5 Sampling Programme

2.5.1 Water Chemistry

Water samples were taken at regular intervals, weekly and bi-weekly, at Sunderland Bridge (km 58.3) and Finchale Abbey (km 78.1) during the period February to August 1972. This programme was designed to establish the variation of important chemical parameters in relation to discharge.

In 1973 the programme was extended to include a site above the industrial effluent (km 73.5) and one below the effluent (km 73.9). The sampling at these four sites in the lower River Wear was carried out between January 1973 and January 1974, at monthly intervals. The location of these sites is shown in Fig. 2.1 and reach information given in 2.3.

Samples were taken on six occasions between March and October, 1973, at four sites on Rookhope Burn shown in Fig. 1.2. Brandon Pithouse Acid Stream A was sampled at its source at monthly intervals, from July 1972 to August 1974. At three monthly intervals, surveys of the whole acid stream complex were made (this work was carried out jointly with J. W. Hargreaves (1977) who gives full details of sampling). The location of all the sites sampled in the Acid Stream catchment is given in Fig. 1.3 and details of the reaches in 2.3.

Four seasonal surveys of the main river and selected sites on its tributaries were carried out in 1973/74: 1 March 1973, 30 June 1973, 10 October 1973 19 January 1974. These surveys comprised the sites A to M illustrated in Fig. 2.1. Geographical details are found in 2.3.

2.5.2 Plant samples, 1967/68

A survey of the mineral composition of aquatic plants occurring at Finchale Abbey (km 78.1) was carried out on material collected in 1967 and 1968. The plants included are given in Table 2.3.

Cladophora glomerata and *Fontinalis antipyretica* were collected from several sites on the

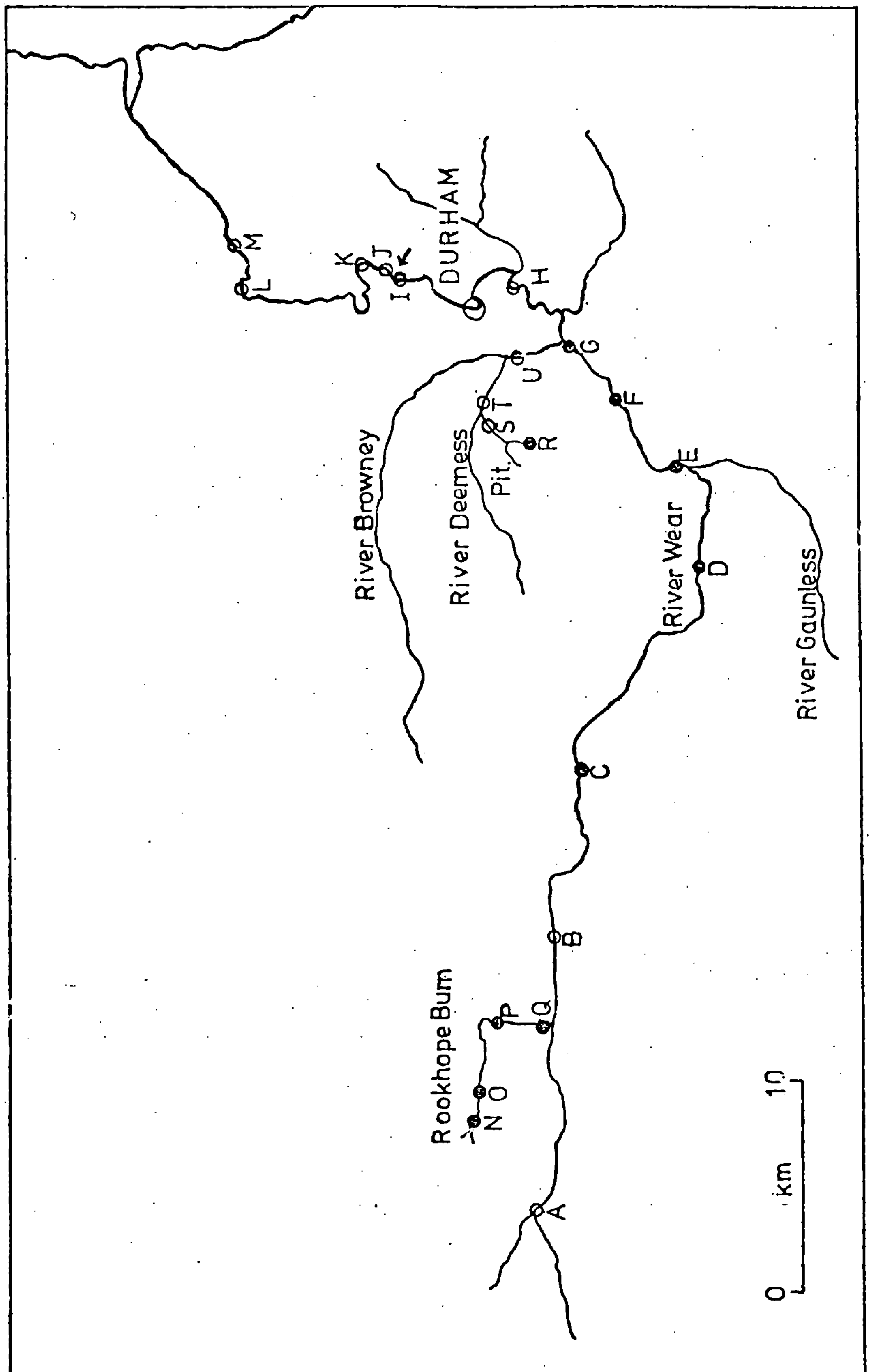

DURHAM
River Browney
River Deerness
Pit.
River Wear
River Gaunless
Rookhope Burn
A
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TABLE 2.3 List of plant species sampled from the River Wear at Finchale Abbey (km 78.1) on various dates during 1967/68

stream no.	date	algae	date	bryophytes	date	angiosperms
0008	27.7.68	*Cladophora glomerata*	27.7.67	*Eurhynchium riparioides*	20.8.68	*Potamogeton crispus*
	13.8.68	*Enteromorpha flexuosa*	27.7.67	*Fissidens crassipes*	20.8.68	*Potamogeton pectinatus*
	13.8.68	*Oedogonium* sp. (9 μm)	27.7.67	*Fontinalis antipyretica*		
	13.8.68	*Vaucheria sessilis*				

River Wear during 1967 and 1968. A number of these samples were chosen to gain some idea of the variation in mineral composition of these plants down the river. Both plants were sampled at the same time at the sites and dates given in Tables 2.4 and 2.5. Full site information is given in 2.3.

2.5.3 Plant samples, River Wear 1972-74

All plants sampled from the River Wear were collected from 20 m stretches of river (2.2.1) at the km marks indicated. Full site information is given in 2.3.

Cladophora glomerata was sampled at intervals during its main growing season at Finchale Abbey (km 78.1) in 1972; dates of collection are presented in Table 2.4.

In 1973, collection was carried out from April to November, at the four sites in the lower River Wear: Sunderland Bridge (km 58.3), above the industrial effluent (km 73.5), below the industrial effluent (km 73.9) at Finchale Abbey (km 78.1). Collection was also carried out, on a single occasion, at sites further upstream (Table 2.4).

Fontinalis antipyretica was collected in 1972, from Finchale Abbey (km 78.1) and divided by eye, into young tips, mature parts and old material (Table 2.5).

This moss was collected, in 1973, from the four main sites in the lower River Wear and on one occasion

TABLE 2.4 List of sites in the River Wear at which *Cladophora glomerata* was sampled during 1968, 1972 and 1973

stream no.	km	site	date
0008	44.0	Bishop Auckland (above River Gaunless)	15. 8.68
	51.1	Willington	15. 8.68
	70.4	Durham Sands	16. 8.68
	78.1	Finchale Abbey	13. 8.68
	80.6	Cocken Bridge	13. 8.68
	90.0	Lambton Bridge	16. 8.68
	78.1	Finchale Abbey	1. 4.72
	78.1	Finchale Abbey	25. 4.72
	78.1	Finchale Abbey	9. 5.72
	78.1	Finchale Abbey	24. 5.72
	78.1	Finchale Abbey	14. 7.72
	24.3	Wolsingham	26. 8.73
	35.2	Witton-le-Wear	26. 8.73
	44.3	Bishop Auckland (below River Gaunless)	26. 8.73
	51.1	Willington	26. 8.73
	58.3	Sunderland Bridge	29. 4.73
	73.5	above effluent	29. 4.73
	73.9	below effluent	29. 4.73
	78.1	Finchale Abbey	29. 4.73
	58.3	Sunderland Bridge	18. 5.73
	73.5	above effluent	18. 5.73
	73.9	below effluent	18. 5.73
	78.1	Finchale Abbey	18. 5.73
	58.3	Sunderland Bridge	14. 8.73
	73.5	above effluent	14. 8.73
	73.9	below effluent	14. 8.73
	78.1	Finchale Abbey	14. 8.73
	58.3	Sunderland Bridge	4. 9.73
	73.5	above effluent	4. 9.73
	78.1	below effluent	4. 9.73
	58.3	Finchale Abbey	4. 9.73
	73.5	Sunderland Bridge	20.11.73
	73.9	above effluent	20.11.73
	73.9	below effluent	20.11.73
	78.1	Finchale Abbey	20.11.73

TABLE 2.5 List of sites in the River Wear at which *Fontinalis antipyretica* was sampled during 1968, 1972 and 1973

stream no.	km	site	date	
0008	44.0	Bishop Auckland (above River Gaunless)	15. 8.68	undivided
	51.1	Willington	15. 8.68	undivided
	70.4	Durham Sands	16. 8.68	undivided
	78.1	Finchale Abbey	13. 8.68	undivided
	80.6	Cocken Bridge	13. 8.68	undivided
	90.0	Lambton Bridge	16. 8.68	undivided
	78.1	Finchale Abbey	7. 5.72	divided
	58.3	Sunderland Bridge	29. 4.73	divided
	73.5	above effluent	29. 4.73	divided
	73.9	below effluent	29. 4 73	divided
	78.1	Finchale Abbey	29. 4.73	divided
	58.3	Sunderland Bridge	14. 8.73	undivided
	73.5	above effluent	14. 8.73	undivided
	73.9	below effluent	14. 8.73	undivided
	78.1	Finchale Abbey	14. 8.73	undivided
	58.3	Sunderland Bridge	20.11.73	undivided
	73.5	above effluent	20.11.73	undivided
	73.9	below effluent	20.11.73	undivided
	78.1	Finchale Abbey	20.11.73	undivided

divided into 30 mm sections from the tip (Table 2.5).

Samples of *Ranunculus penicillatus* var. *calcareus* were collected from three of the four sites in the lower River Wear: above industrial effluent (km 73.5), below industrial effluent (km 73.9) Finchale Abbey (km 78.1). The plant was not collected from Sunderland Bridge (km 58.3) as it did not occur at the site at that time. For comparative purposes, a sample was also collected from the River Tweed at Gala Ford (km 75.5). All samples were divided into root, stem and leaf. All samples were collected on 14 August 1973.

2.5.4 Plant samples, Rookhope Burn 1973

Plants were collected from the river on two occasions in 1973 from the four sites located in Fig. 1.2 and listed in Table 2.6. Many of the algae are transitory in their occurrence and were therefore collected only once. The more permanent vegetation sampled, comprised the alga *Lemanea fluviatilis*, and the bryophytes; *Scapania undulata*, *Drepanocladus fluitans* and *Hygropypnum ochraceum*. The only angiosperm to occur in sufficient quantity to sample was the emergent hydrophyte, *Mimulus guttatus*. The collection sites again consisted of 20 m stretches (2.2.1). The head tributary, North Grain Sike, was sampled because of the wealth of plant material and the presence of *Drepanocladus fluitans* which also occurs in Brandon Pithouse acid streams. Table 2.5 gives the details of the plants collected.

TABLE 2.6 List of plant species sampled from four sites in the Rookhope Burn catchment during 1973

stream no.	km	site	date	algae	date	bryophytes	date	angiosperms
0115	-0.5	North Grain Sike	16.5.73	*Mougeotia* sp.	16.5.73	*Scapania undulata*		
					4.9.73	*Scapania undulata*		
					16.5.73	*Drepanocladus fluitans*		
					4.9.73	*Drepanocladus fluitans*		
0012	-8.5	Upper Rookhope Burn	16.5.73	*Spirogyra* sp.	16.5.73	*Scapania undulata*		
					4.9.73	*Scapania undulata*	4.9.73	*Mimulus guttatus*
					16.5.73	*Hygrohypnum ochraceum*		
					4.9.73	*Hygrohypnum ochraceum*		
0012	-3.9	Lower Rookhope Burn	16.5.73	*Stigeoclonium tenue*	16.5.73	*Hygrohypnum ochraceum*		
					4.9.73	*Hygrohypnum ochraceum*	4.9.73	*Mimulus guttatus*
0012	-0.6	Eastgate	16.5.73	*Lemanea fluviatilis*	16.5.73	*Hygrohypnum ochraceum*	16.5.73	
				Lemanea fluviatilis	4.9.73	*Hygrohypnum ochraceum*	4.9.73	

2.5.5 Plant samples, Brandon Pithouse acid streams, 1973/1974

Samples were taken of the complete range of macrophytic flora, present in both Acid Streams A and B on various occasions during 1973/1974 (Table 2.7). The moss *Drepanocladus fluitans* was also collected at particular sites down the main stream to study the effects of an increasing pH gradient (Table 2.8).

TABLE 2.7 List of plant species sampled from Brandon Pithouse acid streams during 1973/74

stream no.	reach no.	km	site	date	algae	date	bryophytes	date	angiosperms
0127	01	-3.6	stream A (1)	2.8.74	*Euglena mutabilis*	14.6.73	*Drepanocladus fluitans*		
						15.4.74	*Drepanocladus fluitans*		
0125	01	-0.6	stream B (76)	14.6.73	*Hormidium rivulare*	14.6.73	*Drepanocladus fluitans*	2.8.74	*Juncus effusus*
				15.4.74	*Hormidium rivulare*	14.6.73	*Dicranella* sp.		

TABLE 2.8 List of sites on Brandon Pithouse acid streams at which *Drepanocladus fluitans* was sampled on 14 June 1973

stream no.	reach	km	site
0127	01	-3.6	stream A (1)
	03		channel (3)
	05		below reservoir (5)
	07	-2.9	below confluence with stream B (8)
	08		above farm track (9)
	09		bog (10)
	11	-1.6	upper Eshwood (12)
0125	01	-0.6	stream B (7b)

CHAPTER THREE

3. SITE DESCRIPTIONS

3.1 Introduction

Descriptions are given of the main sites in each area of the River Wear system studied.

Details of the taxonomy of the species mentioned are given in 2.4 and the exact geographical locations of the sites are recorded in 2.3. In describing the substratum the sizes have been graded according to the 'Wentworth Scale' (Table 3.1). It has already been mentioned (2.2.1) that 20 m lengths were used for sampling except in the case of Brandon Pithouse acid streams. In this case 10 m 'reaches' (2.3.) were adopted, partly because of its small size and partly to ensure continuity with other work carried out (Hargreaves, 1977).

Relevant features of the four main sites in the lower River Wear are described in 3.2.1 to 3.2.5 and illustrated in Figs 3.1 and 3.2. These diagrams have been compiled from observations at summer low flows. The distribution of the major species is given together with substratum characteristics and a qualitative estimate of current velocity and direction.

The four sites chosen for study in the Rookhope Burn catchment are described in 3.3.

A summary of the relevant sites in Brandon Pithouse acid streams is given in 3.4. Further details of the microflora found in the individual reaches are given by Hargreaves (1977).

TABLE 3.1 The 'Wentworth Scale' of substratum size

		mm
sheet rock		>4096
Boulders	very large	2048 - 4095
	large	1024 - 2047
	medium	512 - 1024
	small	256 - 512
Cobbles	large	128 - 256
	small	64 - 128
Pebbles	very coarse	32 - 64
	coarse	16 - 32
	medium	8 - 16
	fine	4 - 8
	very fine	2 - 4
Sand	very coarse	1 - 2
	coarse	0.5 - 1
	medium	0.25 - 0.5
	fine	0.125 - 0.25
	very fine	0.0625 -0.125
Silt and clay		< 0.0625

Details are included in 2.3 of the sites studied in 1967/68. The location of all the sites sampled in the present study is shown in Fig. 2.1.

3.2 Sites on lower River Wear

3.2.1 Sunderland Bridge (km 58.3)

The 20 m length chosen for study lay just downstream of the Northumbrian Water Authority flow gauging station, located under the bridge. At this point the river flowed through the bridge in deep channels before entering the shallower region of the sampling area. A small effluent entered intermittently from a pipe situated on the south bank adjacent to the bridge. The substratum varied from large sandstone boulders to sand and silt. Fig. 3.1a shows the relation between substratum, flow and flora at low flow.

The predominant macrophytic algal vegetation was *Cladophora glomerata* and *Vaucheria sessilis*, although *Stigeoclonium tenue* and *Ulothrix zonata* occurred in small quantities. *Cladophora* varied considerably in form according to its position in the river. In the slower, deeper parts filaments often exceeded 2 m. However, in the shallower parts the filaments were usually considerably shorter and more branched, looking younger and 'healthier'. Species of encrusting green and blue green algae and mats of diatoms were also present at times.

The most obvious and persistent mosses noted were *Fontinalis antipyretica* and *Eurhynchium riparioides*, although several other species were also evident; some of these have been recorded by Whitton and

Buckmaster (1970) and in more detail by Holmes and Whitton (1977).

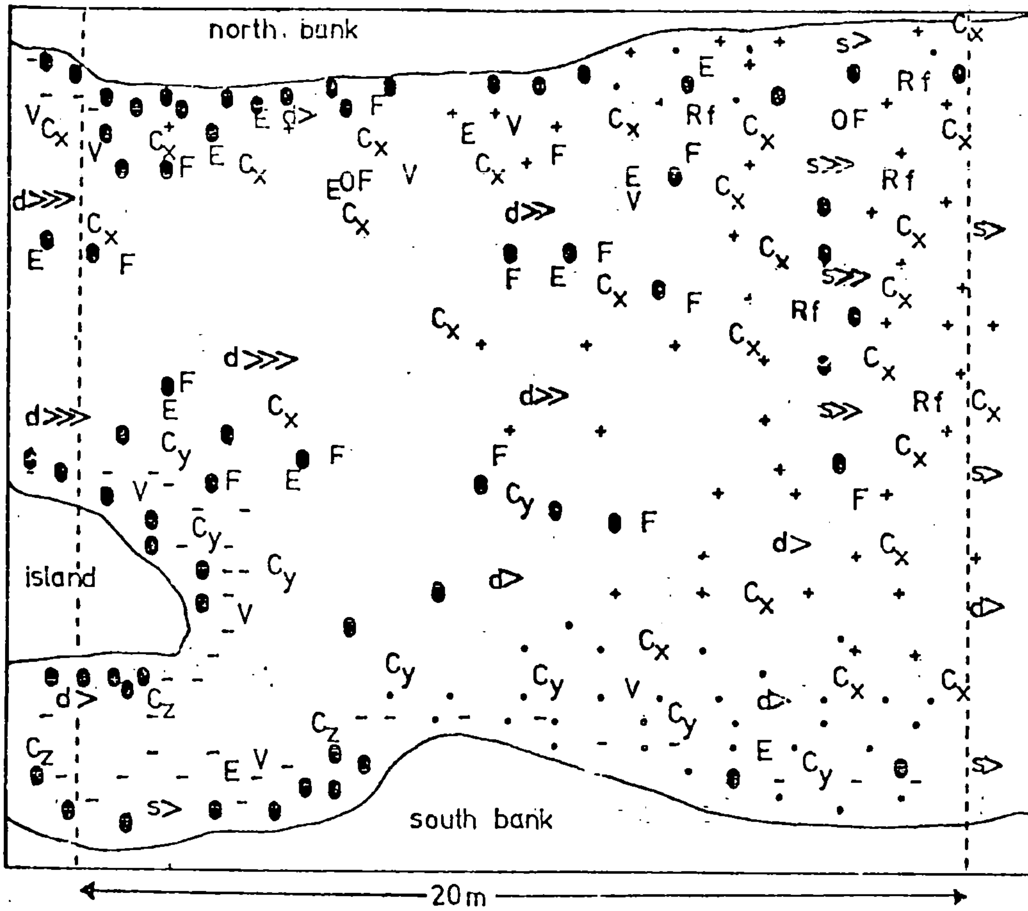
Aquatic angiosperms were found mainly in the deeper parts of the sampling area; these included *Myriophyllum spicatum*, *Elodea canadensis*, *Potamogeton crispus* and *Callitriche stagnalis*. The only angiosperm found in the shallower parts was *Ranunculus fluitans*; small fragments of this became established during 1973.

3.2.2 Above industrial effluent (km 73.5)

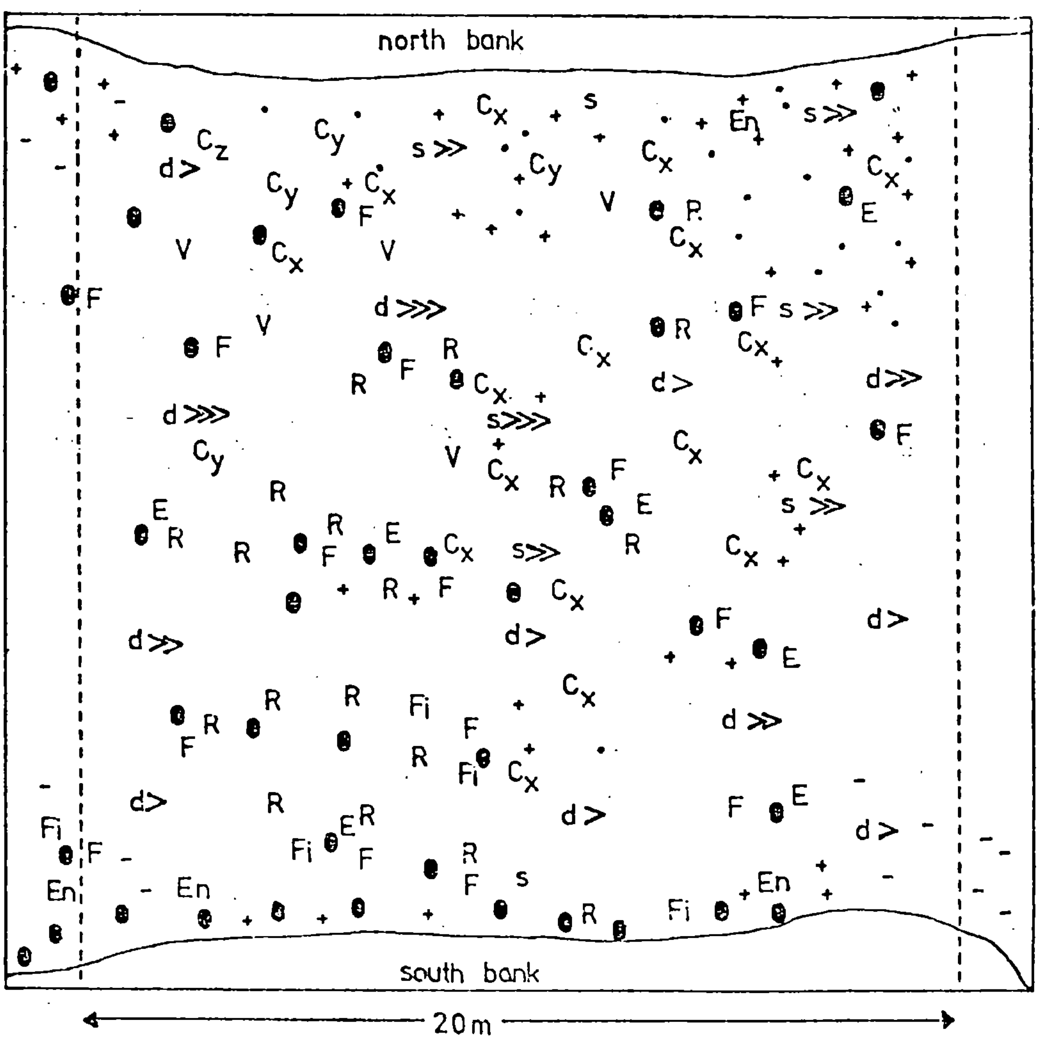
The site lay 100 m upstream of the outfall of the industrial effluent. It was a rather more shaded site than any of the others with heavy tree cover on the banks of the river. The substratum consisted mainly of a mixture of medium and small boulders interspersed by small cobbles and pebbles; on the northern bank the shallower parts became rather sandy.

The algal flora was similar to Sunderland Bridge with obvious macrophytic growths of *Cladophora glomerata* and *Vaucheria sessilis*. During the summer months *Enteromorpha flexuosa* flourished in the still water near the banks.

Two of the mosses recorded at km 58.3 were also present in large quantities; *Fontinalis antipyretica* and *Eurhynchium riparioides* were found together with clumps of *Fissidens crassipes*, appressed to many boulders. However, the most abundant macrophyte present was *Ranunculus penicillatus* var. *calcareus*. A diagrammatic illustration is given in Fig. 3.1b.



(a)



(b)

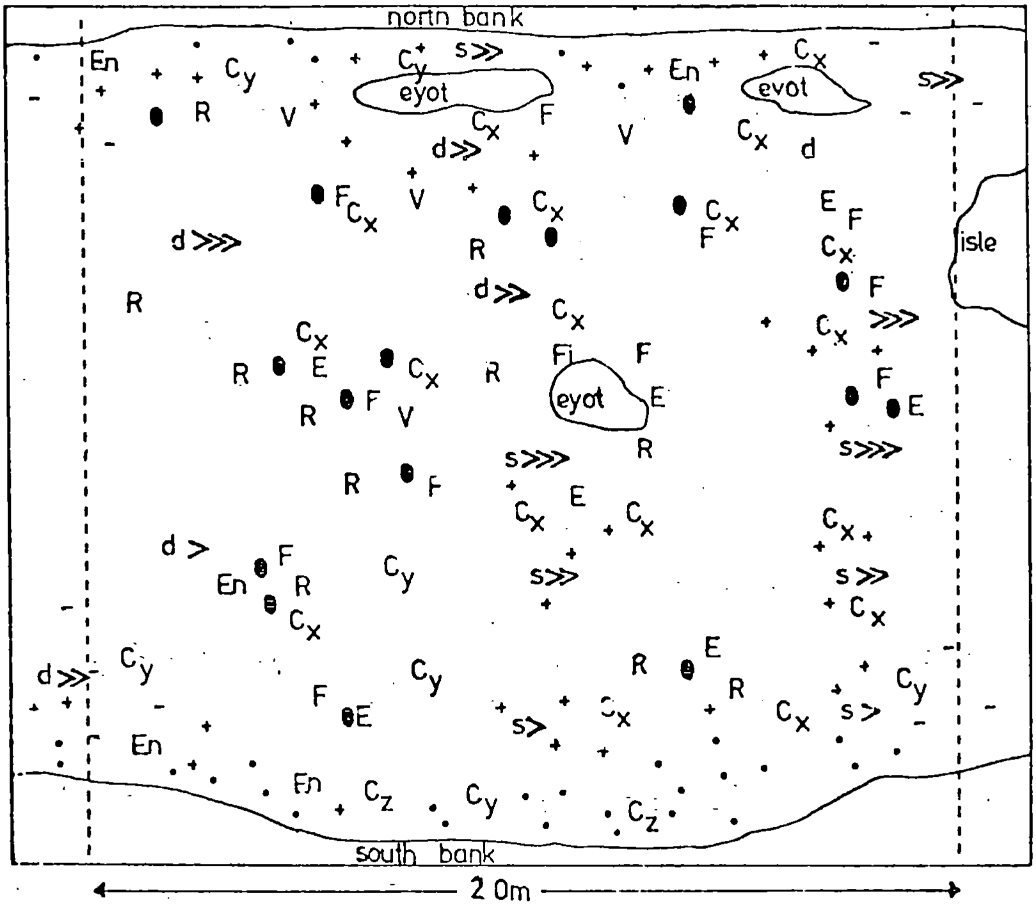
3.2.3 Entry of industrial effluent (km 73.6)

The treated effluent enters the river at km 73.6 by a submerged pipe. At times of exceptionally low flow (< 2 $m^3 s^{-1}$; at Sunderland Bridge gauging station), the pipe became exposed. Occasionally large amounts of foam were present which spread across the river, making the mixing profile obvious. The foam was caused by the presence of polyvinyl alcohols in the effluent. Full mixing appeared to have occurred by km 73.9 where the site downstream of the effluent was located.

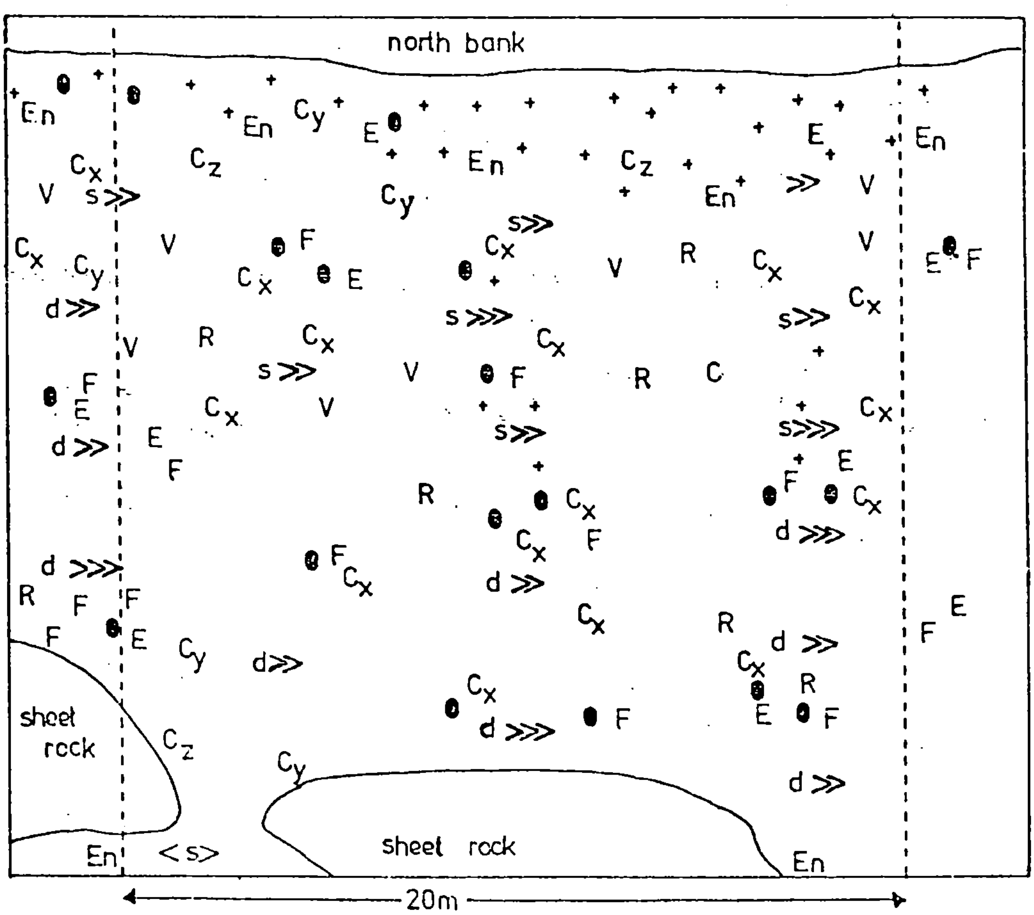
3.2.4 Below industrial effluent (km 73.9)

The site was located in a shallow fast flowing stretch of river with an open aspect. The substratum was much more sandy than either that of km 58.3 or km 73.5 although there were a large number of small and medium sized boulders. The shallowness of the water led to the presence of one or two eyots in midstream. The fastest flowing water was found in the downstream part of the site in a small riffle.

The flora comprised the same species as that upstream of the effluent although *Cladophora glomerata* showed increased cover whilst *Ranunculus penicillatus* var. *calcareus* was reduced. In the slower shallow parts near each bank *Cladophora* tended to have very long filaments (>2 m) but the alga was found at its healthiest towards the middle, in the faster flowing water (Fig. 3.2a).


north bank
eyot
eyot
isle
eyot
south bank
2 0m

(a)


north bank
sheet rock
sheet rock
20m

(b)

3.2.5 Finchale Abbey (km 78.1)

The site was chosen in a deep sandstone cutting, shaded on the south bank by a rock wall and overhanging trees. At low flow large areas of sheet sandstone were exposed towards the south bank leaving shallow cut off pools. The main stream of the river was fast flowing and fairly deep becoming shallower towards the northern side; here the substratum became a mixture of cobbles and pebbles.

The obvious algal flora was similar to the other sites; large areas of the main stream bed were covered by *Cladophora glomerata* and *Vaucheria sessilis*. Whitton and Buckmaster (1970) have recorded the presence of *Oedogonium* sp. (9 μm) and *Lemanea fluviatilis* at this site but neither was present in any quantity during the period of study. A large number of encrusting algae were found, including *Hildenbrandia rivularis*, in the main flow of the river. Just as at other sites below Durham, *Enteromorpha flexuosa* was present in summer towards the banks of the river. During late summer considerable growths of *Melosira varians* became obvious.

A variety of mosses flourished although the bulk of these consisted of *Fontinalis antipyretica*, *Eurhynchium riparioides* and *Fissidens crassipes*. Others recorded in small amounts included *Leptodictyum riparium* and *Grimmia alpicola*.

Apart from *Ranunculus penicillatus* var. *calcareus*, few angiosperms were found in the fast flowing water. However, this plant did not cover the river bed as much as it did at the two sites a few kilometres upstream. Some of the important features are illustrated in Fig. 3.2b.

3.3 Sites on Rookhope Burn

3.3.1 North Grain Sike (- km 0.5)

The site was located on a small tributary close to the headwaters of Rookhope Burn. The substratum consisted mainly of shale and included a small waterfall on which the main vegetation grew. In the very shallow water of the upstream part of the site quantities of *Stigeoclonium tenue* and *Hormidium rivulare* were found, mainly in the early part of the year. During the summer these tended to be replaced by considerable growths of *Mougeotia* sp. This species tended to coat the rock surface.

The bryophytes present were restricted to the face of the waterfall in a thick mat. *Scapania undulata* dominated the vegetation although patches of *Drepanocladus fluitans* were entangled with this.

3.3.2 Upper Rookhope Burn (- km 8.5)

The site was positioned in the upper reaches of the main river, downstream of Groverake mine (- km 8.5). The stream bed consisted mainly of small boulders, cobbles and pebbles. The volume of water passing through the site was considerably greater than that passing through the site at the headwaters. Macrophytic vegetation covered only a very small part of the sampling area. The presence of macrophytic growths of algae depended upon the season and prevailing conditions.

In spring growths of *Ulothrix zonata* were noted together with some *Mougeotia* sp. In summer and early autumn large growths of *Spirogyra* sp. were recorded together with some *Zygnema* sp.

Tufts of *Scapania undulata* were present on the downstream side of the boulders but the growth was less luxuriant than that in North Grain Sike.

The only other bryophyte present was *Hygrohypnum ochraceum*, although its growth was atypical. The moss tended to occur towards the stream bank rather than in the main flow.

Higher plants were restricted to the occurrence of *Mimulus guttatus* in the shallower parts of the site.

3.3.3 Lower Rookhope Burn (- km 3.9)

This site was located downstream of Rookhope Village at - km 3.9, about 300 m below the outfall of a small sewage works. Small boulders covered most of the stream bed. The algal growth was again only present for short periods. Early in the year the whole of the river bed became covered with a thick growth of *Stigeoclonium tenue*. This diminished rapidly in summer and was replaced by less abundant filaments of *Mougeotia* sp. together with some *Hormidium rivulare*.

Among the bryophytes only *Hygrohypnum ochraceum* was found. This covered both submerged and emergent boulders at low flow.

The only angiosperm in the stream at this point was again *Mimulus guttatus*.

3.3.4 Eastgate (Rookhope Burn, - km 0.6)

This site was positioned upstream of the Northumbrian Water Authority flow gauging station at Eastgate, 0.6 km from the confluence with the River Wear. At this point the river flowed very rapidly down sandstone and limestone steps.

Stigeoclonium tenue was found in very small quantities in the slower flowing water especially early in the year. The only other macroscopic alga was *Lemanea fluviatilis* which flourished throughout the summer in the fastest current, firmly attached to the solid substratum. *Hygrohypnum ochraceum* and *Hygroamblystegium fluviatilis* were found towards the banks of the river.

No angiosperms were found at this site.

3.4 Sites on Brandon Pithouse acid streams

3.4.1 Introduction

The two sites of primary importance in accumulation studies are:

the source of Acid Stream A (site 1),

the source of Acid Stream B (site 7b).

Other sites were selected at intervals down the stream to collect data from the increasing pH gradient. In all cases 10 m reaches were used (2.3). A summary of the sites in acid parts of the stream ($pH<4$) is given in Table 3.2.

TABLE 3.2 Summary of site descriptions for Brandon Pithouse acid streams (sites 1 - 12)

stream no.	reach no.	km	site no.	river	substratum	plant species	flow	aspect
0127	01	-3.6	1	stream A	clay	*Euglena mutabilis*, *Drepanocladus fluitans* moss protonema (*D. fluitans*) *Dicranella* sp.	fast	open
	02		2		clay	*Euglena mutabilis*, *Drepanocladus fluitans*, moss protonema (*D. fluitans*) *Dicranella* sp.	fast	open
	03		3		shale and coarse sand	small patches of *Euglena mutabilis* no mosses	medium	shaded
	04		4		silt and organic debris	extensive mats of *Drepanocladus fluitans*	almost still	open
	05		5		shale and silt	mats of *Drepanocladus fluitans*, occasional *Euglena mutabilis*	fast	open
	06		6		shale and silt	small stands of *Drepanocladus fluitans* occasional *Euglena mutabilis*	fast	open
	07		8		friable precipitate (Fe hydroxides)	some coated strands of *Drepanocladus fluitans*	fast	shaded
	08		9		clay and precipitates	small mats of *Drepanocladus fluitans*	fast	shaded
	09		10		organic material	very large quantities of *Drepanocladus fluitans*	slow	part shaded
	10		11		clay	stands of *Drepanocladus fluitans*	medium	open
	11	-1.6	12		clay and silt	small stands of *Drepanocladus fluitans*	medium	shaded
0125	01	-0.6	7b	stream B	clay & silt	*Hormidium rivulare*, *Drepanocladus fluitans*, *Dicranella* sp. *Juncus effusus*	slow/ still	open
	02		7		clay and silt	small amounts of *Drepanocladus fluitans*	medium	open

3.4.2 Source of Acid Stream A (0115.01)

Measurement of the stream at its source showed that it was 20 to 50 mm deep and 300 to 500 mm wide. Mats of *Euglena mutabilis* adhered closely to the clay substratum and were always fully submerged. *Drepanocladus fluitans* was found in both protonemal and adult form, in the main flow. Some *Dicranella* sp. occurred in the damp splash zone of the stream banks. The discharge of the stream remained consistently in the region of 0.3 l s^{-1} (1.3.5).

3.4.3 Source of Acid Stream B (0125.01)

This site comprised a series of seepages into slow flowing water, 500 mm deep and about 1 m across. *Hormidium rivulare* was abundant in the deep water. *Drepanocladus fluitans* and *Dicranella* sp. flourished on the banks in and around the seepages. Stands of *Juncus effusus* were found in the vicinity, many of which were partially submerged, growing in the acid water.

CHAPTER FOUR

4. WATER CHEMISTRY

4.1 River Wear system

4.1.1 Introduction

The complete results of the water chemistry of the River Wear system are presented in Appendix A.1 (Tables A.1a to A.1i). Table A.1a shows the variation found between four replicate samples; these were taken on a single occasion from two sites in the lower River Wear. The coefficient of variation for the majority of elements analysed is 5% or less. However, Mn, Fe, Al and Pb all have large coefficients of variation (20 to 30%) on this occasion. Other samples show coefficients nearer 10%. Variation in Cd results could not be calculated as the concentrations were lower than the detection limit (0.0001 mg l^{-1} Cd). Other analyses for this element indicate a variation, in the region of 10% at low concentration. These coefficients increase markedly as the detection limit is approached. At the higher concentrations encountered in many sites the variations are smaller (5% or less). In Rookhope Burn, for example, the maximum coefficients of variation recorded were 5% for Zn and 1.1% for Pb. Analysis of cations in acid stream water was found to be exceptionally reproducible (the coefficients of variation rarely exceeded 1%).

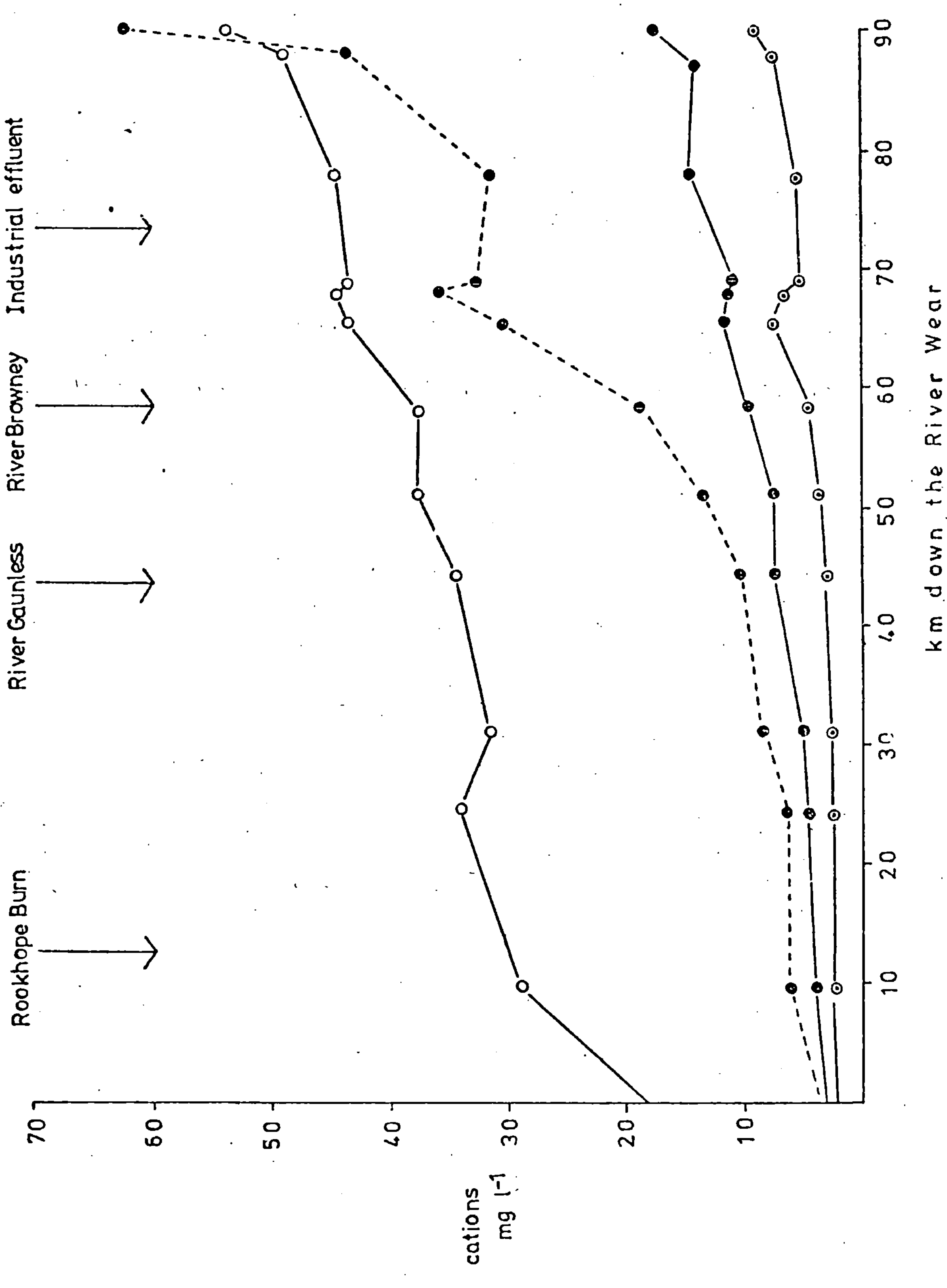
Tables A.1b to A.1f show results based

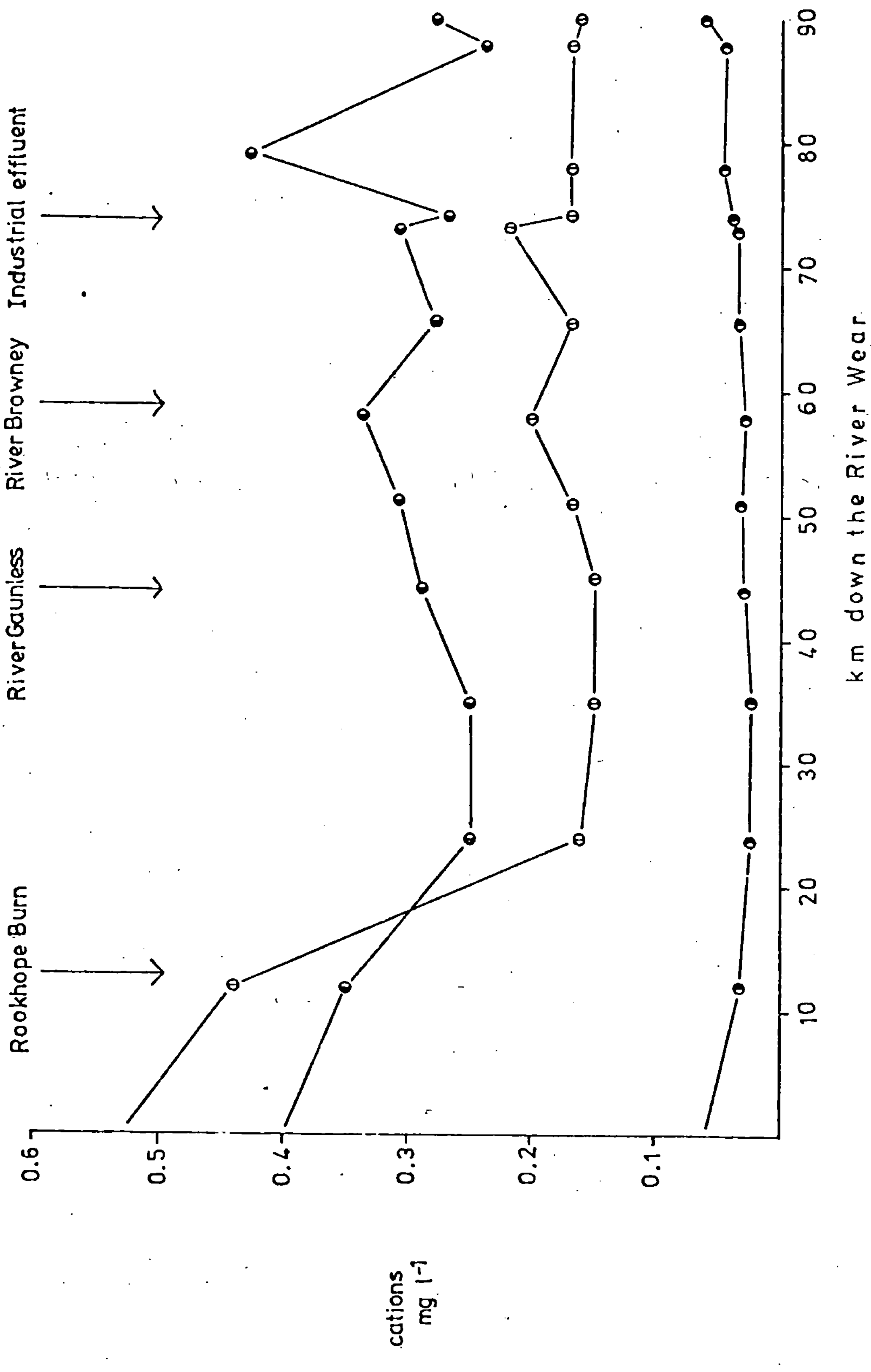
on single analyses except where otherwise stated. It should also be pointed out that most of the results presented were achieved after refinement of techniques (2.1.2). Similarly, a change in analytical method for NO_3-N allowed the detection limit of this anion to be lowered.

4.1.2 Seasonal surveys of River Wear and selected tributaries

The means calculated from the data for four seasonal surveys are presented in Figs 4.1 to 4.4; the primary water chemistry data is found in Tables A.1f to A.1i. These surveys covered the period from March 1973 to January 1974 and were taken at medium to low flows. All major cations increase steadily from the source to the tidal limit of the River Wear. An increase in Mg and Ca, the main hardness elements, occurs with the entry of the River Gaunless (km 44.1). The entry of the River Browney at km 58.4 causes noticeable increases in K, Mg, Ca and a marked increase in Na concentration; the latter continues to rise rapidly in the reaches below Durham. Fluctuations in Na, Mg and Ca occur at the entry of the industrial effluent (km 73.6).

Fig. 4.3 shows the changes in heavy metal content in the fresh-water stretch of the river; the pattern contrasts markedly with Fig. 4.1. The overall trend shown for the elements Zn, Cu, Pb and Cd is a decrease from the upper to the middle reaches of the River Wear. The entry of Rookhope Burn (km 12.6) seems to cause some increase in Pb concentration but does not increase that of Zn, although


Rookhope Burn
River Gaunless
River Browney
Industrial effluent
cations
mg l-1
70
60
50
40
30
20
10
10
20
30
40
50
60
70
80
90
km down the River Wear


Rookhope Burn
River Gaunless
River Browney
Industrial effluent
cations
mg l-1
0.6
0.5
0.4
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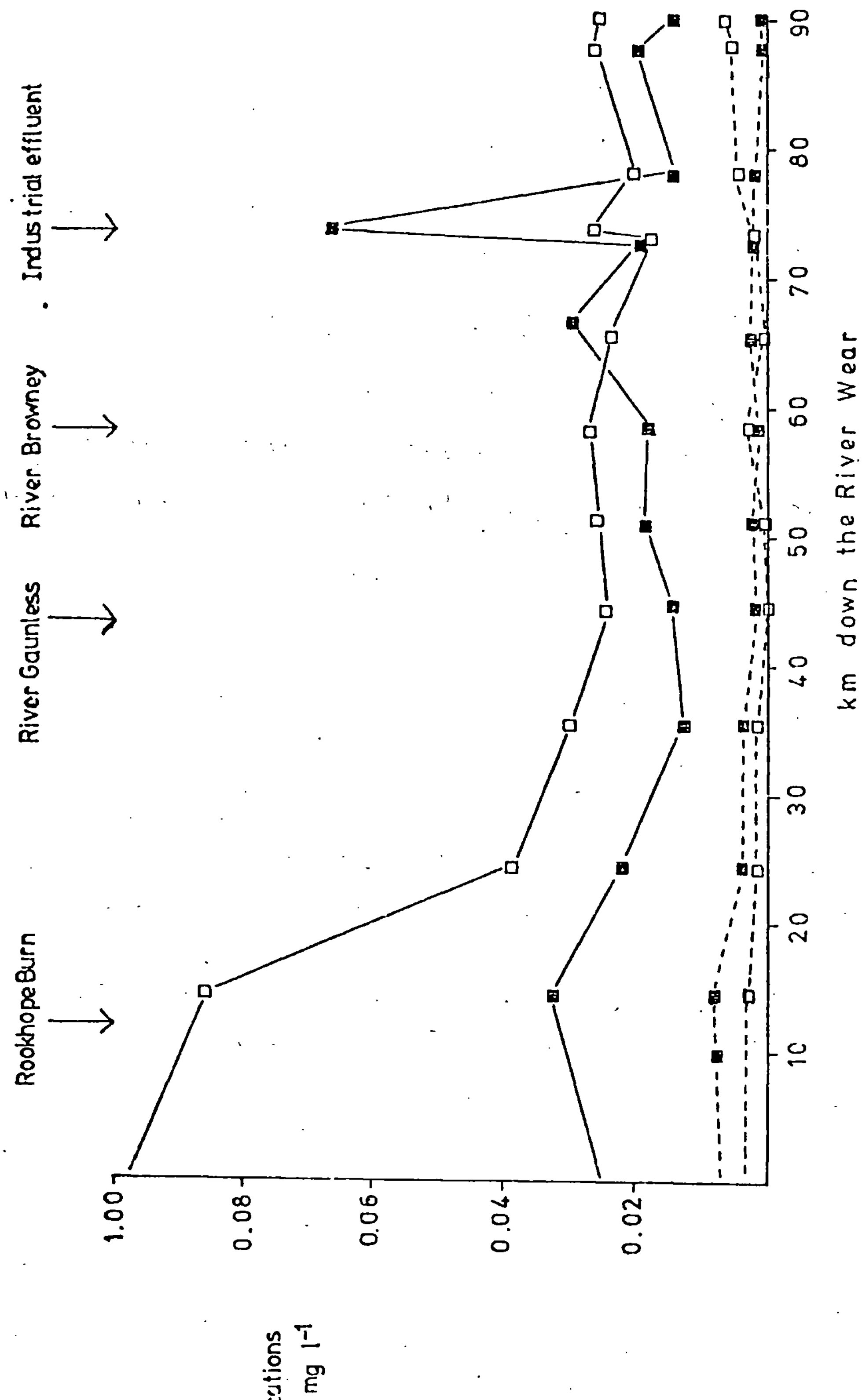
km down the River Wear


Rookhope Burn
River Gaunless
River Browney
Industrial effluent
cations
mg l-1
1.00
0.08
0.06
0.04
0.02
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20
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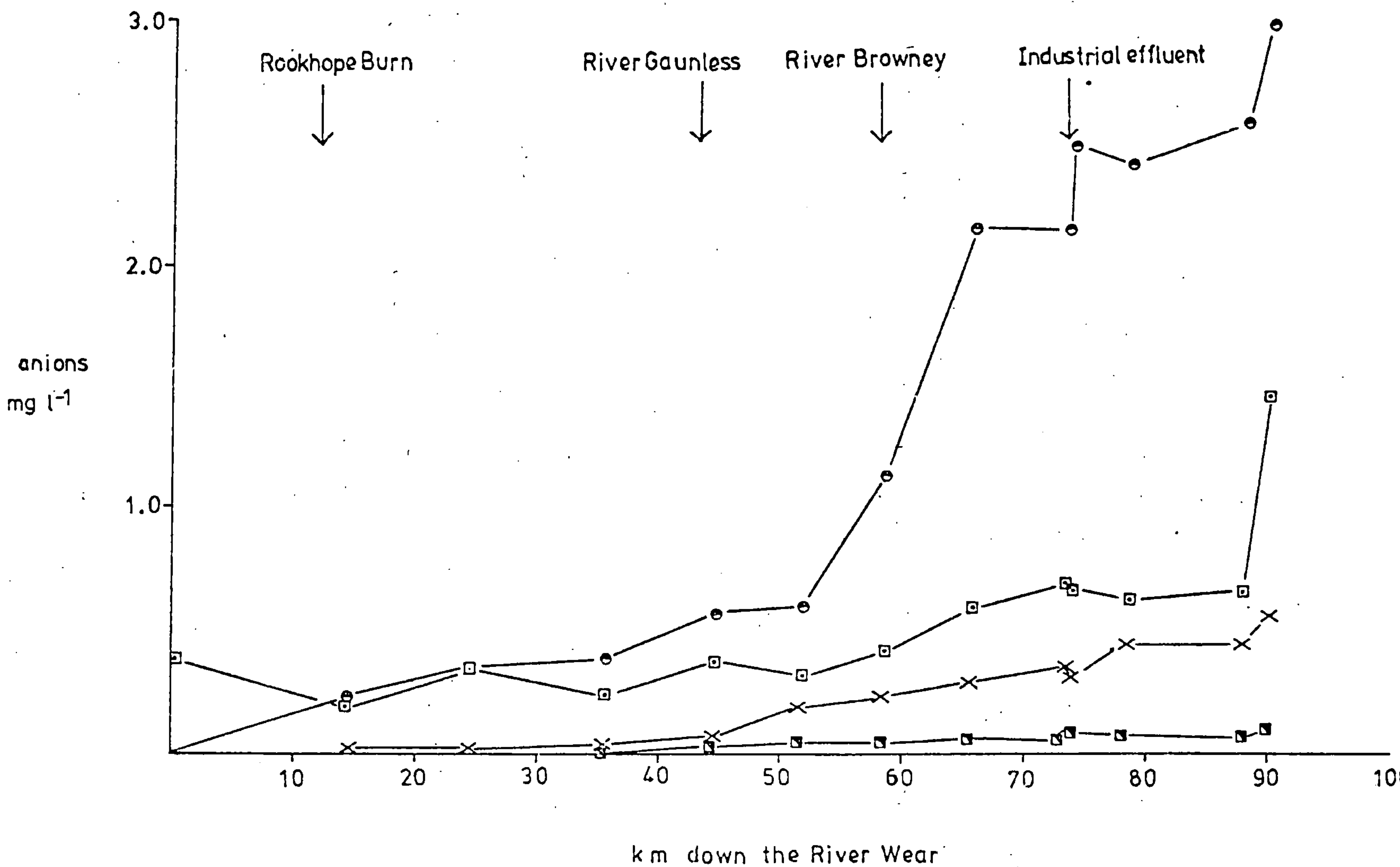
90
km down the River Wear



Rookhope Burn
River Gaunless
River Browney
Industrial effluent
3.0
2.0
1.0
anions
mg l-1
10
20
30
40
50
60
70
80
90
100
km down the River Wear

the concentration of this metal remains relatively high. Concentrations of Cu and Cd are apparently unaffected by the entry of this tributary. There is a steady decrease in all these elements from Stanhope (km 14.6) to Bishop Auckland below the River Gaunless (km 44.3). However Pb rises marginally between Witton-le-Wear and Bishop Auckland. Zn, Cu and Cd remain at a steady concentration as far as km 73.5 but Pb concentrations fluctuate between km 44.3 and km 73.5.

Marked increases occur in Zn and Pb concentrations at the site below the industrial effluent (km 73.9). The effect of these increases is markedly reduced in the reaches before Finchale Abbey (km 78.1) where concentrations return to the same level as those at km 73.5. Further data concerning the heavy metal concentrations at the sites in the region of the industrial effluent are presented in 4.2.4. The concentrations of all these elements fluctuate less dramatically as far as the tidal limit at km 90.0.

Fig. 4.2 shows the variation in concentration of Mn, Fe and Al. All three elements have high concentrations in the upper stretches but fall sharply downstream from Weardale. The concentration of Mn remains remarkably steady throughout the middle and lower parts of the river but increases towards the tidal limit. Concentrations of Fe and Al exhibit a similar pattern throughout the fresh water part of the river; there is a gradual dilution downstream followed by fluctuations in the lower stretches.

The concentrations of anionic nutrients in the main river are shown in Fig. 4.4. The pattern shown by these elements is remarkably similar to that of the major cations; there is a steady increase in nutrients from source to tidal limit. NO_3-N concentrations rise rapidly in the middle and lower stretches of the river. Most of these increases coincide with the centres of population and the consequent sewage outfalls. The River Browney also increases the nutrient concentrations in the lower River Wear. The unusually high NH_3-N concentrations shown in the upper part of the river are suspect. It cannot be ruled out that these data are an artefact caused by analytical error; the limitations of the method are mentioned in 2.1.3.

4.2 Lower stretches of River Wear

4.2.1 Introduction

The lower reaches are those fresh water parts of the River Wear from Sunderland Bridge (km 58.3) to Lambton Bridge (km 90.0).

Data showing the relation of nutrient and heavy metal concentrations to discharge are given in 4.2.2. There are a number of other factors affecting the river in this region. The only major tributary entering the Wear is the River Browney; some of the effects of this tributary have already been pointed out in connection with the seasonal surveys (4.1.2). There are many other smaller influences on the chemistry of the river, for example, the entry of Old Durham Beck (km 66.7), the outfall from Durham Sewage Works (km 71.0), possible effects of run-off from the A1(M).

and A690 trunk roads (km 72 to 74). Some effects of the effluent which enters at km 72.6 have already been noted in 4.1.2. Data specifically concerned with the effects of this are presented in a later section (4.2.4). Influences on the chemistry of the lowest section of the river, (km 76.9 to km 90.0) include: some pumped mine water and the entry of two small but highly polluted tributaries, Lumley Park Burn (km 88.1) and Chester Burn (km 88.6).

4.2.2 Relation of water chemistry to discharge

Scatter diagrams showing discharge effects on concentration of two major cations (K, Mg) and two heavy metals (Zn, Pb) at the Northumbrian Water Authority gauging station (km 58.3) are presented in Fig. 4.5. These data have been abstracted from Tables A.1c and A.1d covering the period March 1972 to January 1974.

Both the major cations, Mg in particular, show clear negative trends which indicate a dilution effect; the greater the flow the lower the concentration. However, this relationship is not necessarily linear. Other major cations Na, Ca and two nutrient elements N and P show very similar scatter patterns to Mg.

The scatter diagrams for the two heavy metals show no clear trend. The highest flows are associated with both highest and lowest concentrations of Zn and Pb. A careful study of all the flow data shows that the highest concentrations of Zn and Pb occurred in the first high flow after a long spell of low flow (Northumbrian

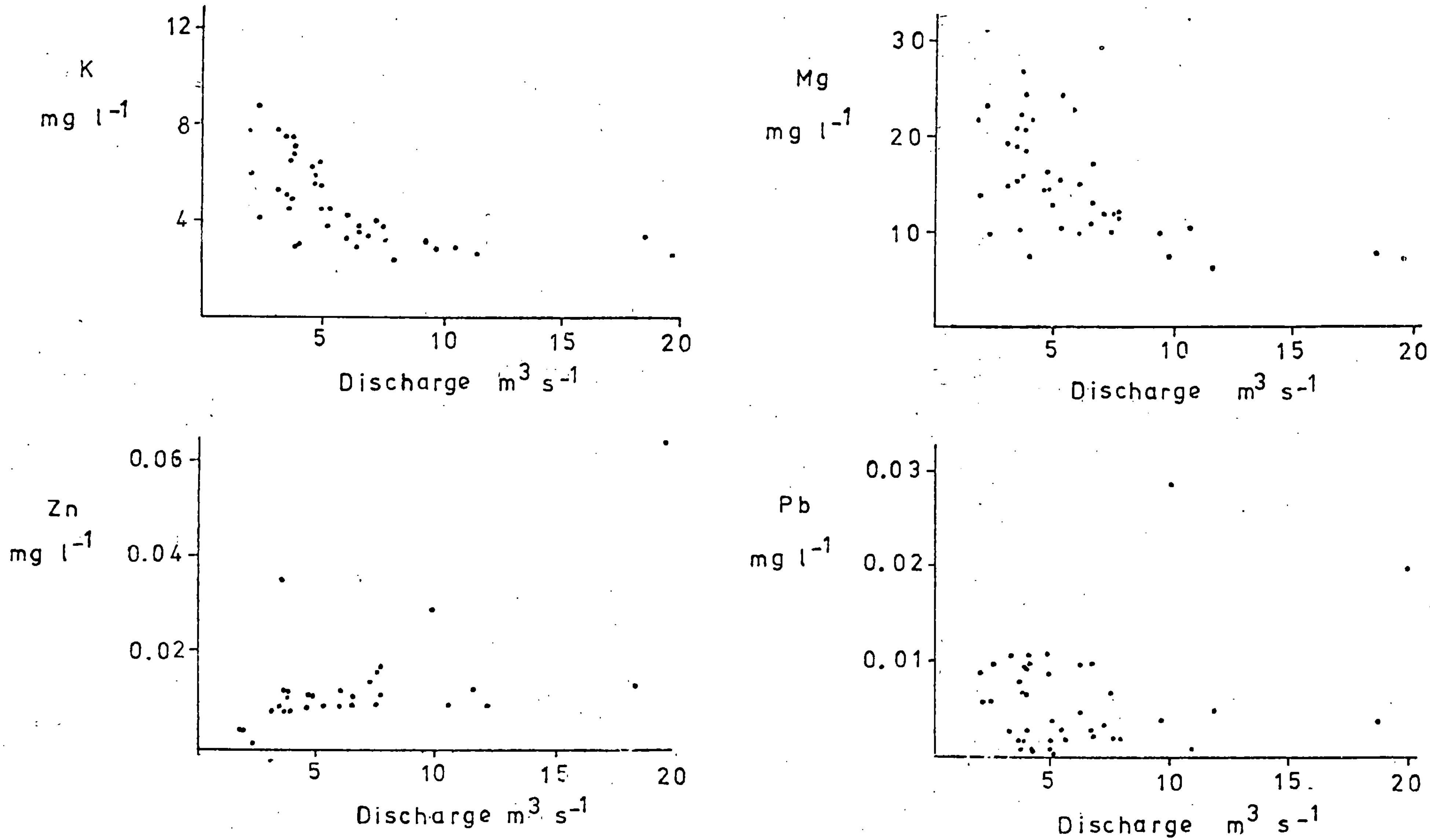


Fig. 4.5 Scatter diagrams showing concentrations of selected metals against discharge at Sunderland Bridge (km 58.3).

Water Authority flow data 1972 to 1974). Some of the very low concentrations of these elements encountered at high flows occurred towards the end of a sustained period of high flows.

In general, it appears that heavy metal concentrations in the lower reaches of the River Wear are not directly related to discharge. None of the other trace elements analysed (Cu, Mn, Fe, Al) showed any particular trend; however, the highest values seem to be associated with the lowest flows. A study of the data of Sunderland and South Shields Water Co. for Finchale Abbey (km 78.1), over the period 1964 to 1970, showed no clear relationship for either Mn or Fe with flow (taken at Northumbrian Water Authority gauging station, km 58.3). Nevertheless, these data indicated that the highest concentrations of these elements occurred at the highest flows e.g. Mn 0.50 mg l^{-1}, Fe 2.28 mg l^{-1} on 5 November 1967 (flow at Sunderland Bridge gauging station, 257.6 $m^3\ s^{-1}$). It must be made clear that the highest flows considered during the period of study, 1972 to 1974, are in the region of 20 $m^3\ s^{-1}$ and flood conditions of the order mentioned above did not occur during that period.

4.2.3 Influence of River Browney

Chemical data are presented in Tables A.1b and A.1c for various sites in the lower River Wear. The period covered by the studies is March 1972 to November 1973. Data in A.1b are from two important sites: Sunderland Bridge (km 58.3) and Finchale Abbey (km 78.1).

The parameters determined give an idea of the general chemistry of this part of the river. The water is fairly hard (from Mg and Ca values) and alkaline (pH 7.9 to 8.3). Conductivity, major cations, nutrient elements and chloride are consistently higher at the downstream site. The average levels of Zn and Pb are slightly higher at Sunderland Bridge (km 58.3). The maximum concentrations of Zn and Pb recorded at either site in 1972 were Zn, 0.018 mg l^{-1} and Pb, 0.012 mg l^{-1}. Data for Cd were not always collected and when analysed only occasionally exceeded the detection limit (0.0001 mg l^{-1}).

The differences between the two sites are summarised in Fig. 4.6, abstracted from Table A.1b. The importance of the River Browney has already been noted in 4.1.2 and 4.2.3. Table 4.1 shows the effects of the River Browney on the chemistry of the main river by taking the mean of the four seasonal surveys, at the one site above and the two sites below the entry of the tributary. There is a marked increase in conductivity of the River Wear below the point of entry. Much of this can be attributed to the considerable increase in Na salts. Noticeable increases in Mg and Ca have already been mentioned in 4.1.2. The mean concentrations of heavy metals indicate low concentrations of these in the River Browney, with little effect on the River Wear. In the case of Pb however, there is a major increase in the main river between km 58.3 and km 65.5; there are not sufficient data for these reaches to attribute the increase to any particular source; the mean concentration of Pb in

TABLE 4.1 Effect of River Browney on chemistry of River Wear. Mean concentrations in mg l^{-1}; n = 4

stream no.	km	site	cond. µmhos	Na	Mg	Ca	Zn	Mn	Pb	PO_4-P
0008	58.3	Sunderland Bridge	295	16.5	9.0	37.9	0.027	0.027	0.016	0.244
0014	-6.1	River Browney	502	44.3	19.2	49.5	0.009	0.039	0.006	0.522
0008	65.5	Shincliffe Bridge	440	30.8	12.9	44.2	0.024	0.042	0.031	0.323
0008	78.1	Finchale Abbey	440	33.7	14.1	45.6	0.021	0.033	0.015	0.335

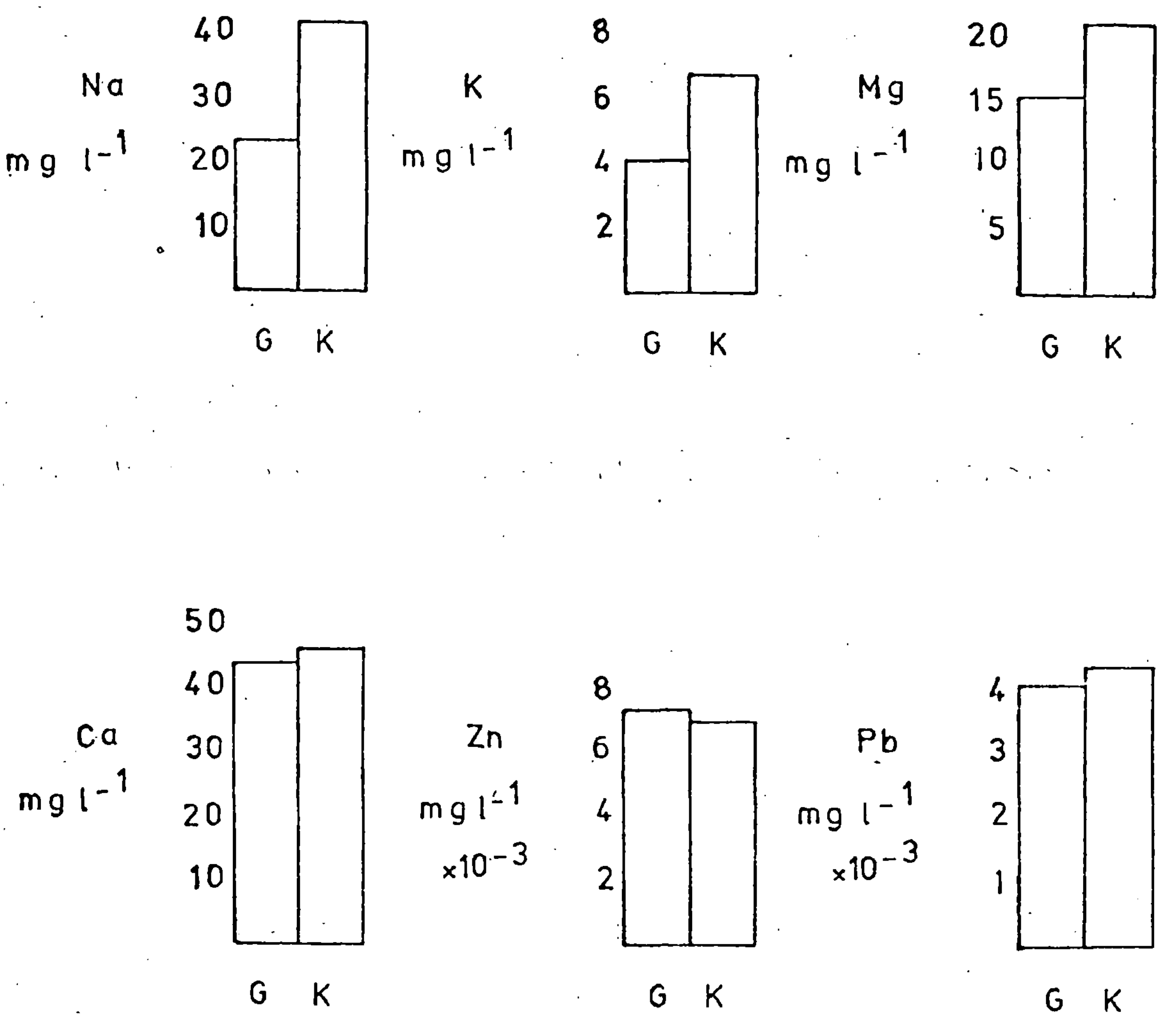


Fig. 4.6 Concentration of cations at Sunderland Bridge (km 58.3) and Finchale Abbey (km 78.1). Mean values in 1972 n ≐ 27.

G Sunderland Bridge K Finchale Abbey

the River Browney however, is very low: 0.006 mg l^{-1}. Anomalous data have also been recorded for other metals e.g. Zn, Cu and Al in the lower River Wear, River Browney and its catchment. At sites below the entry of the River Browney for example, at km 73.5 concentrations of Zn, 0.139 mg l^{-1}, Cu, 0.043 mg l^{-1} and Al, 1.10 mg l^{-1} were recorded on 31 May 1973 (Table A.1c). The following high concentrations of the same three elements have previously been recorded in the River Deerness, a tributary of the River Browney: Zn, 1.07 mg l^{-1}; Cu, 0.40 mg l^{-1}; Al, 0.20 mg l^{-1} (4 September 1972). It is therefore possible that occasional high concentrations of these elements originate from a source in this part of the catchment. anomalous chemical results make the identification of point sources of pollution difficult.

The River Browney undoubtedly has a marked effect on the nutrient concentrations in the River Wear; Table 4.1 shows an increase of more than 30% in PO_4-P concentration. All reaches downstream of the entry point of the River Browney are high in forms of dissolved N.

During the summer low flow period of 1973 the PO_4-P concentrations in the lower reaches remained above 0.4 mg l^{-1} for most of this time. By comparison data from Sunderland and South Shields Water Co. for the period 1960 to 1970 show PO_4-P reaching a maximum of 0.53 mg l^{-1} on two occasions (18 June 1962 and 10 April 1970) but rarely exceeding 0.4 mg l^{-1} at any other time.

4.2.4 Influence of industrial effluent

The chemical data obtained for the region of the industrial effluent are presented in Table A.1c. Table 4.2 shows the mean concentrations of selected elements at the four sites: kms 58.3, 75.5, 75.9 and 78.1 for the period January to November 1973. The anomalous results for Zn and Cu (31 May 1973) referred to in 4.2.3 have been omitted for the purposes of calculating the mean values. These figures are therefore the result of either eleven or twelve analyses.

It can be seen that the two major cations K and Mg are higher at the three sites below Durham and remain remarkably constant at these sites. This reflects the differences in nutrient status, generally, between Sunderland Bridge and the other sites. The sites above and below the effluent and at Finchale Abbey were closely comparable in nutrient terms. Table 4.2 also shows the mean values for three heavy metals Zn, Cu and Pb, one of which, Cu, is known not to occur in significant quantities in the industrial effluent; and therefore acts as a reference for the other heavy metals. The pattern at the four sites for these elements is very different from the major cations. Sunderland Bridge shows marginally higher values of Zn and Pb, possibly because it is far enough upstream to be influenced by the higher concentrations of these elements found in the upper stretches.

The most significant increases occur at the site downstream of the industrial effluent. Zn increases by 30% and Pb by 25%. The metal Cu (not present

TABLE 4.2 Mean concentrations of selected cations at sites in the lower River Wear, 1973. Concentrations in mg l^{-1}; n = 12.

stream no.	km	site	K	Mg	Zn	Pb	Cu
0008	58.3	Sunderland Bridge	5.35	14.30	0.014	0.009	0.003
0008	75.5	above effluent	6.94	17.12	0.013	0.009	0.003
0008	75.9	below effluent	6.88	17.17	0.017	0.012	0.003
0008	82.9	Finchale Abbey	6.90	17.43	0.012	0.008	0.003

in the effluent) is remarkably constant at all four sites. A few kilometres downstream at Finchale Abbey the mean values for Zn and Pb have returned to the level found upstream of the effluent as mentioned in 4.1.2. The importance of the water chemistry at these four sites in relation to the accumulation of heavy metals by plants is discussed in 5.2.3.

Results for the sites above and below the industrial effluent in the Winter 1974 survey (Table A.1i) are exceptionally high. Zn is given at a concentration of 0.038 mg l^{-1} above and 0.060 mg l^{-1} below the effluent; and Pb at 0.040 mg l^{-1} above and 0.230 mg l^{-1} below the effluent. Such high results are either erroneous or caused by a flush of metals in the river.

The only other heavy metal studied was Cd. This was not often recorded above its detection limit at these sites (0.0001 mg l^{-1}). On a single occasion results a factor of ten, higher than normal, were recorded at all four sites (30 March 1973; see Table A.1c).

4.3 Rookhope Burn

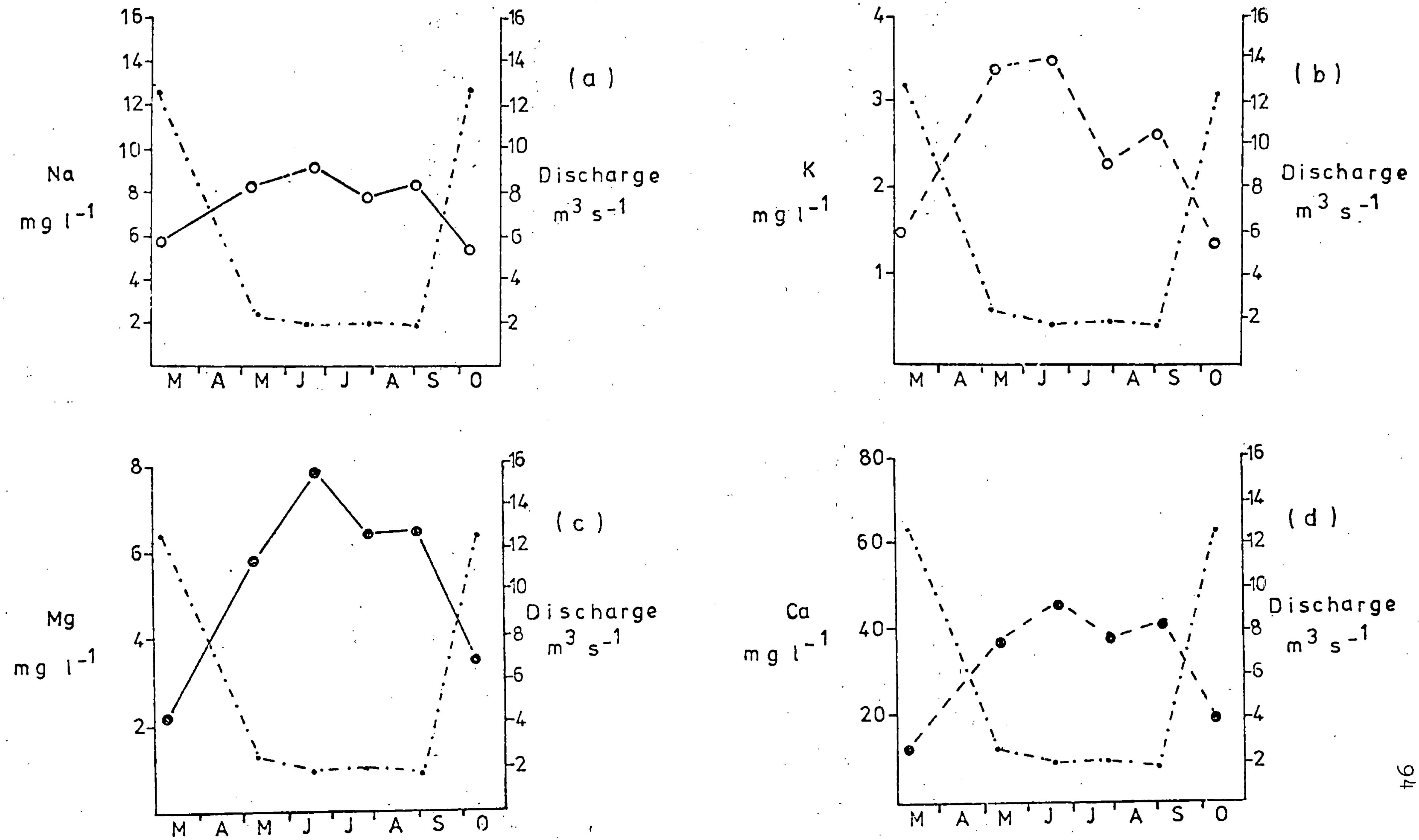
4.3.1 Introduction

The results of six surveys of Rookhope Burn between March and October 1973 are presented in Table A.1b. The water chemistry varies considerably from the headwaters to Eastgate. This reflects the changes in drainage noted in 1.3.4. Throughout its length small streams enter, some of which significantly affect the chemistry, as does run off from the spoil heaps associated with the mining in the area (1.3.4.).

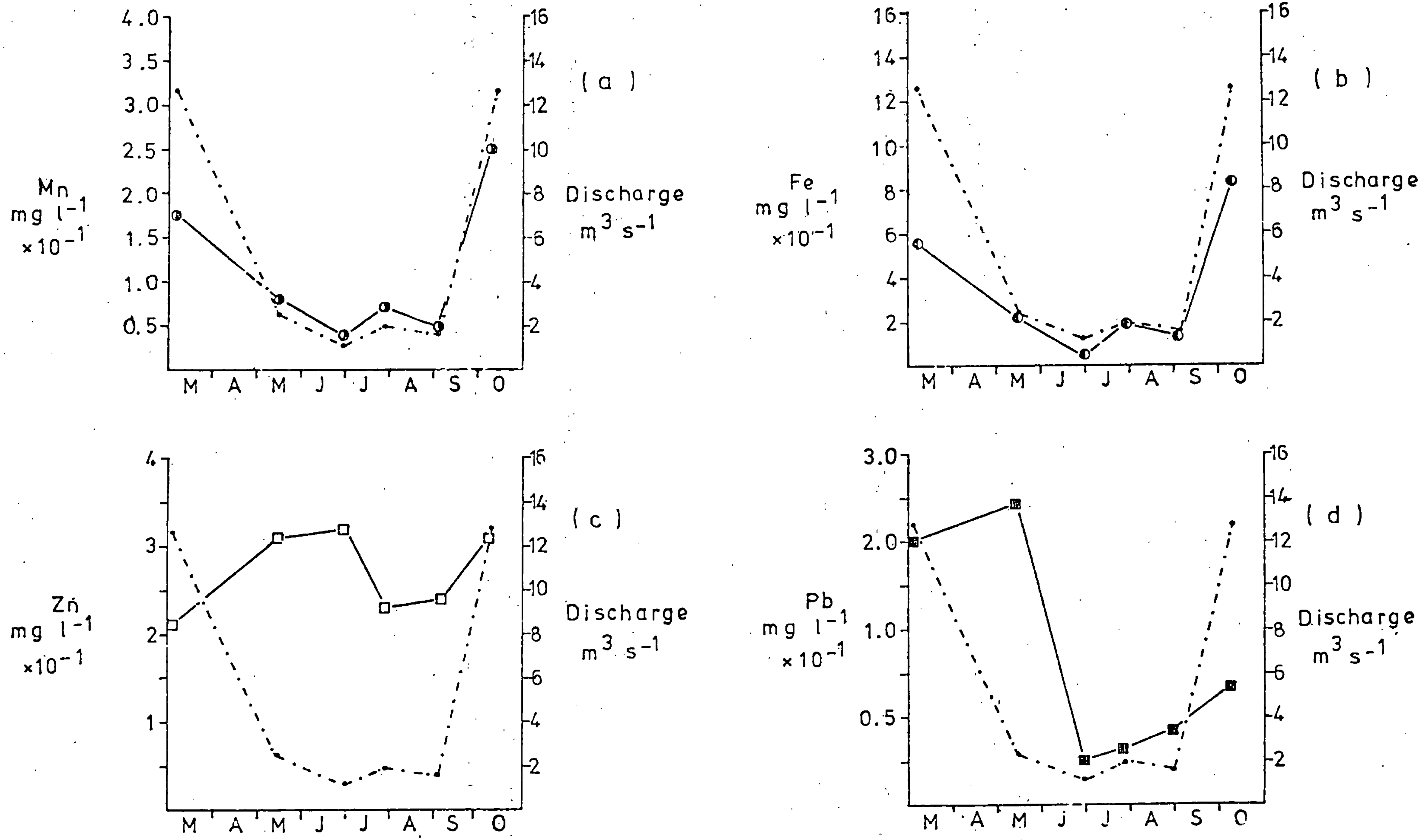
The waters of North Grain Sike are soft and acid, draining almost entirely peat bog land. The head waters and upper reaches are also subject to wash out from many disused lead mines and their waste. These relics of the lead mining era can influence the heavy metal content of the water. Mining still continues by the riverside as illustrated by the presence of two working mines upstream of Rookhope Village: Groverake (- km 11.0) and Red Burn mine (- km 6.1). A flourspar crushing plant is sited by the river near Rookhope Village and a small sewage works is found downstream (- km 4.2). Both of these almost certainly affect the chemistry of the river.

4.3.2 Relation of water chemistry to discharge

The concentrations of selected elements and discharge at Eastgate over the period March to October 1973 are shown in Figs 4.7 and 4.8. The results for Na, K, Mg and Ca all show increased concentration during the summer low flow period (Figs 4.7a,b,c,d). The concentration of all four elements are low at the spring and autumn high flows. This pattern indicates a strong negative relation with discharge similar to that found in the main river at Sunderland Bridge (km 58.3; 4.2.2).
The concentrations of Mn and Fe on the other hand, change positively with discharge (Figs 4.8a and b). This indicates a wash out of these elements (together with Al) from the moorland. These elements are known to be associated with suspended material, notably clay particles. This positive relation with discharge is not seen in the



(a)
Na
mg l⁻¹
Discharge
m³ s⁻¹
16
14
12
10
8
6
4
2
M A M J J A S O
(b)
K
mg l⁻¹
Discharge
m³ s⁻¹
4
3
2
1
(c)
Mg
mg l⁻¹
Discharge
m³ s⁻¹
8
6
4
2
(d)
Ca
mg l⁻¹
Discharge
m³ s⁻¹
80
60
40
20



Mn
mg l-1
×10-1
Discharge
m3 s-1
(a)
Fe
mg l-1
×10-1
Discharge
m3 s-1
(b)
Zn
mg l-1
×10-1
Discharge
m3 s-1
(c)
Pb
mg l-1
×10-1
Discharge
m3 s-1
(d)
M A M J J A S O

main river at km 58.3 presumably because it is well away from the influence of moorland water. Figs 4.8c and d shows that Zn and Pb do not have any clear relation to discharge.

4.3.3 Surveys of Rookhope Burn

The mean changes in concentration of selected elements from the headwaters of Rookhope Burn to Eastgate are shown in Table 4.3. K and Mg are seen to increase rapidly on passing downstream; in the lower reaches the concentrations of these elements level out. Other macro-elements Na, Ca and also pH show similar increases in the upper part of the river (see A.1d). The concentrations of Zn, Pb and Cd are highest at the site downstream of the village (- km 3.9), where much of the mining activity has been and still is centred. The lower reaches are fed by many small streams few of which show high concentrations of heavy metals. These streams therefore tend to have a diluting effect on the concentrations in the main river. In the upper reaches of the stream the only anionic nutrient present in measureable quantities is NH_3-N; the concentrations of this form of N decreases down the stream. There are notable increases in PO_4-P, NO_2-N at the site below Rookhope Village (- km 3.9). This site is influenced by a sewage outfall at - km 4.2. There is a reduction in the concentration of nutrients at Eastgate presumably caused by the diluting influence of numerous nutrient-poor streams.

TABLE 4.3 Mean concentrations of selected cations at sites in Rookhope Burn catchment. Concentrations in mg l^{-1}; n = 6.

stream no.	km	site	K	Mg	Zn	Cu	Pb	Cd
0115	-0.5	North Grain Sike	0.9	1.3	0.834	0.012	0.018	0.0012
0012	-8.5	Upper Rookhope Burn	1.58	3.4	0.090	0.010	0.050	0.0011
0012	-3.9	Lower Rookhope Burn	2.53	5.4	0.411	0.014	0.987	0.0097
0012	-0.6	Eastgate	2.45	5.4	0.270	0.010	0.082	0.0011

4.4 Brandon Pithouse acid streams

4.4.1 Introduction

The chemistry of Brandon Pithouse stream is remarkable because of the exceptionally low pH. Chemical data are presented from the source to the junction with the River Deerness in Table A.1e. These were obtained from the mean of surveys between July 1972 and August 1974.

The first section of Acid Stream A has a pH of 2.6. The subsidiary Stream B which seeps from the base of the coal tip has a pH of 2.8. The source of acidity is thought to be a combination of chemical and bacterial oxidations of Iron pyrites (FeS), resulting in the production of mainly sulphuric acid (H_2SO_4) (Hargreaves, 1977).

Although the discharge of the stream is very small compared to other study areas the significance of research lies in the low pH which causes high concentrations of heavy metals including Zn, Cu, Co and Ni. The pH increases below the confluence of Streams A and B, giving rise to a gradient of increasing pH and decreasing heavy metal content.

4.4.2 Chemical gradient

The gradient is illustrated by changes in pH from 2.6 at the source of Stream A to 7.2 at km -0.1 from the junction with the River Deerness. As a result of this increase in pH the mean conductivity decreases from 1870 μmhos to 616 μmhos.

The pH of stream A remains constant for the first 300 m of its course; consequently the chemistry of the stream remains reasonably stable e.g. mean K increases from 0.95 to 2.2 mg l^{-1}; mean Mg decreases from 61.4 to 53.3 mg l^{-1}; the mean Zn concentration decreases slightly from 1.13 to 0.93 mg l^{-1}; mean Cu decreases from 0.69 to 0.52 mg l^{-1}; and the mean Fe decreases from 99.6 to 78.7 mg l^{-1}. These slight falls in concentration of most metals cause a reduction in mean conductivity from 1870 to 1550 μmhos.

The entry of stream B markedly affects the concentrations of Na, K, Mg and Ca. Table 4.4 compares the chemistry of some of the major sites. Although Stream B runs at a similar pH, the alkali metals are very different. This could be caused by the difference in source; Stream B has a diffuse source seeping from under the coal tip whereas Stream A is a point source springing from underground (1.3.5). The high concentrations of these metals cause a very large increase in these elements in the main stream, below the confluence. The pH rises sharply at this point to 3.5 (site 8) but this does not affect the very soluble alkali metals.

A sharp fall in the concentrations of soluble Fe is seen as a result of this increase in pH. There is a visible precipitation of ferric hydroxides at this point. The other metals decrease in concentration only slightly here but continue to fall steadily down the stream; many of the trace elements occur in quite high concentrations viz. Zn, Cu, Mn, Fe, Al, Co and Ni whereas

Pb and Cd only occur in relatively low concentrations presumably reflecting their status in the local strata.

The concentration of anions tend to show a steady decrease from the source e.g. mean SO_4-S (the highest in concentration) decreases from 454 to 338 mg l^{-1} over the first 500 m. The high concentrations of SO_4-S in Stream B (616 mg l^{-1}) causes an increase in the main stream below the confluence: up to 508 mg l^{-1}.

One of the key plant nutrients PO_4-P markedly decreases with the increase in pH to 3.5; this is probably precipitated with the ferric hydroxides mentioned above. There is however an increase in NO_3-N at this point.

TABLE 4.4 Mean concentration of selected elements at important sites in Brandon Pithouse acid streams. Concentrations in mg l^{-1}, n = 8.

stream no.	reach no.	km	river and	pH	cond. µmhos	Na	K	Mg	Ca	Zn	Cu	Mn	Fe	Al	Pb	PO_4-P	SO_4-S
0127	01	-3.6	Stream A source	2.6	1870	12.9	0.95	61.4	59.4	1.13	0.69	6.1	99.6	26.8	0.024	0.350	454
0125	01	-0.6	Stream B source (7b)	2.8	2000	157	7.6	145	136	1.23	0.33	8.7	17.5	28.7	0.010	0.014	616
0127	07	-	Stream A below conf. with B (8)	3.5	1600	157	12.5	105	108	0.84	0.27	5.5	24.0	21.2	0.009	0.020	508
0022	06	-0.1	Red Burn 100m from conf. with River Deerness	7.2	616	442	7.5	38.2	85.1	0.053	0.008	1.3	0.57	0.09	0.001	0.001	42

CHAPTER FIVE

5. COMPOSITION AND ACCUMULATION OF HEAVY METALS

5.1 Plant species in River Wear

5.1.1 Introduction

A variety of plants present in the three study areas of the River Wear system have been analysed for thirteen metal elements. Heavy metal composition data have been related to the chemistry of the surrounding water by calculating enrichment ratios.

The primary data and statistical analysis of all samples are presented in Appendix A.2. All data are expressed in $\mu g\ g^{-1}$ ($mg\ kg^{-1}$) dry weight plant material; this is in line with the standardisation of data suggested by Bowen (1966).

Analysis is presented of a range of plant material collected in 1968 (Table A.2a). More detailed studies of *Cladophora glomerata* (Tables A.2b to A.2e); *Fontinalis antipyretica* (Tables A.2f to A.2i); and *Ranunculus penicillatus* var. *calcareus* (Table A.2j) in the River Wear, follow.

5.1.2 Survey of metal composition of plants 1967/68

A range of plants occurring at Finchale Abbey (km 78.1) in the lower River Wear was studied. The floristic changes and simple chemistry of this site are well documented (see also 3.1. and 3.2.5); and a number of commonly occurring aquatic plants are present. Examples of algae, bryophytes and angiosperms collected during 1967/68 were analysed to assess which might be suitable for further investigation. Particular attention was paid to amounts of heavy metals present in various plants. The survey reveals a wide range of concentrations of all elements in the plants sampled. Generally macro-elements are higher in concentration than heavy metals. Na concentrations of the algae and mosses are less than 0.05% of the dry weight (the lowest of the major cations) but the two species of *Potamogeton* have a much higher content (approximately 1% Na).

The concentrations of K tends to be high in the region of 2 to 3% for the algae and higher plants but rather less (about 0.5%) in the three species of moss. Mg concentrations are less than 1% in all plants analysed but highest in the algae. Most species contain particularly high amounts of Ca; in the region of 2% of the dry weight.

Immense variation is found in trace element content of the 9 species analysed. Mn, Fe and Al are accumulated particularly by the mosses, Mn reaching as much as 4.8% dry weight of *Fissidens crassipes*.

Heavy metal contents in relation to the macro-elements K and Mg are summarised in Table 5.1. *Cladophora glomerata* and *Vaucheria sessilis* show higher concentrations of Zn, Co and Ni than *Oedogonium* sp. and *Enteromorpha flexuosa*. The mosses exhibit greater accumulation of the heavy metals, notably Zn, Pb, Co and Ni; heavy metals in the algae and higher plants are an

TABLE 5.1 Mean composition of selected metals in plants sampled from Finchale Abbey (km 78.1) in 1967/68. Concentrations in $\mu g\ g^{-1}$ dry weight; n = 4.

	K	Mg	Zn	Cu	Pb	Cd	Co	Ni
Cladophora glomerata	25780	2741	195	42.1	79.7	1.63	135	154
Enteromorpha flexuosa	22067	11005	48.7	7.7	17.8	1.62	6.5	18.2
Oedogonium sp. (9 µm)	20202	6430	51.1	7.4	36.0	1.63	11.5	19.2
Vaucheria sessilis	2771	5229	536.2	33.8	81.5	4.01	136	131
Eurhynchium riparioides	6044	3724	1139	38.2	183.0	3.9	289	1058
Fissidens crassipes	5338	3594	2148	57.2	318.3	8.1	513	1388
Fontinalis antipyretica	4461	2045	4142	19.9	245.3	1.68	149	363
Potamogeton crispus	32659	2483	2466	28.2	43.4	1.68	19.8	83.4
Potamogeton pectinatus	33590	5036	1882	15.4	34.4	1.65	40.2	81.3

order of magnitude lower than in the mosses. Results for Cd are exceptionally low in all species and in many cases values are so close to the detection limit that their validity is questionable.

Among the algae, *Vaucheria sessilis* shows the highest concentrations of Zn, Pb and Cd. It is also of wide occurrence in the River Wear. However, practical problems regarding sampling and cleaning (2.2.2) ruled out a more extensive investigation into its use as an indicator plant. *Enteromorpha* and *Oedogonium* were not used in further studies for several reasons; both plants have only low concentrations of Zn, Cu and Pb, the former species has a restricted and variable occurrence in the river while the latter was not found in sufficient quantities to sample, during the period of study. *Cladophora* shows conveniently measurable quantities of trace elements, its occurrence is widespread in the nutrient rich reaches of the River Wear and it has a longer growing season than many other algae (Whitton 1970). This organism, therefore, seemed the most suitable to select for more detailed study.

Among the bryophytes *Fissidens crassipes* shows higher concentrations of heavy metals than either *Eurhynchium riparioides* or *Fontinalis antipyretica*. The moss, however, occurs inconsistently in the lower reaches. *Eurhynchium* is one of the most widespread aquatic organisms; however, its growth habit and tendency to cling to silt ruled out the possibility of further investigation (2.2.2) *Fontinalis antipyretica* was selected because of its widespread occurrence, ease of sampling and appreciable heavy metal content.

Although both species of *Potamogeton* contained measurable quantities of heavy metals, they tend to occupy the deeper reaches of the river and did not occur in many sites; neither of these was therefore used for further investigation. Samples of *Ranunculus* spp. were not available in the river during that period (1967/68).

Unfortunately chemical data for these years did not include heavy metal analysis. Therefore enrichment ratios could not be calculated for any of these plants.

5.2 Accumulation by *Cladophora glomerata*

5.2.1 Variation in samples

The criteria adopted for the sampling of plants in a river have been mentioned in 2.2.1. In order to confirm that the variation within the sites was acceptable six replicate samples were taken at each of the four main sites in the lower River Wear. Plants were carefully selected by eye, to be well branched, dark green 'healthy' specimens from fast flowing sections across the middle of the 20 m sample site, away from the immediate influence of the river banks. The individual samples were washed, dried and analysed as described in 2.2.

A summary of the 11 metals analysed is given in Table 5.2. Variation is smallest for the macro-elements, K, Mg, and Ca; data concerning Na content are less consistent.

TABLE 5.2 Variation in composition of 11 metals in *Cladophora glomerata* at four sites in the lower River Wear. Mean concentrations in $\mu g\ g^{-1}$ dry weight; n = 6.

stream no.	km		Na	K	Mg	Ca	Zn	Cu	Mn	Fe	Al	Pb	Cd
0008	58.3	mean	542	32100	2410	9100	82.2	8.08	4070	733	158	21.4	1.44
Sunderland Bridge		std. dev.	80.8	1730	73	429	20.2	2.28	1170	61.3	19.7	2.3	0.43
		coeff. var. (%)	14.9	5.40	3.0	4.7	24.5	28.2	28.7	8.4	12.4	10.7	29.8
0008	73.5	mean	453	34300	2680	9060	92.8	8.72	2490	551	149	31.4	3.13
above industrial effluent		std. dev.	56.2	1880	181	843	22.3	1.42	495	88.8	29.0	4.1	0.41
		coeff. var. (%)	12.4	5.5	6.8	9.3	24.0	16.2	19.8	16.1	19.4	13.2	13.2
0008	73.9	mean	697	30800	2500	7820	170	9.10	1820	579	190	30.2	2.50
below industrial effluent		std. dev.	407	4500	270	746	38	1.49	425	128	42	3.7	.15
		coeff. var. (%)	58.4	14.6	10.8	9.5	22.9	16.4	23.4	22.1	22.0	12.3	5.0
0008	78.1	mean	458	26000	2710	8800	226	16.6	3260	2920	648	41.2	2.52
Finchale Abbey		std. dev.	100	3500	187	1047	31	2.6	940	1040	198	6.2	0.64
		coeff. var. (%)	21.8	13.4	6.9	11.8	13.6	15.8	28.8	35.6	30.5	15.0	25.2

The coefficients of variation for the trace elements tend to be greater than the macro-elements e.g. Zn varies from 13.6 to 24.5%, Pb from 10.7 to 15.0% and Cd from 6.0 to 29.8%. Other trace elements tend to vary between 20 to 30%. Although the variation is large it nevertheless allows major differences between the sites to be established. In order to reduce the time for preparation and analysis subsequent samples were based on four replicate samples using the criteria already described.

5.2.2 Preliminary study at Finchale Abbey, 1972

The first detailed study of *Cladophora glomerata* was carried out between April and July 1972 at one site, Finchale Abbey (km 78.1).

Among the macro-elements, K varies widely over this period (20000 to 40000 µg g^{-1}) showing no relation to variation of this element in the water. Mg values however, remain much more stable in the plant and apparently independent of the concentration in the water.

The composition of the heavy metals Zn, Cu and Pb is shown in Table 5.3. The chemistry of the water for the same metals, at the times closest to plant collection, is also given. From these data some idea of the enrichment ratios for these heavy metals can be gathered. A wide range of ratio is found in each case; between 8000 and 70000 for Zn; 2000 and 20000 for Pb. It should be noted that much of the water analysis is close to the limit of detection and not taken at exactly the same time as the plant sample. All enrichment ratios for Cu have a value

TABLE 5.3 Accumulation of Zn, Cu and Pb by *Cladophora glomerata* on various dates at Finchale Abbey (km 78.1). Mean concentrations of plant samples in μg g^{-1}; n = 4, mean concentrations in water, at time nearest to sampling, in mg l^{-1}.

	Zn			Cu			Pb		
date	plant	water	ratio	plant	water	ratio	plant	water	ratio
1.4.72	726	0.010	72600	21.7	<0.01	>2170	20.5	0.003	6833
25.4.72	125	<0.010	12500	32.5	<0.01	>3250	21.2	0.001	21200
9.5.72	138	0.016	8625	20.1	<0.01	>2010	14.7	0.003	4900
24.5.72	60	<0.010	>6000	14.0	<0.01	>1400	16.1	0.002	8050
14.7.72	141	0.010	14100	9.2	<0.01	>9200	23.5	0.011	2136

of > 1400 because the concentration of Cu in the water is given as <0.01 mg l^{-1} for samples taken at that time.

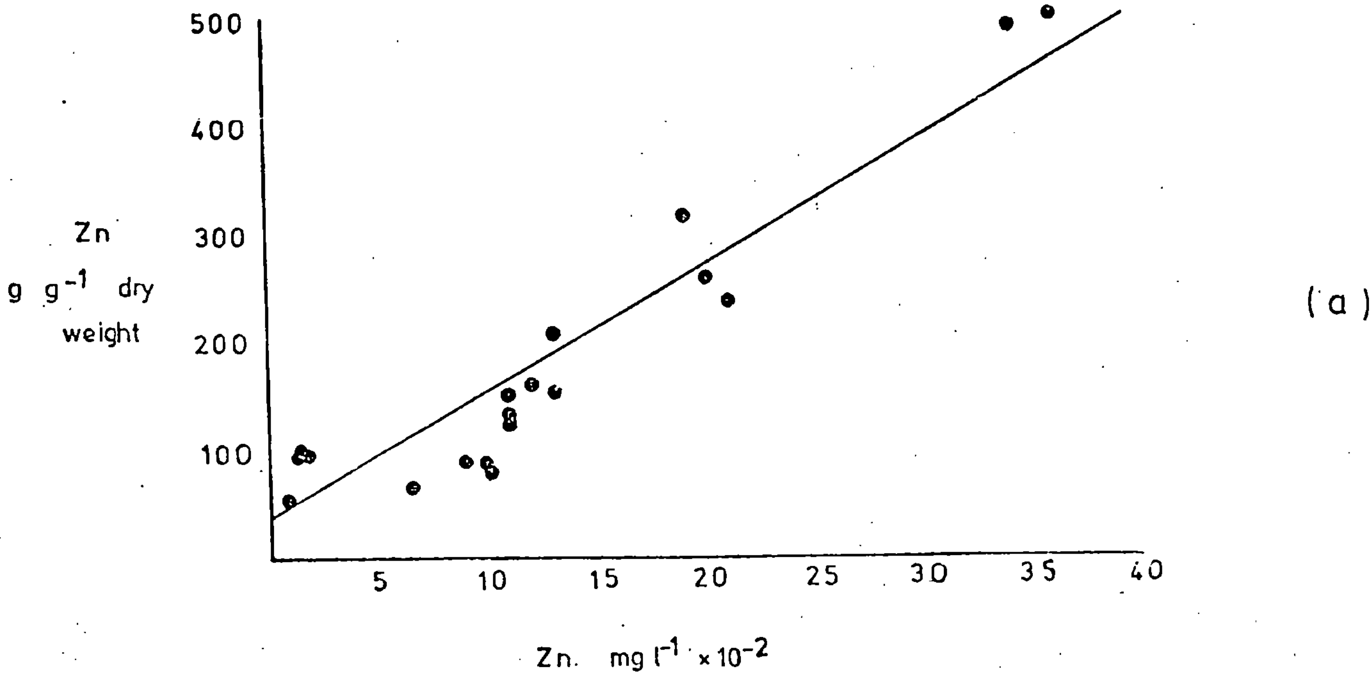
5.2.3 Accumulation in the region of industrial effluent, 1973

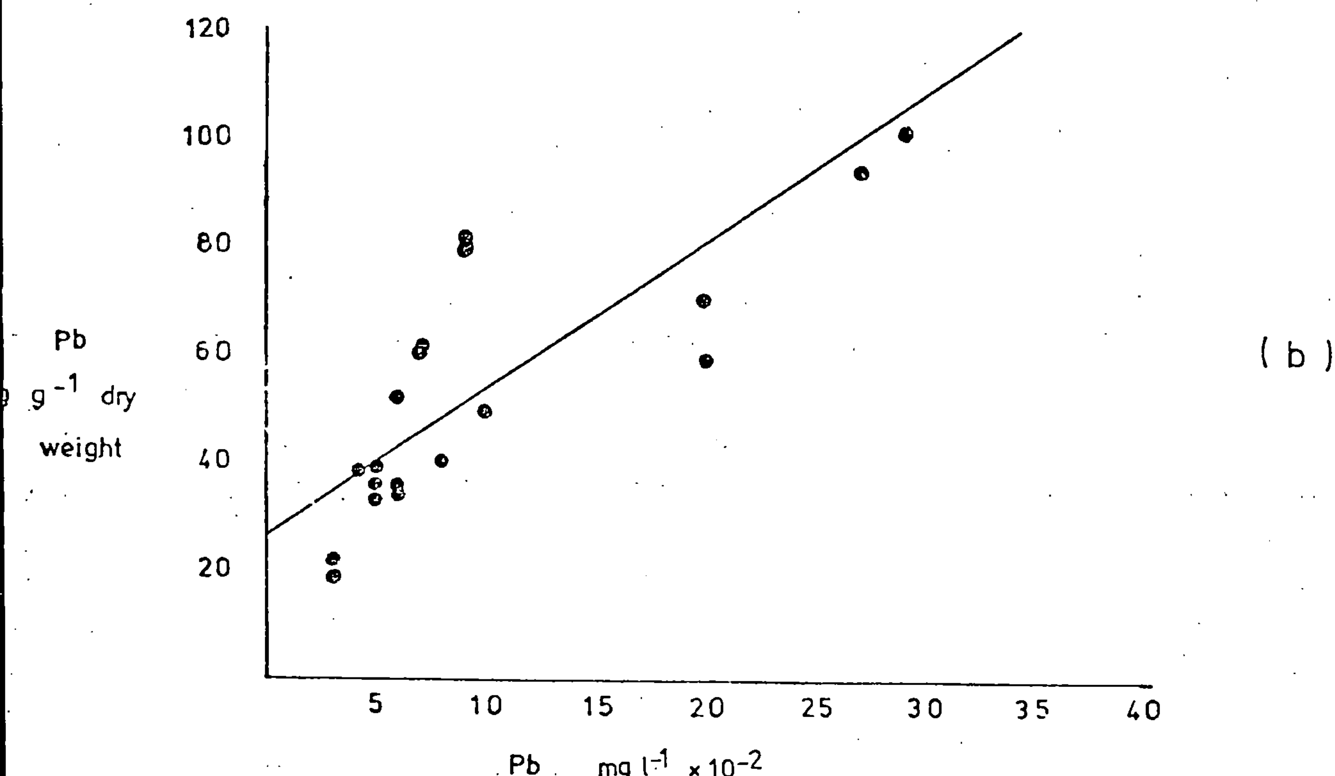
During 1973 data were obtained from the four sites in the lower River Wear to study the effects of the industrial effluent (km 76.6). The relationship between the concentration of heavy metals in *Cladophora* and in the water was established from the data collected in an attempt to use this plant as a quantitative indicator of heavy metals in the river. Fig. 5.1 shows the Zn and Pb concentrations in the water, at the sites in the lower reaches, during 1973, plotted against the Zn and Pb concentrations in *Cladophora*.

For both Zn and Pb there is a clear positive correlation (r values 0944, 0.809 respectively. p, <0.001).

The macro-elements K and Mg in the water plotted against those in the plant show no correlation in either case (r values; K - 0.0884, Mg - 0.156). Therefore these elements are independent of their concentrations in the water. Cu does not give a positive correlation but this is attributable to probable inaccuracy of Cu data at the very low concentrations encountered; this was also noted in 5.2.2.

The proportional relationship for Zn and Pb between *Cladophora* and the water allows the data concerning the composition of the plant and the effects of the industrial effluent to be studied in more detail. The chemistry

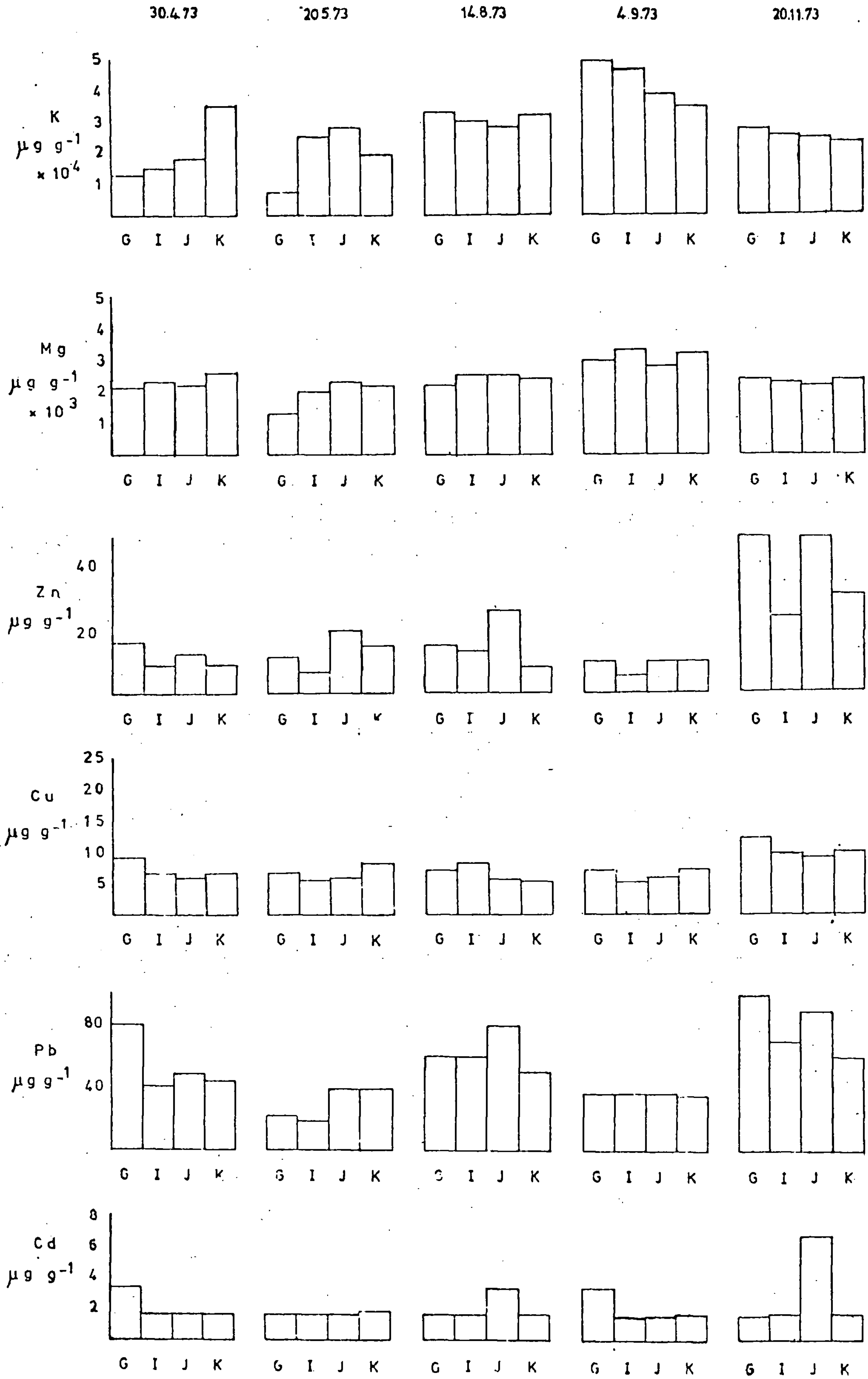

500
400
300
200
100
Zn
g g-1 dry
weight
5
10
15
20
25
30
35
40
Zn. mg l-1 x 10-2
(a)


120
100
80
60
40
20
Pb
g -1 dry
weight
5
10
15
20
25
30
35
40
Pb mg l-1 x 10-2
(b)

of these sites has already been presented (4.2.4) and marked increases were noted for Zn and Pb at the site below the effluent. Fig. 5.2 shows the concentrations in the plant for K, Mg and four heavy metals: Zn, Cu, Pb, Cd, on various dates during 1973. The contents of K vary considerably, however this does not correspond with changes in content of the water (4.1.2). Mg contents are presented to allow comparison of the heavy metals with a stable macro-element.

In the case of both Zn and Pb highly significant increases were found at the site immediately downstream of the effluent on all occasions except 4 September 1973; on this occasion it is known that Pb, at least, was not present in the effluent. The highest concentrations of both elements are generally found at Sunderland Bridge (km 58.3). Perhaps the most important increases are seen below the effluent on 18 May 1973 and 14 August 1973 when both Zn and Pb are between 25 and 50% higher than either of the upstream sites. Unfortunately data are not available from the effluent itself, to confirm the relative increase in plant concentrations. A fall-off in concentrations of both Zn and Pb, similar to those shown by the water chemistry (4.2.3) occurs between km 73.9 and 78.1.

A study of the Cu content of *Cladophora* is of value despite the lack of a clear relationship with the water. Concentrations of Cu do not vary greatly in these reaches of the river although Sunderland Bridge (km 58.3) tends to show highest concentrations (Fig. 5.2).


30.4.73
20.5.73
14.8.73
4.9.73
20.11.73
K
μg g-1
x 10^4
Mg
μg g-1
x 10^3
Zn
μg g-1
Cu
μg g-1
Pb
μg g-1
Cd
μg g-1
G I J K

Unlike Zn and Pb, Cu does not exhibit any significant increases at the site below the effluent; as noted in 5.2.3 Cu is not present in any appreciable quantity in the effluent. This element therefore acts as a useful control for heavy metals (4.2.4).

The concentration of Cd in *Cladophora* is the lowest of all the metals analysed. Results are presented because of its possible occurrence in the industrial effluent. The concentrations are close to the detection limit in all but a few instances; higher values in *Cladophora* are recorded twice at Sunderland Bridge (km 58.3) and twice at the site below the effluent (km 76.9); this is shown in Fig. 5.2. On both occasions the latter results correspond with increases recorded in the water chemistry.

The overall pattern of heavy metal concentration in both plants and water are very similar.

Some attempt to quantify this apparent relationship has already been made for Zn and Pb in *Cladophora*. Enrichment ratios in this plant have also been calculated for the four selected heavy metals (Zn, Cu, Pb and Cd); these are shown in Table 5.4. In a few cases ratios have not been calculated because of anomalous water chemistry results and where 'less than' values occur in the water, only 'greater than' ratios can be given. The majority of enrichment ratios for Zn are in the region of 11000. The ratios for Cu are much lower, the majority being around 2000 and Pb ratios vary from 6000 to 13000, most being close to 7000. These ratios are less variable than those quoted in 5.2.2, mainly because of the improved

TABLE 5.4 Enrichment ratios for Zn, Cu, Pb and Cd in *Cladophora glomerata* at four sites in the lower River Wear, on various dates during 1973.

* Anomalous data for water chemistry, ratio not calculated

site	km	date	Zn	Cu	Pb	Cd
Sunderland Bridge	58.3	29.4.73	13600	1510	*	*
above effluent	73.5	"	8350	1080	*	*
below effluent	73.9	"	11400	710	*	*
Finchale Abbey	78.1	"	9860	880	*	*
Sunderland Bridge	58.3	18.5.73	13100	1600	7400	> 16100
above effluent	73.5	"	9600	1390	6230	> 16100
below effluent	73.9	"	15600	1380	7800	> 16100
Finchale Abbey	78.1	"	14400	1590	9950	> 16100
Sunderland Bridge	58.3	14.8.73	11300	2300	8630	8250
above effluent	73.5	"	11600	2000	8690	> 16300
below effluent	73.9	"	12900	1340	9040	10300
Finchale Abbey	78.1	"	8200	1680	8770	8050
Sunderland Bridge	58.3	4.9.73	50101	>3460	5950	> 32280
above effluent	73.5	"	> 28000	>2450	7200	> 16400
below effluent	73.9	"	> 48800	>2800	6010	> 16600
Finchale Abbey	78.1	"	> 48800	>3610	6620	> 16500
Sunderland Bridge	58.3	20.11.73	14000	6100	13250	> 16100
above effluent	73.5	"	11500	1890	7730	> 16700
below effluent	73.9	"	14600	4550	10420	33500
Finchale Abbey	78.1	"	17600	3290	9830	> 16100
Mean			14500	1900	8300	> 16000

techniques in analysis of water noted in 2.1.2 and because water samples were taken at exactly the same time as collection of plant material.

5.2.4 Other sites 1968 and 1973

Samples of *Cladophora glomerata* were also analysed from other sites on the River Wear both in 1968 (Table A.2e) and 1973 (Table A.2d). Table 5.5 shows data at various sites for major cations, K, Mg and three heavy metals Zn, Cu and Pb, collected during 1968. Table 5.6 shows similar data from a range of sites sampled during 1973. The 1968 samples were all collected within three days of each other to allow reasonable comparison between the sites; whereas plants were collected on the same day from all the sites in 1973. Water chemistry data for the earlier period are not available. Some comparison can be made between the Tables 5.5 and 5.6 although the 1968 survey covers more downstream reaches and that of 1973, covers more upstream reaches. Both sets of samples were taken during low flow conditions in August/September of the respective years. The Wolsingham site (km 24.3) in the 1973 survey was the highest upstream site at which *Cladophora* was found in the River Wear. The highest values of Mg and all three heavy metals are found in the plant at this site; this corresponds with the higher values of the three heavy metals in the water, recorded consistently in 1973. Macro-element values in the plant remain relatively unchanged on passing downstream whereas heavy metals fall steadily, possibly reflecting the gradual decrease in concentrations in the water. The same pattern of steady

TABLE 5.5 Mean Composition of selected metals in *Cladophora glomerata* at various sites in the River Wear, late summer 1968. Concentrations in μg g^{-1}, dry weight; n=4

site	km	date	K	Mg	Zn	Cu	Pb
above Gaunless	44.0	15.8.68	35700	2000	101	5.37	48.7
Willington	51.1	15.8.68	29800	2560	152	8.93	59.4
Durham Sands	70.4	16.8.68	27200	1950	69.2	6.59	48.1
Finchale Abbey	78.3	13.8.68	30800	2080	65.3	4.89	8.2
Cocken Bridge	80.6	13.8.68	41500	1380	65.5	13.9	17.7
Lambton Bridge	90.0	16.8.68	83800	2130	106	10.1	25.0

TABLE 5.6 Mean Composition of selected metals in *Cladophora glomerata* at various sites in the River Wear, late summer 1973. Concentrations in $\mu g\ g^{-1}$, dry weight; n = 4

site	km	date	K	Mg	Zn	Cu	Pb
Wolsingham	22.0	26.8.73	24200	5530	1200	16.9	38.7
Witton le Wear	35.2	26.8.73	39600	2120	230	6.25	92.6
Bishop Auckland	44.3	26.8.73	33200	2240	125	4.64	50.5
Willington	51.1	26.8.73	37200	2430	143	7.46	65.9
Sunderland Bridge	58.3	4.9.73	48600	3000	101	6.93	35.7
Finchale Abbey	78.3	4.9.73	34300	3200	97.5	7.2	33.1

macro-element concentrations and decreasing heavy metal values is evident at the upstream sites used in 1968 (Table 5.5).

A comparison of the same sites in 1968 and 1973 reveals that the composition of *Cladophora* is remarkably constant; K and Mg values are very similar but Zn and Pb values are lower in 1968, at the sites in the middle and lower stretches of the river. Natural variation in the chemistry of the water could account for most of these differences. For the most part it appears that major changes in the trace element concentrations of *Cladophora* did not occur between 1968 and 1973, with the notable exception of results from km 76.9, below the industrial effluent (5.2.3).

5.3 Accumulation by *Fontinalis antipyretica*

5.3.1 Preliminary study at Finchale Abbey, 1972

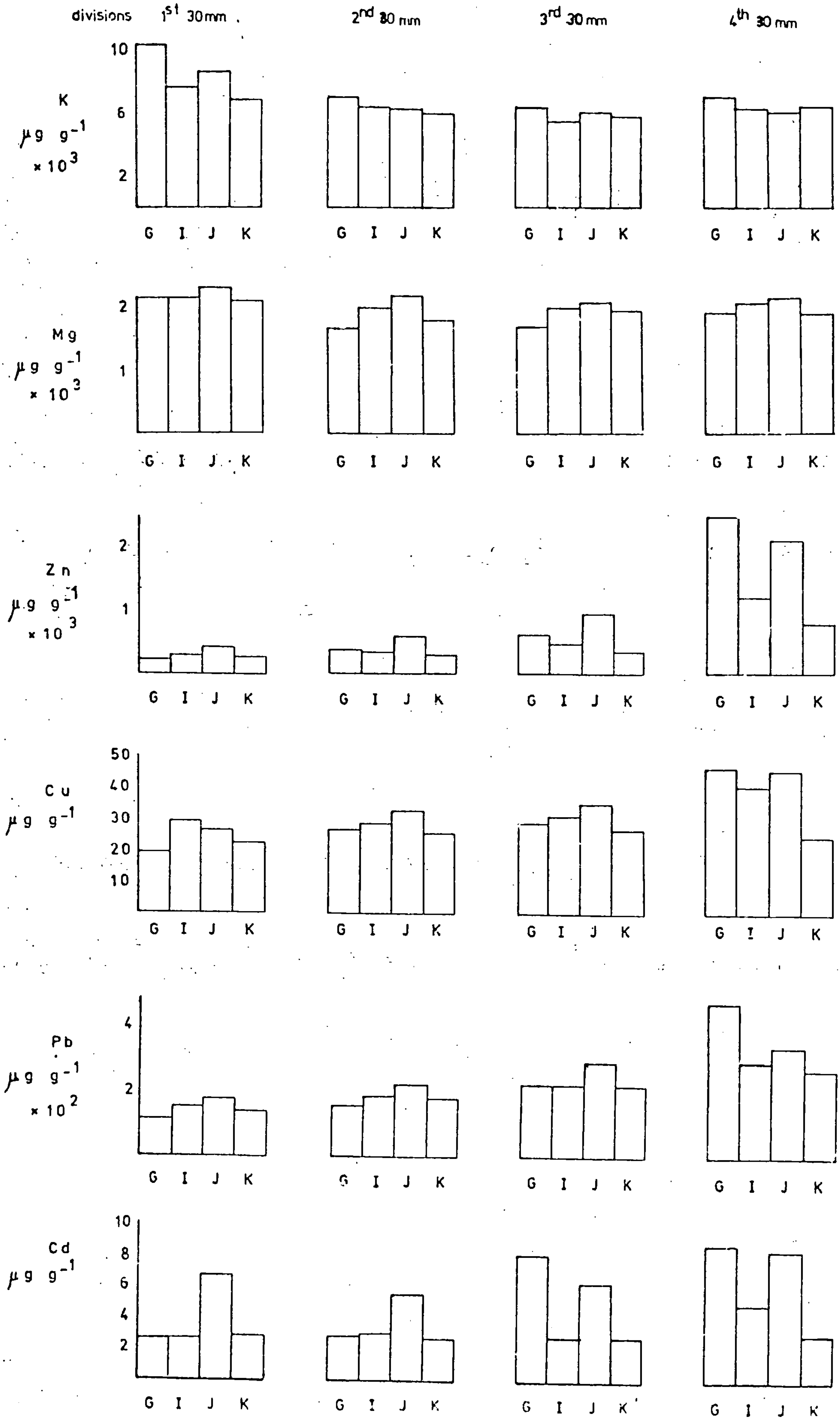
A preliminary examination of *Fontinalis antipyretica* was carried out in 1972. Samples were subjectively divided into growing tips, mature stems and old material (details of the samples are given in 2.5.3).

The data presented in A.2F show a marked tendency for the macro-elements; Na, K, Mg and Ca to decrease in concentration away from the tip whereas the heavy metals increase in concentration in the older material.

5.3.2 Accumulation in the region of industrial effluent, 1973

Data for the metal composition of *Fontinalis antipyretica* were obtained from both divided and undivided samples of the moss. The samples were taken from the sites above and below the industrial effluent in the lower River Wear and the full results are presented in A.2G and A.2H. Division of the samples allows clearer comparison of the metal contents of the plants from the different sites and also relates to different time periods of growth. Fig. 5.3 summarises the composition of divided *Fontinalis* for two of the macro-elements analysed (K, Mg), at the four sites in the region of the industrial effluent. These histograms show a clear tendency for the concentration of both elements to fall away from the tip at all sites but this fall is most marked for K. The differences in K content between sites are not statistically significant ($P < 0.01$) except for samples of the 1st 30 mm. Mg results are fairly stable between sites particularly in the 1st 30 mm where only the sample from below the industrial effluent is significantly higher than the others at $P < 0.01$; the increase is however only marginal.

The contents of heavy metals (Zn, Cu, Pb, Cd) in the different sections and at the different sites vary greatly by comparison with the macro-elements (Fig. 5.3). Cu acts as a control over the other heavy metals as it is known not to occur in any quantity in the industrial effluent. Increases in this element at the site below the effluent are not statistically significant at $P > 0.05$. However, highly significant increases ($P < 0.001$) are found consistently at this site for Zn, Pb and Cd. These increases become even more obvious in the oldest material where the heavy metal concentrations are very much higher.


divisions
1st 30 mm
2nd 30 mm
3rd 30 mm
4th 30 mm
K µg g-1 × 10³
Mg µg g-1 × 10³
Zn µg g-1 × 10³
Cu µg g-1
Pb µg g-1 × 10²
Cd µg g-1
G I J K

This appears to indicate a gradual build up of these metals by the plant as it grows.

Data given in A.2G also show considerable increases in Ni concentrations below the effluent although no regular water chemistry data are available for this element. It therefore seems probable that this element is present in the effluent itself.

Undivided samples from the same four sites also taken in 1973 do not indicate the differential between the sites so clearly although highly significant increases in Zn, Cd and Ni are found below the effluent in the samples taken in November but not in August 1973. Samples of *Cladophora glomerata* (5.2.3) however, showed increases for Zn, Pb, and Cd on both occasions. It is possible that increases are blurred in these undivided samples by the relative proportion of older material containing high concentrations of heavy metals.

Enrichment ratios were also calculated for the four heavy metals of chief interest (Zn, Cu, Pb, Cd) in both divided and undivided samples. These are presented in Table 5.7. Ratios obviously increase away from the tip in the divided samples. It is also clear in all cases, except Cd, that the ratios become more variable in the older material. Ratios for the element Cd have not been calculated for the divided samples because of some anomalous, possibly erroneous water chemistry data. The undivided material shows even greater variability in enrichment ratio than the divided material. It is therefore clear that the youngest material exhibits the most

TABLE 5.7 Enrichment ratios for Zn, Cu, Pb and Cd in divided and undivided *Fontinalis antipyretica*, at four sites in lower River Wear during 1973.

* Anomalous data for water chemistry, ratio not calculated

site	km	date	section	Zn	Cu	Pb	Cd
Sunderland Bridge	58.3	29.4.73	1st 30 mm	18700	3170	11700	*
above effluent	73.5			27100	4780	6040	*
below effluent	73.9			35900	3200	7250	*
Finchale Abbey	78.1			26400	3160	12000	*
Sunderland Bridge	58.3	29.4.73	2nd 30 mm	28700	4350	16400	*
above effluent	73.5			31700	4700	7360	*
below effluent	73.9			52500	4080	9700	*
Finchale Abbey	78.1			31800	3600	17100	*
Sunderland Bridge	58.3	29.4.73	3rd 30 mm	48200	4720	24800	*
above effluent	73.5			47100	5070	9160	*
below effluent	73.9			82200	4300	11800	*
Finchale Abbey	78.1			38200	3690	20400	*
Sunderland Bridge	58.3	29.4.73	4th 30 mm	213000	7680	54700	*
above effluent	73.5			124000	6680	11400	*
below effluent	73.9			186800	5590	14300	*
Finchale Abbey	78.1			86200	3440	22900	*
Sunderland Bridge	58.3	14.8.73	undivided	145400	8570	47900	57000
above effluent	73.5			82500	6880	33600	> 35800
below effluent	73.9			33100	8180	24300	11700
Finchale Abbey	78.1			64500	6430	31200	14100
Sunderland Bridge	58.3	20.11.73	undivided	70600	21800	84700	78400
above effluent	73.5			51400	6740	20300	> 22600
below effluent	73.9			55800	14500	19600	30000
Finchale Abbey	78.1			65700	7600	26800	46500

reliable potential as an indicator. Enrichment ratios for these sections range from 18700 to 35900 for Zn; 3160 to 4780 for Cu, the most stable, and 6040 to 12000 for Pb.

5.3.3 Other sites, 1968

Data are presented in A.21 to show the composition of *Fontinalis antipyretica* at various sites in the River Wear in 1968. The data for K, Mg, Zn and Pb are summarised in Table 5.8. Certain trends are clear despite the use of undivided samples. K values fall from the upstream to downstream sites whereas Mg results remain stable. The highest concentrations of both Zn and Pb occur at the site above the entry of the River Gaunless (km 44.0); this was the furthest upstream site from which *Fontinalis* was sampled in 1968. The Zn concentration decreases downstream as far as Lambton Bridge (km 90.0) where there is a marked increase in the concentration of this element. Pb shows a similar trend. These patterns correspond quite closely with those for *Cladophora glomerata* sampled from the same sites at the same period in 1968 (5.2.4). There is, therefore, reasonable evidence to suggest that the water chemistry for the heavy metals followed a similar trend despite the lack of chemical data to confirm this.

5.4 Accumulation by *Ranunculus penicillatus* var. *calcareus*

The content of two macro-elements (K, Mg) and three heavy metals (Zn, Cu, Pb) in *Ranunculus penicillatus* var. *calcareus* from sites in the River Wear and River Tweed

TABLE 5.8 Mean Composition of selected metals in *Fontinalis antipyretica* at various sites in the River Wear, late summer 1968. Concentrations in $\mu g\ g^{-1}$, dry weight; n = 4.

date	stream no.	km	site	K	Mg	Zn	Pb
15.8.68	0008	44.0	Above Gaunless	8460	1920	1250	398
15.8.68	0008	51.1	Willington	8170	1930	883	172
16.8.68	0008	71.1	Durham Sands	7200	2300	835	237
13.8.68	0008	78.3	Finchale Abbey	6500	1880	473	100
13.8.68	0008	80.0	Cocken Bridge	6610	2080	297	100
16.8.68	0008	90.0	Lambton Bridge	5500	3160	632	169

is summarised in Table 5.9; the composition data for all elements analysed are presented in A.2J. Samples were divided into root, stem and leaf in order to establish the distribution of metals through the plant.

The two macro-elements show a markedly different distribution to the heavy metals; K is consistently highest in the stem whereas Mg is almost equally distributed in the three parts. Zn shows the most consistent distribution; highest in the leaves, almost double the concentration in the roots, in each case, and lowest in the stem. Cu does not exhibit the same marked differences except in the sample from the River Tweed in which the concentration in the leaves is significantly higher than either the stem or root. Pb is also highest in the leaves, in all cases but lowest in the roots.

There is little difference in heavy metal content between the samples from the River Wear except for a significant increase ($P < 0.001$) in Zn concentration in the leaves of the plant at the site below the industrial effluent (km 76.9) compared with the site above the effluent (km 76.5).

A comparison of *Ranunculus* from the River Tweed at Galashiels (km 75.5) with that from the River Wear shows similar concentrations of the macro-elements K and Mg, but Zn and Pb concentrations in the River Tweed sample are considerably lower. On the other hand Cu concentrations are higher in all parts of the River Tweed sample. This may reflect to some degree differences in the heavy metal status of the two rivers. A comparison of heavy metal

TABLE 5.9 Mean Composition of selected metals in divided *Ranunculus penicillatus* var. *calcareus* at three sites in the lower River Wear and one site in the River Tweed. Concentrations in $\mu g\ g^{-1}$, dry weight; n = 4.

stream no.	km	site	part	K	Mg	Zn	Cu	Pb
0008	73.6	above effluent	root	40900	3000	1340	33.6	123
			stem	48500	2910	565	25.7	97.6
			leaf	21500	3010	2000	35.4	24.8
0008	73.9	below effluent	root	35300	2900	1320	23.8	12.5
			stem	52600	2570	376	33.5	59.4
			leaf	21800	3260	2420	29.9	24.8
0008	78.1	Finchale Abbey	root	41500	3020	1460	37.5	131
			stem	56600	2820	553	33.6	59.9
			leaf	22500	3390	2440	32.0	28.5
0011	75.5	Gala Ford (R. Tweed)	root	27600	2480	287	115	35.4
			stem	59700	2080	81.9	51.5	10.7
			leaf	27200	2700	394	70.3	19.8

concentrations in both water and plant material together with the enrichment ratios at Finchale Abbey (km 78.1) on the River Wear and Gala Ford (km 75.5) on the River Tweed is given in Table 5.10. Although the enrichment ratios for the heavy metals are radically different at the two sites, the higher Cu concentrations in the River Tweed plant are in agreement with consistently higher concentrations of this element in the water (Holmes,1975). Similarly. Zn and Pb concentrations are consistently higher in the River Wear than in the River Tweed and the concentration of these elements is also markedly higher in the *Ranunculus* from the River Wear.

5.5 Plant species in Rookhope Burn

5.5.1 Introduction

A range of aquatic plants from the four sites on Rookhope Burn were analysed. The composition data are given in A.2K (algae), A.2L (bryophytes and A.2M (angiosperms). Enrichment ratios have also been calculated in an attempt to gauge the accumulation of heavy metals by the plants.

The changes in flow, substratum and chemistry outlined in 3.3 and 4.3.3 resulted in a changeable flora at each site. The sites sampled and the dates of collection of plant material have been given in 2.5.4.

Before presenting detailed results for the metal composition of the species found in the river, some general comments can be made on the metal concentrations found.

TABLE 5.10 Accumulation of Zn, Cu and Pb in *Ranunculus penicillatus* var. *calcareus* at one site on the River Wear and one site on the River Tweed. Mean concentrations in μg g^{-1} dry weight plant; n = 4; concentration in water at time of sampling in mg l^{-1}.

stream no.	km	site	organ	Zn plant	Zn water	Zn ratio	Cu plant	Cu water	Cu ratio	Pb plant	Pb water	Pb ratio
0008	78.1	R. Wear (Finchale Abbey)	root	1460	0.010	146000	37.5	0.003	12500	131	0.006	21800
			stem	553	0.010	55300	33.6	0.003	11200	59.9	0.006	9980
			leaf	2440	0.010	24400	32.0	0.003	10670	28.5	0.006	4750
0011	75.5	R. Tweed (Gala Ford)	root	287	0.007	41000	115	0.012	9580	35.4	0.002	17700
			stem	81.9	0.007	11700	51.5	0.012	4300	10.7	0.002	5350
			leaf	394	0.007	56300	70.3	0.012	5860	19.8	0.002	9900

The pattern of composition encountered is similar to the other aquatic plants in the River Wear, system so far mentioned. K again shows the highest concentration of the macro-elements in the majority of plant samples and Na tends to be the lowest of the four major elements analysed. One notable exception to this is the emergent hydrophyte *Mimulus guttatus* which has Na values an order of magnitude higher than other aquatic plants studied.

In general, heavy metal concentrations are higher than plants analysed from the lower River Wear. Fe concentrations are particularly high in the bryophytes reaching 8.6% dry weight in one sample of *Scapania undulata*. Heavy metal values vary greatly from plant to plant and site to site but the highest concentrations are found consistently at Upper Rookhope (- km 8.5) and lower Rookhope (- km 3.9) where the river receives the largest volumes of wash out and adits from the lead mining area (4.3.3).

5.5.2 Accumulation by Algae

The accumulation of heavy metals by the various species of algae analysed varies greatly. Table 5.11 summarises the heavy metal composition, water chemistry and enrichment ratios for four species of algae found at the sites in the Rookhope Burn catchment. Direct comparison of the sites is not possible using these data as different algae are present at each site. However, with the exception of *Mougeotia* sp. concentrations of Zn and Pb are an order of magnitude higher than any of the algae collected from the lower River Wear (Table 5.1) as indeed

TABLE 5.11 Accumulation of Zn, Cu and Pb by algae in Rookhope Burn on two occasions in 1973. Mean concentrations in µg g^{-1} dry weight plant; n = 4, concentration in water at time of sampling in mg l^{-1}

stream no.	km	site	date	species	Zn plant	Zn water	Zn ratio	Cu plant	Cu water	Cu ratio	Pb plant	Pb water	Pb ratio
0115	-0.5	North Grain Sike	16.5.73	*Mougeotia* sp.	135	0.131	1030	29.8	0.015	1990	75.9	0.049	1690
0012	-8.5	Upper Rookhope	16.5.73	*Spirogyra* sp.	2450	0.100	24500	32.6	0.017	1920	4210	0.090	13400
0012	-3.9	Lower Rookhope	16.5.73	*Stigeoclonium tenue*	3960	0.520	7620	50.0	0.022	2270	2270	0.390	5820
0012	-0.6	Eastgate Rookhope Burn	16.5.73	*Lemanea fluviatiles* (young)	1310	0.310	4230	56.2	0.020	2810	553	0.172	3210
0012	-0.6	Eastgate Rookhope Burn	4.9.73	*Lemanea fluviatilis* (old)	2890	0.240	12040	88.7	0.010	8870	1110	0.04	25810

are the concentrations in the water. The Cu concentrations on the other hand, are of a similar order to River Wear algae in both plant and water. This shows up clearly in the consistent enrichment ratios encountered of about 2000; this is closely comparable to ratios given for *Cladophora glomerata* in the lower River Wear (Table 5.4).

A marked difference can be seen between the heavy metal composition of young and old *Lemanea fluviatilis*; the concentrations of all three metals are about double in the older material.

5.5.3 Accumulation by Bryophytes

A summary is given, in Table 5.12, of the heavy metal contents of the two bryophytes sampled from Rookhope Burn. The concentrations of these elements in the surrounding water are also presented together with the enrichment ratios calculated from these data. Some comparison can be made between the sites. The Zn and Pb contents of *Scapania undulata* are an order of magnitude higher at the upper Rookhope site than at the North Grain Sike site on each sampling occasion. However, the water chemistry at the time of sampling does not show a similar increase; thus the enrichment ratios are widely different. Although the concentration of Cu is similar in the plant at both sites and on both occasions the enrichment ratios again differ because of the concentration of this element in the water.

Similar inconsistencies between the heavy metal content of the plant and the chemistry of the water, at the time of sampling, occur when comparing the three

TABLE 5.12 Accumulation of Zn, Cu and Pb by bryophytes in Rookhope Burn on two occasions in 1973. Mean concentrations in μg g^{-1} dry weight plant; n = 4, concentration in water at time of sampling in mg l^{-1}.

stream no.	km	site	date	species	Zn plant	Zn water	Zn ratio	Cu plant	Cu water	Cu ratio	Pb plant	Pb water	Pb ratio
0115	-0.5	North Grain Sike	16.5.73	*Scapania undulata*	150	0.131	1140	33.1	0.015	2210	281	0.045	6240
0012	-8.5	Upper Rookhope	16.5.73	*Scapania undulata*	2450	0.100	24500	38.9	0.017	2290	2430	0.090	27000
0015	-0.5	North Grain Sike	4.9.73	*Scapania undulata*	266	0.015	17730	38.8	0.002	19400	607	0.009	67330
0012	-8.5	Upper Rookhope	4.9.73	*Scapania undulata*	3890	0.030	129700	43.4	0.002	21700	3320	0.024	138300
0012	-8.5	Upper Rookhope	16.5.73	*Hygrchypnum ochraceum*	4530	0.100	45300	32.5	0.017	1910	3380	0.090	39560
0012	-3.9	Lower Rookhope	16.5.73	*Hygrohypnum ochraceum*	3960	0.520	7620	226	0.022	10270	4630	0.390	11870
0012	-0.6	Eastgate Rookhope	16.5.73	*Hygrohypnum ochraceum*	3500	0.310	11290	124	0.020	6200	3920	0.172	22790
0012	-8.5	Upper Rookhope	4.9.73	*Hygrohypnum ochraceum*	3600	0.030	120000	38.4	0.002	19200	3770	0.024	157080
0012	-3.9	Lower Rookhope	4.9.73	*Hygrohypnum ochraceum*	16480	0.330	49300	326	0.017	19180	4300	0.051	84310
0012	-0.6	Eastgate Rookhope	4.9.73	*Hygrohypnum ochraceum*	11790	0.240	49120	198	0.010	19800	3640	0.043	84650

lower sites on Rookhope Burn at which *Hygrohypnum ochraceum* occurs; ratios for Zn vary from approximately 7000 to 120000, and ratios for Pb from 12000 to 160000. It is therefore quite clear that neither of these bryophytes is reflecting the chemistry of the water at the time of sampling. However in the case of both *Scapania* and *Hygrohypnum* the concentrations of Zn and Pb are abnormally high whereas Cu concentrations are an order of magnitude less; this corresponds with the overall water chemistry. Thus in general terms the plants give a guide to the metal status of the river.

5.5.4 Accumulations by Angiosperms

The only aquatic angiosperm, *Mimulus guttatus*, occuring in any quantity in Rookhope Burn was divided into root, stem and leaf. Data concerning the macro-element content of the divided plant at each of the two sites sampled show that K in common with other plants has the highest concentration of any element analysed; being in the region of 4 to 6% dry weight. This is considerably higher than other truly aquatic plants studied. Mg content is also higher than other plants reaching 0.7% dry weight in the leaves. Trace element content is consistently greatest in the submerged roots of the plant and decreases through the stem to the leaves. The composition data are presented in A.2M. Further data presented here are confined to the heavy metal content of the submerged roots; these data are compared with the concentrations in the surrounding water using the enrichment ratio and are presented in Table 5.13. The same pattern of concentration

TABLE 5.13 Accumulation of Zn, Cu and Pb by *Mimulus guttatus* roots in Rookhope Burn on 4 September 1973. Mean concentration in $\mu g\ g^{-1}$ dry weight plant; n = 4, concentration in water at time of sampling in $mg\ l^{-1}$

						Zn			Cu			Pb		
stream no.	km	site	date	species	part	plant	water	ratio	plant	water	ratio	plant	water	ratio
0012	-8.5	Upper Rookhope Burn	4.9.73	*Mimulus guttatus*	root	1150	0.030	38 330	36.5	0.002	18250	474	0.024	19750
0012	-3.9	Lower Rookhope Burn	4.9.73	*Mimulus guttatus*	root	3840	0.330	11640	222	0.017	13060	5590	0.051	109600

is encountered as in other aquatic plants from Rookhope Burn; Zn and Pb concentrations are high whereas Cu concentrations are much lower by comparison. Enrichment ratios for the two sites at which the plant occurs are again widely different. Such data can give only a very generalised picture of the conditions in the water and possibly the sediment.

5.6 Plant species in Brandon Pithouse acid streams

5.6.1 Introduction

The range of macroscopically obvious vegetation occurring at the sources of Acid Streams A and B, at a pH of 2.6, was analysed to show metal composition; the data are given in A.2N. The most abundant aquatic plant present, *Drepanocladus fluitans*, was analysed at points down the stream as the pH rises from 2.6 to 4.5 The same organism was also analysed from North Grain Sike (pH 4.5 to 5) for comparative purposes; these data are presented in A.2O. Analysis of the moss was also carried out after division into 30 mm sections (Table A.2P). Full details of the dates and species collected from the various sites have been given (2.5.5). Aspects of the metal composition with particular reference to the heavy metals are summarised in the following sections. Certain heavy metal data are related to the water chemistry using enrichment ratios in order to establish any differences in metal accumulation in an acid environment of low pH.

5.6.2 Survey of accumulation by plants

The concentration of two macro-elements, K and Mg, and eight heavy metals in two species of algae, two species of bryophyte and an emergent hydrophyte are summarised in Table 5.14. A pattern of metal composition similar to that described for plants from the other two sampling areas emerges. K again tends to be the element with the highest concentration relative to the other metals. Two notable exceptions to this are *Euglena mutabilis* and *Dicranella* sp., in which Fe concentrations are in excess of 1% and 3% dry weight respectively. Such high concentrations of Fe have been recorded for other mosses (*Fissidens crassipes*, A.2A) but not for algae. Mg concentrations are in the region of 0.1 to 0.2% in all cases. Concentrations of other heavy metals, particularly Mn, are surprisingly low.

It has already been shown (4.4) that the concentrations of certain heavy metals are high in those acid stream waters: Zn, 1.13 mg l^{-1}, Cu, 0.69 mg l^{-1}, Co, 0.21 mg l^{-1}, and Ni, 0.47 mg l^{-1}, at the source of Stream A. Concentrations in the water of other heavy metals are exceptional: Fe, 99.6 mg l^{-1}, at the source of Stream A, Al, 28.7 mg l^{-1} and Mn, 8.7 mg l^{-1}, at the source of Stream B.

Apart from the Fe concentrations already mentioned, the low concentrations of heavy metals are all the more surprising in view of the water chemistry. This is clearly illustrated in the enrichment ratios given in Table 5.15. All ratios shown with the exception of Pb are several orders of magnitude lower than any encountered for algae, bryophytes or angiosperms in areas of higher pH.

TABLE 5.14 Mean composition of 10 metals in plants from the sources of Brandon Pithouse acid streams on various dates in 1973 and 1974. Concentrations in $\mu g\ g^{-1}$ dry weight plant; n = 4.

stream no.	reach no.	site	date	species	K	Mg	Zn	Cu	Mn	Fe	Al	Pb	Co	Ni
0127	01	source stream A	2.8.74	*Euglena mutabilis*	2760	2210	121	29.7	127	14400	3000	8.94	6.59	8.94
0125	01	source stream B	14.6.73	*Hormidium rivulare*	7760	1640	59.9	42.9	131	6690	1360	5.58	5.58	5.58
0125	01	source stream B	14.6.73	*Dicranella* sp.	10400	1030	56.9	22.5	87.2	30000	1690	8.93	6.54	6.87
0127	01	source stream A	14.6.73	*Drepanocladus fluitans*	14700	1160	72.3	82.5	42.9	9920	770	13.8	9.50	6.10
0125	01	source stream B	2.8.74	*Juncus effusus*	14700	916	37.8	27.9	49.9	1230	270	3.32	4.78	7.06

TABLE 5.15 Enrichment ratios for eight heavy metals in plants from the sources of Brandon Pithouse acid streams.

stream no.	reach no.	site	date	species	Zn	Cu	Mn	Fe	Al	Pb	Co	Ni
0127	01	source Stream A	2.8.74	*Euglena mutabilis*	98.4	35.3	20.7	145	112	1490	26.4	19.0
0125	01	source Stream B	14.6.73	*Hormidium rivulare*	44.0	119	15.1	48.2	476	930	22.3	14.0
0125	01	source Stream B	14.6.73	*Dicranella* sp.	41.8	625	10.0	171	58.9	1490	26.2	17.2
0127	01	source Stream A	14.6.73	*Drepanocladus fluitans*	63.4	120	7.0	99.6	28.8	1061	47.5	13.0
0125	01	source Stream B	7.8.74	*Juncus effusus*	22.6	43.6	5.7	7.1	9.4	1665	36.8	17.7

5.6.3 Accumulation by *Drepanocladus fluitans*

The metal composition of *Drepanocladus fluitans* from three sites of increasing pH on Acid Stream A and a site of higher pH on North Grain Sike, is presented in Table 5.16. Among the macro-elements Na shows a marked decrease at the sites of higher pH. Only minor differences occur between sites for the other major elements although the Ca concentration in the sample from North Grain Sike is about double those from Acid Stream A. Some of the heavy metals tend to show an increase in concentration at the sites of higher pH, notably Zn, Mn, and Al. However the pattern of increase in heavy metals becomes clearer when enrichment ratios are calculated; these are presented for eight heavy metals at the same four sites of increasing pH in Table 5.17. In every case the relative accumulation increases at the higher pH values. For the majority of elements the increase between pH 2.6 and pH 5 is greater than an order of magnitude. The increase from pH 2.5 to 3.5 tends to be small except in the case of Fe. The greatest increases in the ratio occur between pH 3.5 and 4.5. Data from North Grain Sike (pH 5) have been included despite the great differences in the streams because of the occurrence of *Drepanocladus fluitans* and the pH at a level above which the moss occurs in Acid Stream A.

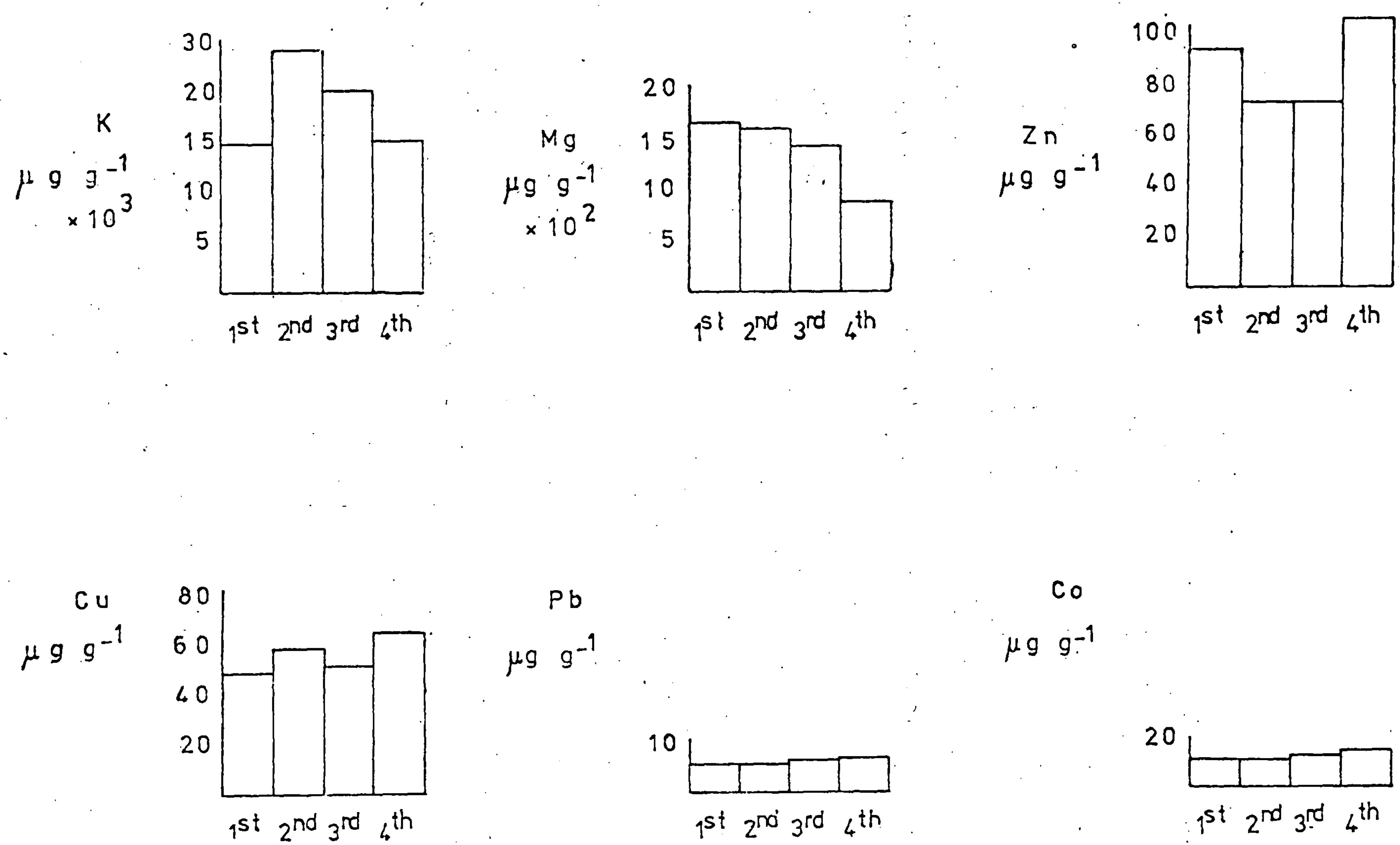
A study of the data from sub-divided *Drepanocladus fluitans*, illustrated in Fig.5.4, reveals a similar, although less distinct pattern of metal composition to sub-divided *Fontinalis antipyretica* described in 5.3.2. An overall decrease in concentration of the two

TABLE 5.16 Mean composition of 12 metals in *Drepanocladus fluitans* at sites of increasing pH. Concentrations in $\mu g\ g^{-1}$ dry weight plant; n = 4.

stream no.	reach no.	site	date	pH	Na	K	Mg	C	Zn	Cu	Mn	Fe	Al	Pb	Ca	Ni
0127	01	source Acid Stream A	14.6.73	2.6	1430	14700	1160	1960	72.3	82.2	42.9	9920	772	13.8	9.50	6.10
0127	08	Acid Stream A (9)	14.6.73	3.5	459	13600	982	1862	51.2	44.4	41.3	40400	777	17.5	6.16	4.93
0127	11	Acid Stream A (12)	14.6.73	4.5	514	13400	998	1750	50.9	57.1	26.4	33800	497	38.6	5.02	5.02
0115	10	North Grain Sike	16.5.73	5.0	262	11700	1203	3860	122	42.6	301	25300	636	12.6	7.73	4.95

TABLE 5.17 Enrichment ratios for eight heavy metals in *Drepanocladus fluitans* at sites of increasing pH.

stream no.	reach no.	km	site	date	pH	Zn	Cu	Mn	Fe	Al	Pb	Co	Ni
0127	01	-3.6	source Acid Stream A	14.6.73	2.6	63.4	120	7.0	99.6	28.8	1060	47.5	13.0
0127	08	-2.9	below confluence with Stream B	14.6.73	3.5	53.1	148	8.0	3700	42.0	3530	55.4	19.7
0127	12	-1.6	upper Esh Wood	14.6.73	4.5	424	1390	12.4	33500	257	3220	836	68.7
0127	10	-0.5	North Grain Sike	16.5.73	5.0	923	2840	201	32400	2500	6600	-	-


K
µg g-1 ×10³
30
20
15
10
5
1st 2nd 3rd 4th
Mg
µg g-1 ×10²
20
15
10
5
1st 2nd 3rd 4th
Zn
µg g-1
100
80
60
40
20
1st 2nd 3rd 4th
Cu
µg g-1
80
60
40
20
1st 2nd 3rd 4th
Pb
µg g-1
10
1st 2nd 3rd 4th
Co
µg g-1
20
1st 2nd 3rd 4th

major cations (K and Mg) occurs away from the tip. Among the heavy metals Zn does not show a clear trend to increase in older material whilst the other elements studied show only an insignificant increase away from the tip.

CHAPTER SIX

6. DISCUSSION

6.1 Influence of major chemical parameters on heavy metals in River Wear system

6.1.1 Introduction

It was suggested in Chapter One that studies in a range of different chemical environments could help establish some of the factors affecting the accumulation of heavy metals by aquatic plants and also enable their use as quantitative indicators to be assessed.

The need to understand the chemical forms of heavy metals in river water was stressed so that the availability of these elements to aquatic plants could be established (1.2.1).

The results presented in Chapter Four and Appendix A.1 show the variation of pH, major cations, nutrient anions and discharge in the River Wear and particular parts of its catchment.

Important differences have been shown for chemical parameters in each of the three areas studied. These parameters not only have a marked effect on the concentration and speciation of heavy metals but also affect the vegetation.

The influence of some of the major chemical parameters on the heavy metal content of the water can be clarified by comparing these parameters in the main study areas. Two representative sites have been chosen from the River Wear, Rookhope Burn and Brandon Pithouse Acid Stream A; chemical data are shown in Table 6.1.

6.1.2 pH

A range of pH values was established in the River Wear system from 2.6 in Brandon Pithouse acid streams to 7.8 in the main river at Finchale Abbey (km 78.1).

pH is fundamental by controlling directly the solubility of most cations and anions and indirectly by influencing oxidation states and complexes. (Stumm and Morgan, 1970; Stumm and Bilinski, 1972; Elder, 1975). Furthermore, the inter-relationship of pH with major cations such as Mg and Ca is of great importance regarding the buffering of natural waters (Cholnoky, 1960); fluctuations in pH are certain to cause radical changes in chemical speciation and availability. The upland streams of Weardale (Table 6.1) exemplify the variability of pH and consequently other chemical parameters. The lower reaches of the River Wear constitute a better buffered system with the pH values consistently in the region of 7 to 8. Increases in Ca and Mg in the lower stretches of the River Wear are mainly attributed to the influence of the River Gaunless (km 44.1). The remarkable consistency of pH in Brandon Pithouse acid streams illustrates a very different buffering system. The effects of pH have been shown in increasing the metal concentration (4.4.2) and reducing the relative accumulation of heavy metals (5.6.3). This is further discussed in 6.3.6 and 6.4.

TABLE 6.1 Summary of major chemical parameters affecting River Wear and tributaries; concentrations of elements in mg l^{-1}, n = 4

stream	reach	km	site	pH	Na	K	Mg	Ca	PO_4-P	NO_3-N
River Wear 0008	03	0.0	Wearhead	6.6	4.4	2.7	2.8	19.1	< 0.005	< 0.2
	75/76	78.1	Finchale Abbey	7.8	33.6	5.9	14.1	45.6	0.335	2.4
Rookhope Burn 0012	10/11	-0.5	North Grain Sike (stream 0115)	5.0	4.8	1.0	1.2	4.2	< 0.005	< 0.2
	60/61	-0.6	Eastgate	6.8	6.6	2.0	4.2	25.1	0.006	< 0.2
Brandon Pithouse Acid Stream A 0127	01	-3.6	source	2.6	12.9	1.0	61.4	59.4	0.35	0.4
	10	-1.6	site 11	3.5	85.6	6.9	65.0	84.0	0.048	1.1

6.1.3 Major cations

The four major cations found in the River Wear system are: Na, K, Mg, Ca. Rarely, were any of these elements encountered at concentrations of <1 mg l^{-1}. Lower concentrations of K were recorded in upland streams draining peat bog e.g. Wearhead (km 0.0) and North Grain Sike (- km 0.5). Concentrations of K as low as 0.04 mg l^{-1} have been recorded at the source of Brandon Pithouse Acid Stream A. It has been suggested that such a low concentration could be limiting to plant growth (Hargreaves *et al.*, 1975).

A steady increase has been shown in Na, K, Mg and Ca down the River Wear (4.1.2); this is well illustrated in Table 6.1 by the difference between Wearhead (km 0.0) and Finchale Abbey (km 78.1). Similar increases are obvious for Rookhope Burn and Brandon Pithouse Acid Stream A (Table 6.1).

The relatively low values recorded for major elements in North Grain Sike (- km 0.5) are not unusual in streams draining moorland. It has already been mentioned (6.1.2) that such poorly buffered streams present a very unstable chemical environment which could influence the availability of ions for accumulation by plants.

Concentrations of Ca and Mg are of particular importance in river systems for several reasons.

(i) Both elements contribute to the buffering capacity of natural waters (6.1.2) and have a major effect upon the precipitation of other ions. At

Wearhead (km 0.0) and Eastgate (- km 0.6), Ca values are high compared with moorland streams (Table 6.1). It is expected that the 'harder' water reduces the load of heavy metals carried by a river; marked decreases have been reported at Eastgate in Zn, Pb and Cd (Table 4.3). However, this decrease is by no means conclusive because of the effects of dilution (4.3.3).

(ii) It has been suggested that Mg and Ca play an important role in the stability of many chemical complexes in natural waters, particularly those involving other divalent cations (Stumm and Morgan, 1970).

(iii) The effects of Ca in reducing the toxicity of heavy metals to aquatic organisms are well documented (Carpenter, 1930; Jones, 1938). More recent studies have shown that both Ca and Mg can bring about a marked reduction in the toxicity of Zn to *Hormidium* spp. in 'normal' and low pH situations (Hargreaves and Whitton, 1977; Say and Whitton, 1977).

(iv) Table 6.1 shows that Brandon Pithouse Acid Stream A contains higher concentrations of Mg and Ca than any of the other streams studied. In other streams at <pH 3, very high concentrations have been recorded; Mg >2400 mg l^{-1}, Ca >500 mg l^{-1} (Hargreaves *et al.*, 1975). It seems reasonable to suggest that such high concentrations could affect the speciation and availability of other cations.

It is therefore clear that Mg and Ca, combined with effects of pH, can have an important effect on the chemistry of other divalent metals, consequently affecting the availability of these for uptake by aquatic plants.

6.1.4 Anionic nutrients

The concentrations of nutrient anions are very low in the upland parts of the River Wear system (Table 6.1). This factor is important in determining the occurrence of certain aquatic plants. It has been pointed out by Whitton (1970) that the genus *Cladophora* appears to avoid waters low in phosphate and nitrate. Similar considerations may well affect the presence or absence of other potential indicator species.

The concentration of nutrients is one among many factors affecting the rate of growth and productivity of aquatic plants. In the lower River Wear concentrations of dissolved forms of N and P are high (Table 6.1), and were especially high during the low flows of summer 1973 (4.2.3). Such high concentrations almost certainly affected the growth of a number of aquatic plants. Some effects of growth on accumulation and the use of certain species as indicators of heavy metals are discussed in 6.4.

It is also possible that high concentrations of dissolved forms of P affect the chemistry of other cations (1.2.2) in the lower stretches of the River Wear.

An example of the possible effect of phosphate on heavy metals has been given by Stumm and Morgan (1970). In the presence of a 10^{-2} M ligand ($H_2PO_4^-$), a 10^{-3} M solution of Fe^{3+} was precipitated at around pH 4.5 but precipitation did not occur until pH 7.5 of the ligand was citrate. This may be relevant to the situation in Brandon Pithouse Acid Stream A where high concentrations of PO_4-P are present (Table 6.1). In this case Fe^{3+} is precipitated at pH 3.5 to 4 and the dissolved orthophosphate is markedly reduced at the same time.

6.1.5 Organic compounds and colloids

Some of the possible effects of fulvic/humic complexes and their occurrence in the River Wear have already been noted (1.2.2). The coloured waters of upland streams such as North Grain Sike certainly contain large quantities of such compounds. Precipitation of brown organic material also occurred in some samples from the main River Wear after a few days and a reduction in heavy metal content was observed at the same time.

Other suspended and colloidal material also occurs in samples from the River Wear system especially at or just after periods of high flow. The effects of these and discharge on heavy metals are discussed in 6.2.

6.2 Aspects of the chemistry of heavy metals

6.2.1 Introduction

The main sources of heavy metals in rivers have been reviewed in 1.2.2. Three of the sources are clearly illustrated by the chemical data presented from the River Wear system (4.2.4, 4.3.3, 4.4.1).

(i) Past and present mining activities have given rise to elevated concentrations of Zn, Pb and Cd in the Weardale region of the Alston mineralised block.

(ii) An industrial effluent has caused increases of Zn, Pb and possibly Cd in the lower River Wear.

(iii) Acid drainage from Brandon Pithouse coal tip was shown to be associated with high concentrations of Zn, Cu, Mn, Fe, Al, Co and Ni.

Some suggestions can be made concerning the analysis and speciation of heavy metals together with other factors which have a bearing on the accumulation of these elements by aquatic plants.

6.2.2 Chemical speciation

It has been noted in 1.2.2 that there is a lack of easily applicable, practical methods of determining the state of heavy metals in river water. According to Wilson (1976) there is a general lack of understanding concerning the chemical form in which heavy metals are present. Biological interpretation of their effects therefore becomes even more difficult.

Before discussing the validity and interpretation of data from the River Wear System further clarification of the theoretical speciation of heavy metals in natural water is required. Table 6.2 shows such a classification as it applies to river water. The boundary lines between each section are not clear cut. The first two sections are almost entirely hypothetical arising from *in vitro* studies. Filtration or even dialysis to the 10 nm true aqueous solution level is not possible. Filtration to the 100 nm level also presents difficulties mainly through contamination (J.P.C. Harding, pers. comm.). Practical data, therefore, rarely coincide with the rigorous

TABLE 6.2 Theoretical classification of heavy metal species in river water (After Stumm and Bilinski, 1972)

FILTRABLE FRACTION		size
Truly dissolved	Free metal ions co-ordinated with water aquo solutions	
Inorganic complexes	Oxidation states of ions also complexes such as hydroxo and polyhydroxo	
		10 nm
Truly chelated complexes	Likely to be a very small proportion in river water	
Colloidal organic complexes	Such as Fe and Mn complexed with humic/ fulvic acids	
		100 nm
NON-FILTRABLE FRACTION		
Larger colloids	Such as hydroxides	
Dispersed solids and precipitates		1000 nm
Particulate matter	Suspended solids	
Large particulate matter	Includes algae etc.	

chemical analysis required to identify the chemical state of heavy metals in river water. Filtered samples may therefore refer to the removal of anything from large particulate material to larger colloids. Data presented in the present study refer to water passed through a No.2 'Sinta' funnel which has a maximum pore size of 45 μm. However, it should be pointed out that use of these filters gradually reduces the pore size such that particles of 10 μm are retained. However only particulate matter has been removed and data can therefore be defined as 'total' heavy metal concentration, including dispersed and colloidal material. There is some justification for using total values, as Keulder (1975) has shown an increase in Zn^{65} uptake by *Scenedesmus obliquus* in the presence of colloidal clays.

For heavy metal data to be useful and comparable, reasonable precautions regarding collection, filtration, contamination and storage must be observed (Wilson, 1976).

6.2.3 Validity of heavy metal data

Methods used in collection and storage of samples for heavy metal analysis have been described in 2.1 Some further comments are useful in clarifying the data, bearing in mind the foregoing statements regarding speciation.

(i) Maximum precautions were taken to avoid heavy metal contamination, by using acid soaked glassware.

(ii) Chemical change was kept to a minimum by carrying out heavy metal analysis on return to the laboratory.

(iii) Attempts to carry out full speciation were not made. However in some cases it is felt worth while speculating as to the possible form of heavy metals.

(iv) It seems likely in stream conditions that colloidal material may contribute to a pool of available heavy metals.

(v) Enrichment ratios have therefore been calculated on the basis of 'total' heavy metal defined in 6.2.2.

Certain anomalous results, recorded in 4.2.4, occurred in turbid samples, taken at high flows. It is probable that these data resulted from the presence of large colloidal or even fine particulate matter which could easily pass through a sintered glass filter. However it must be stressed that the majority of samples were taken at times of stable flow when the influence of such fractions is minimal.

6.2.4 Availability of heavy metals to aquatic plants

The likely importance of adsorption in uptake mechanisms (1.2.3.) may be fundamental in assessing the availability of heavy metals to aquatic plants. The possibility of adsorption or ion exchange from various chemical species present in water onto the plant surface was noted in 1.2.2.

Factors affecting this adsorption are the pH and oxidation state of the metal in question. Iron gives a clear example of changes in adsorption capacity; at below pH 3.5 Fe tends to be in the Fe^{3+} aquo form and not in its hydroxo complex $Fe(OH)_n$ and is much less strongly adsorbed at the lower pH (Stumm and Morgan, 1970). It seems reasonable to suggest that such a situation could exist in the conditions of very low pH in Brandon Pithouse acid streams although other factors must not be ignored. It has already been pointed out (6.1) that Ca and Mg or other competing ions as well as pH could influence the degree and type of inorganic complexation. Other factors including the presence of organic chelators and colloids could also affect the adsorbative properties of any given metal ion. Such physico-chemical phenomena must have a profound influence upon the availability of heavy metal ions for adsorption.

The presence of fulvic/humic acids in the River Wear, particularly its upper catchment, has already been mentioned in 6.1.5. Such compounds are known to have a 'solubilising' effect upon heavy metals (1.2.2). It is not yet clear whether the heavy metals held by these organic complexes (as opposed to inorganic complexes) are more or less available to aquatic organisms. However the processes involved are likely to be either adsorption or ion exchange at surface interfaces.

6.2.5 Effects of discharge on metal concentrations in the River Wear system

Discharge has already been shown to have a marked effect on the concentration of certain metal ions in most areas of the River Wear System (4.2.2, 4.3.2). It is thus an important parameter in controlling the concentration of metal ions surrounding aquatic plants.

According to Wilson (1976) the overall picture of the relationship between metal concentration and discharge is inconsistent. However, clear inverse relationships between discharge and concentration were noted for both the River Wear and Rookhope Burn, in 4.2.2 and 4.3.2, for K and Mg. Positive relationships were noted for Fe, Mn and Al in Rookhope Burn (4.3.2) but not in the lower River Wear for the same elements. The positive relationship in Rookhope Burn can be explained by increased run-off from the surrounding moorlands. These elements in particular are known to form complexes with the organic compounds associated with run-off from peat areas (1.2.2). Such an explanation is consistent with the hypothesis put forward by Hellman (1970) and Wilson (1976) that there is a decrease in the filtrable fraction with dilution and an increase in the non-filtrable fraction as discharge increases. This relationship is masked in the lower River Wear by the increase in run-off from non-peaty sources.

The situation for Zn and Pb is more complicated. Zn tends to increase with decrease in discharge where it is relatively high in concentration (0.2 mg l^{-1}) in Rookhope Burn (Fig. 4.8) but in very dilute solution (<0.02 mg l^{-1}) in the lower River Wear, this increase is not apparent (Fig 4.5a). Pb shows no clear relationship at either Eastgate (km -0.6) or Sunderland Bridge (km 58.3). This could well reflect its unstable chemical state.

The influence of discharge on the availability of metals to plants has yet to be clarified although some changes in equilibria and chemical speciation must occur. For example Hellman (1970) has pointed out the relatively minor effect whereby the amount of Zn adsorbed by suspended material decreases with increasing flow. Such a situation could well apply to other surface interfaces such as adsorption onto the surface of aquatic plants. Although the overall effect of increasing non-filtrable clay colloids may well increase the amount of exchangeable cations available (Keulder, 1975).

6.3 Accumulation of heavy metals by aquatic plants in relation to their use as monitors

6.3.1 Introduction

It has been suggested (1.2.3.) that the literature supplies some evidence for the practical use of aquatic plants as indicators of heavy metals. This was partly based on the ability of many aquatic plants to adsorb divalent heavy metals onto their surface.

It seems reasonable to suggest that a considerable proportion of the total heavy metal is available for such adsorption or ion exchange (6.2.4.). Subsequent steady assimilation into the cells has been suggested as a later stage in the uptake mechanism for several divalent heavy metals, notably Zn^{65} (1.2.3). Bearing these two processes in mind, the claim that many aquatic organisms can quantitatively indicate and integrate the concentration of a number of trace elements in their environment (Goldberg, 1965) seems probable.

The selection of suitable indicator plants in fresh running waters therefore relies, to a large extent on the enrichment ratios (1.2.3.). It is expected that these ratios will remain the same if the conditions affecting the plant and the water also remain constant. Direct use of this can be made in monitoring specific sites (6.3.8). Where variation in the ratio is encountered it is useful to suggest certain parameters affecting this so that within limits the plants concerned could still be used as indicators. Some of the factors affecting accumulation of heavy metals are therefore particularly relevant. An overall assessment of the advantages and limitations of potential indicator plants can now be given in the light of other work.

6.3.2 Factors affecting the accumulation of heavy metals by algae

Some comparisons can be made with data from the literature in an attempt to define some of the factors which affect the accumulation of heavy metals by algae.

Data have been restricted to fresh water algae as it is felt that the situation in the marine environment, especially concerning the chemistry of heavy metals in the water, is too different for valid comparison.

In many cases radioactive isotopes such as Zn^{65} have been used in both experimental and field situations to establish the relative accumulation of the stable isotope. Enrichment ratios (concentration factors) are the usual way of expressing this accumulation (1.2.3). In general the data vary greatly from species to species or even within the same species.

Data are presented in Table 6.3 to show the mean enrichment ratios for heavy metals in a number of

TABLE 6.3 Heavy metal enrichment by freshwater algae.

organism	area	reference	Zn	Cu	Pb	Cd
Cladophora glomerata	R. Wear	Present study	14500	1900	8300	16000
Cladophora glomerata	Deadman Bay, Ontario	Keeney *et al.*(1976)	2900	2200	16000	49000
Cladophora glomerata	Main Duck, Ontario	"	1000	1900	20000	18000
	Lake Erie	"	-	1000	-	-
	Spokane River	"	-	2500	-	-
	U.S.S.R.	Timofeeva-Resovskaya *et al.* (1961)	-	-	-	17400
Cladophora fracta	U.S.S.R.	"	-	-	-	16200
Mougeotia sp.	Rookhope Burn	Present study	1000	2000	1700	-
Mougeotia sp.	U.S.S.R.	Timofeeva-Resovskaya *et al.* (1961)	-	-	-	36600
Spirogyra sp.	Rookhope Burn	Present study	24500	1920	13400	-
Spirogyra sp.	U.S.S.R.	Timofeeva-Resovskaya *et al.* (1961)	31500	-	-	-
Stigeoclonium tenue	Rookhope Burn	Present study	7600	2300	5800	-
Lemanea fluviatilis	" "	" "	8000	5800	14500	-

fresh water algae from the River Wear system, compared with similar organisms from the U.S.S.R. (Timofeeva-Resovskaya, *et al.* 1961) and Canada (Keeney *et al.*, 1976). Timofeeva-Resovskaya *et al.* (1961) calculated the ratios from radioactive isotope data, whereas field information was used by Keeney *et al.* to calculate their ratios.

All data presented show considerable enrichment of all four heavy metals. Considerable differences in ratio are obvious for *Cladophora glomerata*; Zn ratio is much higher in the River Wear than at the Canadian sites. On the other hand, Pb ratios are lower in the Wear; whereas those for Cd are of the same order of magnitude. This variation in ratio is not unexpected as some chemical and physiological parameters are likely to be very different between the various sampling areas. Ratios for Cu are remarkably similar. This might indicate a similar availability despite variation in other factors.

Spirogyra sp. from Rookhope Burn shows a similar enrichment ratio for Zn, to that of a *Spirogyra* sp. from the U.S.S.R. but data for the other heavy metals are not available for comparison.

Three species from Rookhope Burn all show marked enrichment of Zn and Pb (5.5.2): *Lemanea fluviatilis* *Spirogyra* sp. *Stigeoclonium tenue*. *Mougeotia* sp. from Rookhope Burn shows low enrichment of Zn, Cu and Pb but considerable enrichment of Cd in the species from the U.S.S.R.

There are insufficient data, particularly for important chemical parameters to draw conclusions concerning the factors affecting accumulation. Further research into the range of enrichment ratios and factors such as pH and the concentration of major ions would help establish specific effects on accumulation.

Experimental data in the fresh water environment are sparse. Harvey and Patrick (1967) found concentration factors for Zn^{65} in the region of 3000 to 4000 for three species of green algae grown in continuous culture. These data fall within the range of enrichment ratios for green algae given in Table 6.4. They also concluded that uptake may be related to surface/volume ratio rather than taxonomic group. This may have some bearing upon the variation in enrichment ratios encountered. For example, *Cladophora glomerata* sampled in the River Wear was always highly branched thus increasing its surface area/volume ratio consequently increasing the area for adsorption of metal ions and possibly the overall accumulation.

Among the few fresh water experimental data are those of Gileva (1964) who carried out ratio-active isotope experiments with *Cladophora fracta* including the heavy metal Zn. This author found enrichment ratios were remarkably stable at concentrations of 10^{-4} M, or less, for a number of elements. He concluded that at these low concentrations the concentration within the plant depends entirely on the concentration in the surrounding medium. Unfortunately the concentrations used for Zn were so high that the data show a reduction in enrichment ratio due to saturation. Nevertheless the principle of proportionality between plant concentrations and low concentrations of elements in the surrounding medium was clearly demonstrated under closely defined experimental conditions.

6.3.3 Algae as monitors of heavy metals

It has already been noted (1.2.3) that a number of authors have suggested the use of algae, particularly green filamentous algae as possible quantitative indicators of heavy metals in fresh water.

One of the chief limitations in attempting to find indicator plants is their distribution. No single species of macrophytic alga exists throughout the River Wear system. This necessitates the use of different plants in different circumstances and brings about the problem of selection of suitable species.

In the present study most attention has been devoted to the use of *Cladophora glomerata* as a monitor of the industrial effluent (km 76.6) in the lower River Wear. This study (5.2.3) clearly illustrates the proportional relationship between the heavy metals Zn and Pb in the water and the plant. The concentrations accumulated (up to 500 $\mu g\ g^{-1}$ Zn and 100 $\mu g\ g^{-1}$ Pb (dry weight) show the advantage of analysing the plant since concentrations in the water were low (0.024 $mg\ l^{-1}$ Zn and 0.009 $mg\ l^{-1}$ Pb; maximum). The effect of the effluent also became obvious (Figs 5.4 and 5.5); the concentration of Zn almost doubled in most cases, relative to the site upstream of the effluent and the concentrations of Pb and Cd were also significantly increased.

The widespread occurrence of this alga in the nutrient rich parts of the River Wear system and also in many other rivers, could allow its use as a monitor to to be extended. However, there are limitations which must be taken into consideration.

(i) Differences in morphology and rate of growth could alter the amount of heavy metal accumulated. Careful selection of the plant is necessary when sampling to ensure that qualitatively similar plants are selected (2.2.1, 5.2.1).

(ii) The distribution of the plant tends to be restricted to areas of high nutrient and it has been suggested that *Cladophora glomerata* cannot withstand high concentrations of heavy metals (Whitton, 1970).

(iii) The occurrence of the plant is seasonal it occurs in the River Wear from March to November. It also tends to have two distinct growth peaks in spring and autumn (Whitton, 1970). There may also be a marked decrease during the hottest months (Whitton, 1970) at which time it becomes easily removable by summer floods, as occurred in 1973.

Preliminary metal composition and accumulation studies carried out, revealed other algae displaying a potential for use as monitors of heavy metals.

Lemanea fluviatilis (5.5.2) is widespread in both heavy metal polluted and unpolluted sites in the upstream part of the River Wear system. Investigations carried out on this organism by Leeder (1972) in Rookhope Burn and in the present study showed that this organism accumulates large concentrations of heavy metals, notably Zn and Pb. In a survey of *Lemanea fluviatilis* at sites in Britain and Europe J.P.C. Harding and B.A. Whitton (pers. comm.) have shown good correlation between Zn concentrations in plant and water. They have also found, in field experiments that the alga reflects very rapid changes in Zn concentrations in the water.

Other algae collected did not show the same potential for a variety of reasons. *Vaucheria sessilis*, although widespread in the lower Reaches of the River Wear was always associated with large amounts of silt (2.2.2); the rigorous and time consuming washing procedure precluded its use as an indicator organism. Algae of a transient nature such as *Enteromorpha flexuosa*(5.1.2), *Stigeoclonium tenue*, *Mougeotia* sp. and *Spirogyra* sp. (5.5.2), although showing measurable quantities of heavy metals do not grow for sufficiently long periods to be realistic monitors other than in exceptional circumstances.

Algae, in general, show a number of advantages as monitors of heavy metals. These organisms can obtain their nutrient only from the surrounding water (Davis *et al.* 1958). It is clear that they can accumulate large concentrations of apparently useless but toxic heavy metals such as Pb and Cd. This is important because both of these elements are particularly toxic and cumulative poisons in mammals (Bowen, 1966).

Furthermore, many of these algae should integrate the concentration of heavy metals over the time period of growth, as illustrated by *Cladophora*, thus levelling out fluctuations in water chemistry. Selected species can, therefore, be used as an adjunct to, if not a total replacement for, analysis of the water, as already suggested (1.1). Where concentrations in the water are normally so low as to be difficult to detect, the ability of these organisms to concentrate heavy metals is of obvious value, especially as occasional 'flushes' of heavy metals are likely to be retained by the plant material.

6.3.4 Factors affecting the accumulation of heavy metals by bryophytes

The age and morphology of bryophytes have a very considerable effect upon the amount of heavy metals accumulated. The increases in concentration in older material have an obvious effect upon the enrichment ratio which also increases in the older parts of the plant (5.3.2).

It is also noticeable that the majority of bryophytes studied accumulate heavy metals, particularly Mn and Fe much more than any of the algae or angiosperms studied. Similar enrichment of heavy metals in bryophytes has also been noted by Dietz (1973). He suggested in the case of both Mn and Fe that the elements are not necessarily completely incorporated but may be bound to the surface as iron hydroxides or manganese oxihydrate. Such purely physical accumulation is likely to reduce the effectiveness of these plants as indicators for Mn and Fe, as the accumulation is not dynamic.

Dietz (1973) has also calculated enrichment ratios for a number of trace elements including the heavy metals, Zn, Cu and Pb in *Fontinalis antipyretica* and *Hygroamblystegium*; the species name is not given for this organism but it seems reasonable to assume that it is the common river moss *H.fluviatile* . Accumulation data for these elements and species including the range of enrichment ratios and water chemistry are compared with similar data for *Fontinalis* from the River Wear (Finchale Abbey, km 78.1) in Table 6.4.

The range of water chemistry data quoted for the River Ruhr is greater than that for the River Wear. This gives a wide total range of water chemistry for the two areas: Zn 0.009 to 0.28, Cu 0.003 to 0.10, Pb 0.005 to 0.27 mg l^{-1}. Both range and mean enrichment ratios shown for *Fontinalis* are remarkably similar for all three heavy metals. This is all the more surprising as none of these samples were divided. The similarity of enrichment ratio encountered for *Fontinalis* over the wider range of heavy metal concentration might imply that the plant can act as an indicator over a broader range of chemical parameters. Sufficient chemical data is not given to demonstrate this clearly.

Hygroamblystegium shows enrichment ratios of a similar order to the other moss. However enrichment of Cu and Pb are higher. This moss, although present in the River Wear, was not analysed.

In general terms these data help to confirm the hypothesis put forward by Dietz (1973) that 'enrichment of minor elements in water plants is a useful criterion to calculate the average concentration of these elements in water'.

Some experimental work has been carried out using Zn^{65} in *Fontinalis antipyretica* (Pickering and Puia, 1969) in an attempt to establish the mechanism of uptake. These

TABLE 6.4 Comparison of accumulation of heavy metals by aquatic mosses.

Concentrations in water in mg l^{-1}, enrichment ratios calculated on dry weight basis

			Zn				Cu				Pb			
			enrichment ratio			Water	enrichment ratio			Water	enrichment ratio			Water
organism	area	reference	min	max	mean	range	min	max	mean	range	min	max	mean	range
Fontinalis antipyretica	River Ruhr	Dietz (1973)	21600	61800	54400	0.01-0.28	5100	7680	6300	0.01-0.10	18720	19500	19200	0.01-0.27
Fontinalis antipyretica	River Wear	present study	45500	65700	58600	0.009-0.018	3500	7600	5800	0.003-0.007	18000	31200	22000	0.005-0.011
Hygroamblystegium fluviatile	River Ruhr	Dietz (1973)	20160	34200	22500	0.01-0.28	17100	35100	2500	0.01-0.10	37800	47700	41400	0.01-0.27

authors have shown that Zn taken up from the water is strongly bound to the plant cells; only 5% of the Zn^{65} activity was released after repeated washing with distilled water. Concentration factors were also found to be stable from 10^{-4} to 10^{-2} mM (0.0065 to 0.5 mg l^{-1}). At higher concentrations a marked decrease in ratio occurred. These data are essentially similar to those found by Gileva (1964) for *Cladophora fracta* (6.3.2). Such experimental evidence helps to confirm the ability of aquatic plants to accumulate heavy metals, at low concentration, in proportion to the concentration of the surrounding medium.

6.3.5 Bryophytes as monitors of heavy metals

Unlike most algae, bryophytes do not necessarily obtain their nutrient only from the water. The so called 'copper masses' are well known as indicators of heavy metal in the substratum to which they are attached (Shacklette, 1967). In this respect aquatic bryophytes, closely appressed to the rock surface such as *Fissidens crassipes* are less likely to be good indicators of the water because of the possible influence of the substratum on heavy metal concentrations.

One advantage in selecting bryophytes is that a number of species are extremely widespread. *Fontinalis antipyretica* and *Eurhynchium riparioides* occur throughout the length of the River Wear (Holmes and Whitton, 1977), and many of its tributaries. Both plants therefore tolerate a very wide range of nutrients and changes in other chemical parameters (6.3.4.). Neither moss however occurs in Rookhope Burn although this is not necessarily related to the high heavy metal content of the river. *Scapania undulata* and *Philonotis fontana* are often found in heavy metal polluted areas of the River Wear system and the adjacent River South Tyne catchment (Say, 1977). One species is particularly tolerant of low pH; *Drepanocladus fluitans* occurs in North Grain Sike (Rookhope Head) at pH < 5 and thrives in Brandon Pithouse Acid Stream at pH < 3.

A further advantage in the selction of bryophytes for monitoring heavy metals is the tendency to be firmly attached and permanent parts of the aquatic vegetation.

A number of species were ruled out because of contamination and cleaning problems (2.2.2). Unfortunately, this included the widespread *Eurhynchium riparioides*. However, if a rapid method of removing grit from the thallus could be found, this moss would certainly be worthy of further investigation, particularly since the few analyses carried out indicated high concentrations of Zn, Pb, Co and Ni.

One of the most important factors affecting the use of bryophytes as indicators of heavy metals is the distribution of elements through the thallus illustrated by *Fontinalis* (5.3.2) and *Drepanocladus* (5.6.3). In general, the lowest concentrations of heavy metals occur in the tip of these mosses and the highest concentrations in the oldest material close to the point of attachment of the plant. The most consistent data are obtained from the tips since these appear to be the most actively growing part of the plant. The time period which the tips reflect should obviously be the most recent. It is felt that it would be of some use to establish the rate of growth in the field in order to gain a clearer idea of the time period over which metals might be integrated into the plant. The length of tip sampled would then be of more relevance.

Most species of aquatic bryophyte can tolerate drying out when exposed at periods of low flow e.g. *Eurhynchium riparioides Fissidens crassipes* . From the point of view of indicators, mosses which are frequently exposed, such as *Grimmia alipcola* are less useful since they can only indicate heavy metal concentrations while submerged. This imposes a further limitation in the selection of suitable species. As far as possible fully submerged species such as *Fontinalis antipyretica* should be chosen. In the present study examination of the sites at the lowest flows during the summer months enabled the identification of permanently submerged areas; samples were taken only from these areas.

A further advantage in selecting *Fontinalis antipyretica* is that its attachment is well away from the growing shoots, reducing the possibility of contamination from the substratum. Rigorous application of the criteria given should help in selecting the most suitable species for quantitative studies.

Other authors have used aquatic bryophytes as indicators of heavy metals in river water, notably Dietz (1973), whose data have been discussed (6.3.4).

Recently Empain (1976a) has used a number of bryophytes species, including *Fontinalis antipyretica* and *Fissidens crassipes* to indicate levels of heavy metals in the River Somme. This author does not give any details of the chemistry in the water. Nonetheless the data provide an interesting comparison with concentrations found in the River Wear.

The ranges of concentration found in *Fontinalis* for Cu. Mn, Fe, Pb, Cd, Co and Ni are similar if slightly lower than those found in samples from the River Wear (A.2H). For example, in the River Somme, Cu ranges from 15 to 77 $\mu g\ g^{-1}$ dry weight and Pb from 40-90 $\mu g\ g^{-1}$ dry weight. However, *Fissidens* from the River Wear (A.2A) shows markedly higher concentrations of all seven elements than those from the Somme.

Further studies have been carried out on the Rivers Sambre, Meuse and Somme (Empain, 1976b). Profiles of the heavy metal content were produced for several bryophytes from samples taken at intervals down the rivers. These were compared with profiles for the water and sources of heavy metal pollution. He found that aquatic bryophytes, including *Fontinalis antipyretica* integrated the broad variations of concentration of a number of heavy metals in the water. Direct comparison of his data with those from the River Wear system is not possible because of the generalised form of the profiles.

6.3.6 Factors affecting the accumulation of heavy metals by aquatic angiosperms

Apart from variation in the heavy metal content of the water discussed in 6.2.2 and 6.2.4 which applies to all aquatic plants, the most important factor affecting the accumulation of heavy metals by angiosperms is their morphology and means of obtaining nutrients from the water. Sculthorpe (1967) has classified aquatic angiosperms according to their principal growth forms.

Two principal types are encountered in the present study.

(i) Emergent hydrophytes which are rooted in the substratum, such as *Mimulus guttatus* and *Juncus effusus*.

(ii) Submerged hydrophytes which are also rooted in the substratum but with vegetative parts almost completely submerged, such as *Ranunculus penicillatus* var. *calcareus* and *Potamogeton crispus*.

It is not clear in the literature reviewed by Sculthorpe (1967) to what extent plants in the first category are able to obtain nutrients and trace elements directly from the water through the vegetative parts. Adams *et al.* (1973) acknowledged this problem but nevertheless suggested that such plants could still be of value as monitors in the absence of other more suitable species. In the present study, enrichment ratios have been calculated only for the submerged parts. In the case of *Mimulus guttatus* (5.5.4) marked accumulation of Zn and Pb was noted but enrichment ratios were very variable. Leeder (1972) gave very similar results for this species, also in Rookhope Burn. In such cases concentrations in the sediment could well have a distinct effect upon the amounts of heavy metal accumulated.

Many species of submerged hydrophytes can take up nutrients including heavy metals, via both shoots and leaves as well as through the roots (Adams *et al.*, 1973) although the pathways of uptake and movement of nutrients through individual species have not been clearly established (Sculthorpe, 1967). In the study of *Ranunculus penicillatus* var. *calcareus* (5.4) Zn was consistently highest in the leaves, Cu was more or less consistently distributed, Fe, Al and Pb are among the elements with the least stable compounds in water and likely to be found in higher concentration in the sediment whereas Zn, being more soluble, might be more available to the leaves. These assumptions require further research particularly regarding the importance of sediment as a source of mineral elements to rooted aquatic plants and the relative importance of uptake of trace elements directly from the water by the vegetative parts. In his study of enrichment of heavy metals by aquatic plants, Dietz (1973) gives no indication of the distribution of these elements in the different species studied, basing the analysis upon green parts only. The data on elemental composition given by Adams *et al.* (1973) is based on entire plants. Comparison of these data are therefore not possible. However it is interesting to note that the enrichment ratios given by Dietz for Zn, Cu and Pb in the green parts of *Ranunculus fluitans* are very similar in range and mean to those presented for the leaves of *Ranunculus penicillatus* var. *calcareus* from the River Wear.

6.3.7 Aquatic angiosperms as monitors of heavy metals

Aquatic angiosperms have not received the same attention in the present study as aquatic algae and bryophytes. Nevertheless, some comments regarding their use as indicators of heavy metals are pertinent.

(i) Fully submerged plants are likely to give a better indication of the surrounding water than emergent types; the only example given is *Ranunculus penicillatus* var. *calcareus* (5.4). The emergent *Mimulus guttatus* showed very much reduced concentrations of heavy metals in its aerial parts whereas the submerged leaves of *Ranunculus* showed the highest concentrations of these elements.

(ii) The leaves of submerged plants particularly *Ranunculus* give the best indication of heavy metals probably because of the large surface area exposed to the water.

(iii) Many suitable submerged plants are restricted in their occurrence; these plants are rarely found in the smaller upland streams. In the River Wear, *Ranunculus* spp. do not appear until km 26; other submerged species such as *Elodea canadensis*, *Myriophyllum spicatum* and *Potamogeton* spp. show a similar distribution pattern (Holmes and Whitton, 1977).

(iv) It has been pointed out by Adams *et al.* (1973) that individual species may be exceptionally sensitive to particular pollutants. They selected three species for further study in relation to monitoring nutrient pollution including heavy metals. The species chosen were: *Elodea canadensis*, *Potamogeton crispus* and *Myriophyllum exalbescens*. The two former are of common occurrence in the River Wear and many other British rivers. Further investigation of these together with *Ranunculus penicillatus* var. *calcareus* and *R. fluitans*, which are also very common might prove fruitful. Dietz (1973) has also investigated a number of aquatic angiosperms in relation to the accumulation of heavy metals, including *Ranunculus fluitans* and *Myriophyllum spicatum*, finding these species suitable for monitoring heavy metals (6.3.6).

A wide variety of aquatic angiosperms may well have the potential to be used as monitors of heavy metals in rivers.

6.3.8 Monitoring industrial effluent

The present study has shown that the monitoring of a specific effluent is a workable possibility using aquatic plants. This is chiefly because the factors affecting the lower stretches of the River Wear, particularly below Durham, are much the same. Certain advantages and limitations are worth mentioning concerning species used.

Certain species can be used to keep a continuous check on the effluent over most of the year, especially during periods of low flow when pollution would be most serious.

Analysis of *Cladophora glomerata* and the water have indicated that this alga could be used as a reliable indicator of at least Zn and Pb (5.2.3) and probably Cu, Cd and Ni even when concentrations of these elements are difficult to detect in the water. Serious increases in any of the above mentioned heavy metals seem almost certain to show up in plant material.

The tips and other sections of *Fontinalis antipyretica* also appear to indicate changes below the effluent although the sections probably represent longer time periods than *Cladophora glomerata*.

Despite increases in Zn, Pb and Cd which appear to have been up to 100% in plant material below the effluent (6.3.3), the effects seem to be short-lived; plants at Finchale Abbey (km 78.1) showed no apparent signs of elevated heavy metal content during the period of study.

The long term effects of such effluents are difficult to predict but careful monitoring using *Cladophora glomerata* or *Fontinalis antipyretica* would be especially useful in ensuring that any serious pollution could be identified.

The major limitation in the use of plant species concerns the length of the growing season. The two plants mentioned thrive from March to November; it is therefore only the winter period when monitoring could not be carried out. Limitations of the individual plants and the effects of chemical factors have been discussed in the appropriate sections (6.2, 6.3.3).

6.3.9 Accumulation in an environment of low pH

Up to now little attention has been focused on the accumulation of metals at low pH (<3). The present work gives a preliminary study of the accumulation by a range of aquatic plants found in Brandon Pithouse acid streams. It has not been found possible to draw any firm conclusions from the type of data presented but some tentative suggestions can be made regarding the parameters affecting accumulation and guidelines for further research.

The concept of using plants as monitors of heavy metals may still apply in situations of low pH but the marked reduction in enrichment ratios in all species and for most of the heavy metals studied would restrict its use to similar situations.

The importance of the study lies more in the use that can be made of the information obtainable from an extreme and stable environment in improving the understanding of the complex ecosystems of more typical rivers and streams (Whitton, 1972).

The stability of Brandon Pithouse acid streams assists accumulation studies because important parameters such as pH nutrient and metal content remain relatively unchanged (4.4.1).

The low enrichment ratios found for heavy metals in acid stream plants (5.6.2) are of great interest. There is some evidence to suggest that the reduction in ratios for *Drepanocladus fluitans* is related to pH (5.6.3); marked increases in ratio occur at sites of increasing pH although the absolute concentrations of most elements do not change very much.

It is only possible to speculate as to the reason for the reduced enrichment. However, there are several possibilities.

(i) A mechanism exists in these extreme conditions which allows the aquatic plants present to reject the large concentrations of heavy metals surrounding them. Hargreaves and Whitton (1976) have suggested, in laboratory toxicity studies of *Hormidium rivulare* (acid stream population), that an active mechanism may be involved in the resistance of this alga, at low pH to high concentrations of Zn.

(ii) Heavy metals are not available for uptake because of marked changes in chemistry brought about by the low pH. It has been suggested that many cations exist in true aquo solution at pH <3 and that these ions are not as well adsorbed as other inorganic complexes (1.2.2). At higher pH values in more 'normal' streams a large variety of organic complexes and colloids are present from which adsorption and ion exchange can freely occur. As the primary mechanism for uptake of a number of cations probably relies upon some ion exchange adsorbation process (1.2.3), lack of suitable complexes and colloids could consequently reduce the uptake by plants. It is most noticeable in the Brandon streams that there is a lack of coloured organic compounds.

(iii) Under the prevailing conditions the plants are approaching a saturation level of heavy metals thus reducing the enrichment ratio. Saturation levels have been encountered experimentally in accumulation studies (Gileva, 1964; Pickering and Puia, 1969). However, the concentrations of elements are not unusually high in acid stream plants and considerably higher concentrations of many elements have been recorded for *Drepanocladus fluitans* at a site elsewhere.

(iv) Saturation by similar elements might reduce uptake of heavy heavy metals e.g. Mg and Ca are both present in very high concentrations at low pH (6.1.3). It has been suggested by Say and Whitton (1977) that Ca can compete with Zn for uptake in such a way as to reduce the toxicity of the latter to *Hormidium rivulare*.

(v) The concentration of H^+ ions directly reduces the accumulation. Bachmann (1963) found that Zn^{65}

uptake by *Golenkinia paucispina* cells was reduced more by the concentration of H^+ ions than Ca^{2+}, Mg^{2+}, Na^+, and K^+, in that order.

There is an obvious need to clarify the availability and means of uptake of heavy metals by plants from situations of low pH. It is felt that this might be best achieved with radio-active isotope studies.

The absolute concentrations of most elements in acid stream plants are, in most cases, of the same order as similar plants in non-acid environments, except that in all cases Na concentrations are high. A marked reduction in Na concentration, at sites of increasing pH, occurs in *Drepanocladus fluitans* although the significance of this is not immediately clear (5.6.3). Further field studies over as wide a range of pH as possible, might well prove profitable in establishing more fully the effects of this factor on the composition and accumulation of aquatic plants not only in acid conditions but also in a wider field.

6.4 General Conclusion

The use of aquatic plants as quantitative indicators of heavy metals relies on the ability to take up elements proportionally from the available supply in the surrounding water. Sufficient heavy metal must be retained and permanently accumulated to allow integration of the concentration over a given time period.

The simplest way of determining this ability is to calculate the 'enrichment ratio' (1.2.3). However, the use of this ratio oversimplifies the true situation in river waters. A variety of factors affect both the concentration in the water and that in the plant.

It is not clear which chemical species or combination of species is available for uptake from the water (6.2.4). Truly dissolved 'aquo' ions may only form a relatively minor proportion of 'normal' river water. The proportion is likely to be higher in conditions of low pH such as those encountered in Brandon Pithouse acid streams, because of the influence of hydrogen ion concentration. These compounds may not be as available because of the lower capacity of adsorption compared with the hydroxo and polyhydroxo complexes which form at higher pH values (6.2.4).

In general, running waters are unlikely to be composed entirely of these relatively simple, pH dependent inorganic species. Most streams are subject to influxes of a range of natural organic compounds such as the fulvic/humic complexes which have the ability to 'solubilise' heavy metals (6.1.5 and 6.2.4). Furthermore many of these complexes do not necessarily act as simple chelators but may well have colloidal properties. Physico-chemical phenomena of surface exchange and adsorption must have a considerable influence on the availability of all metal ions.

Artificial organic compounds such as pesticides and detergents are also capable of affecting the availability of metal ions. These influences are likely to affect downstream stretches where sewage and industrial effluents together with run-off from arable land tend to increase.

Rivers are also subject to periodic influences of larger colloidal material such as clay minerals. These influxes are often brought about by increase in discharge (6.2.5). It has been suggested that such colloids could increase the surface interactions and therefore bring about increased availability (6.2.5). Even particulate matter could act as an ion exchange reservoir for some heavy metals.

Individual metals may be available in some or all of the above mentioned species. It appears that pH has a fundamental role in the control of side complexations and surface phenomena. Anionic compounds, particularly those of Γ, can also profoundly affect such reactions (6.1.4). Competition between metal ions can also occur in all species, depending upon the proportions of ions present. Easily exchangeable cations, such as Ca and Mg, seem to be particularly important in this respect (6.1.3, 6.2.4, 6.3.9).

All these factors are embraced by the term 'total heavy metal' concentration; the proportions of chemical species differ widely from one stream to another and therefore contribute to the variation of enrichment ratios encountered in the different areas studied.

Empain (1976b) has suggested that accumulation by aquatic bryophytes, actually 'helps in the discrimination of truly available heavy metal, as opposed to total heavy metal concentration'. However, it is important to establish accumulation over a range of chemically different environments, as this helps to elucidate some of the key factors controlling accumulation.

Studies with radioactive isotopes, such as those of Cross *et al.* (1971) have demonstrated that accumulation of Zn^{65} differs from total Zn, probably because of the different availability of the latter in the water (1.2.2).

It has been suggested that chemical speciation might be important in the reduced accumulation in an environment below pH 3 (6.3.9).

There are another set of factors which affect the enrichment ratio as a measure of accumulation. These apply to the plants themselves. It seems fairly certain that ion exchange and adsorption processes are the primary mechanism of uptake of at least divalent heavy metals. This applies to plants unaffected by absorption of ions from the substratum, chiefly algae, some bryophytes and a few angiosperms (1.2.3, 6.2.4, 6.3.1, 6.3.4). However, a proportion of heavy metal may be lost with a change in equilibrium. For example, J.P.C. Harding (pers.comm.) has shown that up to 20% Zn may be lost from *Lemanea fluviatilis* in the field when the Zn concentration of the water decreases after a 'flush' of high concentration. On the other hand, Pickering and Puia (1969) found only 5% loss of Zn^{65}, in experimental situations, when *Fontinalis antipyretica* was transferred to distilled water. This may reflect the difference in uptake of radioactive isotopes compared with uptake from available chemical species in the field mentioned previously and reinforces the need to establish factors controlling availability. However, a slower secondary, energy dependent, binding process has been established for a number of heavy metals in a range of organisms, under experimental conditions (1.2.3).

In the field, there are a number of factors which could affect the rate at which this process might occur, including temperature, oxygen concentration, nutrients and pH. These factors also affect the rate of growth of plants and consequently the time period over which the latter could integrate the heavy metal concentration. The growth rate of *Cladophora glomerata*, in the field, is faster than that of *Fontinalis antipyretica*. These two organisms are therefore likely to indicate the concentrations of heavy metals over different time periods. A short tip of *Fontinalis* might represent a longer period than a young growth of *Cladophora*; differences were noted in the pattern of accumulation above and below the industrial effluent (5.3.2).

Differences in morphology and growth caused by external factors are also likely to alter the enrichment ratio of plants of the same species. Radically different chemical situations were found between the sites in Rookhope Burn (4.3.3). This apparently affected the growth and habit of *Scapania undulata* and *Hygrohypnum ochraceum* and possibly the enrichment ratios. A difference of several orders of magnitude were found at the different sites (5.5.3) for these species.

Enrichment ratios should be similar in situations where physiological and external parameters, other than the concentration of metals, are also similar; simple quantitative monitoring then becomes possible. This was best illustrated by the linear relationships for Zn and Pb found between *Cladophora glomerata* and the water (5. 2.3). It seems likely that a similar relationship exists for Cu and Cd (5.2.3) probably for other heavy metals such as Co and Ni.

In order to use aquatic plants as indicators in a broader way it is necessary to be able to predict enrichment ratios from a knowledge of the key chemical factors in the environment and the physiological state of the selected species. If *Cladophora glomerata* is chosen as an indicator species the restrictions imposed by its physiology should help to reduce the variation in enrichment caused by environmental parameters. For example, *Cladophora* in the field has a restricted pH range, rarely growing at pH <7 (Whitton, 1970). This factor and others associated with it are therefore of minor importance in affecting enrichment ratios. In well buffered situations with high Ca and Mg as well as high nutrients (6.1.2) these factors are also likely to assume less importance. It is possible that the variation, in ratio, in this case, is mainly attributable to physiological factors, including age, contamination with epiphytes and variation in morphology. Apart from adopting strict qualitative criteria in sampling, (2.2.1, 5.2.1), the macro-element content might give a guide to the physiological state of the sample. It is most noticeable that Mg concentrations are consistently in the region of 2000 $\mu g\ g^{-1}$ dry weight. However the sample from the most upstream site in the River Wear (Wolsingham, km 24.3) showed a content of 5500 $\mu g\ g^{-1}$ dry weight. Detailed experimental work might establish whether this or other macro-elements could be used in the standardisation of samples.

If simple criteria could be established for determining the physiological state of any plant, data from a much wider range of sites would be comparable and many rivers could be simply monitored for heavy metal content.

It has already been pointed out (6.3.5) that a number of bryophytes exist in a wider range of environmental conditions and considerably greater variation in enrichment ratios has been noted, e.g. *Scapania undulata* shows a variation in Zn ratio from 1000 to 124000 and *Drepanocladus fluitans* varies from 60 to 920. Where ratios show such a range of variation direct comparison between sites using these species is obviously not possible. It has already been pointed out, however, that careful selection of a standard tip of bryophytes would reduce the variation to some extent.

Data would be more comparable provided that the enrichment ratio could be defined for a certain set of environmental parameters. This is clearly illustrated by the very low ratios encountered at pH <3. *Drepanocladus fluitans* could be used as an indicator of heavy metals provided the pH is limited. Thus heavy metal data from other sites of very low pH might be simply obtained and compared using this species, especially as it is widespread in such streams. In more complex environments factors other than pH would also be involved in establishing the environmental range at which a certain enrichment ratio exists, particularly Ca and Mg and organic/colloidal complexes.

It is therefore possible to summarise the practical criteria and limitations in the use of aquatic plants as quantitative monitors of heavy metals, from the field studies presented.

(i) Species should be widely distributed and easily identified.

(ii) Species should be independent of the substratum for their nutritional requirements but sufficiently attached to withstand periods of high flow.

(iii) The growth and morphology need to be fairly standard between samples, so that the time period represented is approximately the same.

(iv) Species should have a long growing season to allow regular analysis.

(v) Species must accumulate easily measurable concentrations of heavy metals.

(vi) Clearly defined limits need to be established for important chemical factors so that the enrichment ratio can be linked to these. This would allow valid comparison between samples at different sites.

Among the plants studied *Cladophora glomerata* and *Fontinalis antipyretica* display the most potential for simple quantitative use, particularly in lowland stretches of rivers. Such plants could be of particular value in monitoring changes caused by water transfer and abstraction together with the increasing volume of heavy metals entering river systems. A number of other species, particularly attached algae and bryophytes could be used in different but clearly defined ecological situations.

The use of enrichment ratios in selecting suitable species relies on a balance between the environmental conditions and the physiological state of the plant. If both can be established within defined limits the concept of aquatic plants as quantitative indicators of heavy metals in flowing waters could be greatly extended.

SUMMARY

A study was made of a range of aquatic plants from various parts of the River Wear system for 13 metal elements. An attempt was made to relate the heavy metal content of the plants to that of the surrounding water using 'enrichment ratios' so that quantitative indicator organisms could be selected.

A detailed study was carried out of the chemistry of the main river and some of its tributaries in order to establish background concentrations of heavy metals and some of the factors affecting these concentrations.

Three main areas were chosen for investigation.

(i) The lower stretches of the River Wear were studied in the region of an industrial effluent which was known to contain heavy metals.

(ii) Rookhope Burn was studied because of the high concentrations of Zn and Pb present in the water, as a result of past and present mining activities.

(iii) Brandon Pithouse acid streams were studied because of the exceptionally low pH and high heavy metal content of the water.

Surveys of the chemistry of the River Wear revealed low concentrations of heavy metals in the downstream stretches although marked increases occurred in Zn and Pb concentrations below the industrial effluent. Nutrient elements tended to show a steady increase from source to mouth. Macro-elements tended to show an inverse relationship with discharge in the upland tributary, Rookhope Burn and in the main river. Relationships were not clear for most heavy metals despite

much higher concentrations of Zn and Pb in Rookhope Burn. However, positive relationships were noted for Mn, Fe and Al in this tributary but not in the downstream sites of the main river. These relationships were attributed to colloidal run-off from the moorland.

The chemistry and discharge at source of Brandon Pithouse Acid Stream A remained extremely stable over two years of study. High concentrations of Zn, Cu, Mn, Fe, Al, Co and Ni were encountered at pH<3. Decreases in these heavy metals were observed as the pH increased and much precipitation occurred.

Surveys of a number of macroscopically obvious plants were made in each area in order to establish species which accumulated large amounts of heavy metals. This was the first step in the selection of indicator plants. The majority of species analysed contained easily measurable quantities of heavy metals and large amounts of K, Mg and Ca. Concentrations of Na were generally low except in species growing below pH 3. These elements were not directly related to concentrations in the water.

Bryophytes in general, tended to contain the highest concentrations of all heavy metals, especially Mn and Fe.

On the basis of data from these surveys, together with biological and methodological information, various species were suggested as potential indicator plants.

In the lower River Wear *Cladophora glomerata* and *Fontinalis antipyretica* were chosen for further study. Both species were found to accumulate higher concentrations of Zn, Pb and Cd below the industrial effluent compared to a site above this effluent. Increases in Cu were not recorded in either species;

this element was known not to occur in significant quantities in the effluent. A clear linear relationship was shown for *Cladophora glomerata* between concentrations of Zn and Pb in the water and those in the plant at comparable sites above and below the effluent; this allowed its use as a simple quantitative indicator of at least these two elements.

Such relationships were not established for *Fontinalis antipyretica* from the available data. Marked increases in heavy metal content were found in the older parts of this species and it was suggested that the growing tips of the moss were the best indicator of heavy metals.

Studies of *Ranunculus penicillatus* var. *calcareus* showed that the highest concentrations of heavy metals occurred in the roots and leaves. It was suggested that the latter part could be suitable as an indicator. Comparison with the same species from the River Tweed indicated that the heavy metal composition corresponded to the average composition of each river although there were not sufficient data to be conclusive.

Studies of a range of species from Rookhope Burn showed that most plants accumulated relatively large concentrations of Zn and Pb. Most algae were too transient to be practicable as indicator species with the notable exception of *Lemanea fluviatilis*. Bryophytes were found to have a particularly wide variation in enrichment ratio which imposed limitations on their use as indicators.

All species from Brandon Pithouse acid streams showed very low enrichment ratios. Some evidence was presented that pH was the most important factor in the reduction of the ratio.

It was suggested that *Drepanocladus fluitans* could be used as an indicator of heavy metals under comparable conditions of low pH.

The studies carried out show the potential for the practical use of a number of aquatic plants as quantitative indicators of heavy metals. In some circumstances the use may be straightforward, as in monitoring specific effluents where other factors are equal. It was concluded that a range of physiological and environmental factors affected the enrichment ratio; these must be taken into account before more general use of aquatic plants as indicators of heavy metals.

REFERENCES

ADAMS F.S., MACKENZIE D.R., COLE H. & PRICE M.W. (1971) The influence of nutrient pollution levels upon the element constitution and morphology of *Elodea canadensis* Rich. in Michx. *Environ. Pollut.* 1, 285-298.

ADAMS F.S., MACKENZIE D.R., COLE H. & PRICE M.W. (1973) Element constitution of selected aquatic vascular plants from Pennsylvania: submersed and floating leaved species and rooted emergent species. *Environ. Pollut.* 5, 117-147.

ADRIAN W.J. (1973) A comparison of a wet pressure digestion method with other commonly used wet and dry ashing methods. *Analyst, Lond.* 98, 213-216.

ALLEN S.E., GRIMSHAW H.M., PARKINSON J.A. & QUARNIBY C. (1974) *Chemical Analysis of Ecological Materials*, 565 pp., Blackwell Scientific Publications.

A.P.H.A. - AMERICAN PUBLIC HEALTH ASSOCIATION (1971) *Standard Methods for the Examination of Water and Wastewater*, 13th Edn, 874 pp. American Public Health Association Inc., 1790 Broadway, New York.

ANDERSON R.R., BROWN R.G. & RAPPLEYE R.D. (1965) Mineral composition of eurasian water milfoil, *Myriophyllum spicatum* L. *Chesapeake Sci*. 6, 68-72.

BACHMANN R.W. (1963) Zinc-65 in studies of the freshwater zinc cycle. In: Schultz V. & Klement W. (Eds) *Radioecology* 746 pp., pp. 485-96. Reinhold, New York.

BACHMANN R.W. & ODUM E.P. (1960) Uptake of Zn^{65} and primary productivity in marine benthic algae. *Limnol. Oceanogr.* 5, 349-355.

BAKER D.E., GORSLINE G.W., SMITH C.B., THOMAS W.I., GRUBE W.E., & RAGLAND J.L. (1964). Technique for rapid analyses of corn leaves for eleven elements. *Agron. J.* 56, 133-136.

BERTINE K.K. & GOLDBERG E.D. (1972) Trace elements in clams, mussels and shrimps. *Limnol. Oceanogr.* 17, 877-884.

BIRGE E.A. & JUDAY C. (1922) The inland lakes of Wisconsin. The plankton I. Its quantity and chemical composition. *Wisc. Geol. Nat. Hist. Sur. Bull.* 64, 1-222. Quoted in Boyd C.E. & Lawrence J.M. (1967) The mineral composition of several freshwater algae. *Proc. Ann. Conf. S. E. Assoc. Game & Fish Comm.* 20, 413-424.

BOWEN H.J.M. (1966) *Trace Elements in Biochemistry,* 241 pp. Academic Press, New York & London.

BOYD C.E. (1968) Some aspects of aquatic plant ecology. In: *Reservoir Fishery Resources Symposium, Athens, Georgia.* pp. 114-129.

BOYD C.E. (1969) Production, mineral nutrient absorption and biochemical assimilation by *Justicia americana* and *Alternanthera philoxeroides. Arch. Hydrobiol.,* 56, 139-160.

BOYD C.E. & LAWRENCE J.M. (1967) The mineral composition of several freshwater algae. *Proc. Ann. Conf. S.E. Assoc. Fame & Fish Comm.* 20, 413-24.

BRODA E. (1965) Mechanism of uptake of trace elements by plants: experiments with radio-zinc. In: *Isotopes and Radiation in soil-plant nutrition studies.* pp. 207-216. International Atomic Energy Authority, Vienna.

BRODA E. (1972) The uptake of heavy cationic trace elements by micro-organisms. *Ann. Micr.* 22, 93-108. Quoted in Keeney *et al.* (1976).

BROOKES & RUMSBY M.G. (1965) The biogeochemistry of trace element uptake by some New Zealand bivalves. *Limnol. Oceanogr.* 10, 521-527.

BRYAN G.W. (1969) The absorption of zinc and other metals by the brown seaweed *Laminaria digitata. J. mar. biol. Ass. U.K.* 49, 225-243.

BUTCHER R.W. (1933) Studies on the ecology of rivers, I. On the distribution of macrophytic vegetation in the rivers of Britain. *J. Ecol.* 21, 58-91.

BUTCHER R.W. (1947) Studies on the ecology of rivers, VII. The algae of organically enriched waters. *J. Ecol.* 35, 186-91.

BUTCHER R.W. (1955) Relation between the biology and the polluted condition of the Trent. *Verh. int. Verein. theor. angew. Limnol.* 12, 823-27.

CAIRNEY T. & STOREY J.M. (1970) Hydrology and water resources. In: Dewdney J.C. (Ed.) *Durham County and City with Teesside.* 522 pp. pp.75-88. British Association, Durham.

CARPENTER K.E. (1924) A study of the fauna of rivers polluted by lead mining in the Aberystwyth district of Cardiganshire. *Ann. appl. Biol.* 9, 1-23.

CARPENTER K.E. (1925) On the biological factors involved in the destruction of river fisheries by pollution due to lead mining. *Ann. appl. Biol.* 12, 1-73.

CARPENTER K.E. (1928) *Life in Inland Waters*, 267 pp., Sidgwick & Jackson, London.

CARPENTER K.E. (1930) Further researches on the action of metallic salts on fishes. *J. exp. Zool.* 56, 407-22.

CHOLNOKY B.J. (1960) The relationship between algae and the chemistry of natural waters. In: *Proceedings of Specialist Meeting on Water Treatment.* pp. 215-225. Council for scientific Research, National Institute for Water Research, Pretoria, South Africa.

CRISP D.T. (1966) Input and output of minerals for an area of Pennine moorland; the importance of precipitation, drainage, peat erosion and animals. *J. appl. Zool.* 3, 327-348.

CROSBY N.T. (1967) The determination of nitrite in water using Cleve's acid; 1,napthylamine-7, sulphonic acid. *Proc. Soc. Wat. Treat. Exam.* 16, 51-55.

CROSS F.A., WILLIS J.N. & BAPTIST J.P. (1971) Distribution of radioactive and stable zinc in an experimental marine ecosystem. *J. Fish. Res. Bd Can.* 28, 1783-88.

CUSHING C.E. & ROSE F.L. (1970) Cycling of zinc-65 by Columbia River periphyton in a closed lotic microcosm. *Limnol. Oceanogr.* 15, 762-67.

DAVIS J.J., PERKINS R.W., PALMER R.F., HANSON W.C. & CLINE J.F. (1958) Radioactive materials in aquatic and terrestial organisms exposed to reactor effluent. *Proc. Intern. Conf. Peaceful Uses of Atomic Energy Second Cont. Geneva* 18, 423-28.

DIETZ F. (1973) The enrichment of heavy metals in submerged plants. In: Jenkins S.H.(Ed.) *Advances in Water Pollution Research, Proceedings 6th International Conference.* 946 pp., pp.53-62. Pergamon Press, Oxford.

DUNHAM K.C. (1948) *Geology of the Northern pennine Orefield. I. Tyne to Stainmore,* 357 pp. *Mem. Geol. Surv. U.K.* H.M.S.O., London.

DUNHAM K.C. (1959) Non-ferrous mining potentialities of the northern Pennines. In: *Future of non-ferrous Mining in Great Britain and Ireland.* pp. 115-147. Institution of Mining and Metallurgy, London.

DUNHAM K.C. (1969) Practical geology and the natural environment of man - II. *Quart. J. Geol. Soc. Lond.* 124, 101-129.

ELDER J.F. (1975) Complexation side reactions involving trace metals in natural water systems. *Limnol. Oceanogr.* 20, 96-102.

EMPAIN A. (1976a) Estimation de la pollution par métaux lourds dans la Somme par l'analyse des brophytes aquatiques. *Bull. fr. Piscic.* 175, 41-53.

EMPAIN A. (1976b) Les bryophytes aquatiques utilises comme traceurs de la contamination en métaux lourds des eaux douces. *Mem. Soc. Roy. Bot. Belg.* 7, 141-56.

FAILLA M.L., BENEDICT C.D. & WEINBERG E.D. (1976) Accumulation and storage of Zn^{2+} by *Candida utilis*. *J. gen. Microbiol.* 94, 23-36.

FISHMAN M.J. (1966) The use of atomic absorption for the analysis of natural waters. *Atomic Absorption Newsletter* 6, 102-106.

FJERDINGSTAD E. (1950) The microflora of the River Mølleaa with special reference to the relation of the benthal algae to pollution. *Folia limnol. scand.* 5, 1-123.

FOGG G.E. & WESTLAKE D.F. (1955) The importance of extracellular products of algae in freshwater. *Verh. int. Verein. theor. angew. Limnol.* 12, 219-32.

FUGE R. (1972) The chemistry of some mine waters from Cardiganshire. In: *Mineral Exploitation and Economic Geology.* pp. 16-20. Inter Collegiate Colloquium, Sept 22, 1972, University of Wales, Aberystwyth.

GILEVA E.A. (1964) Dynamics of the accumulation of chemical elements by the alga *Cladophora fracta* and the dependence of the accumulation on the concentration of the elements in solution. *Fiziologiya Rast.* 11, 581-86.

GOLDBERG E. (1965) Minor elements in sea water. In: Riley J.P. & Skirrow E.G. (Eds) *Chemical Oceanography* 1, Ch. 5, p. 163. Academic Press, New York & London.

GORSUCH T.T. (1959) Recovery for analysis of trace elements in organic and biological material. *Analyst, Lond.* 84, 135-73.

GUTKNECHT J. (1963) Zn^{65} uptake by benthic marine algae. *Limnol. Oceanogr.* 8, 31-38.

GUTKNECHT J. (1965) Uptake and retention of cesium-137 and zinc-65 by seaweeds. *Limnol. Oceanogr.* 10, 58-66.

HAMMOND E.W. (1959) A rapid method for the determination of nitrate in drinking water using 3, 3' dimethylnapthidene. *Proc. Soc. Wat. Treat. Exam.* 8, 173-75.

HARGREAVES J.W. (1977) *Ecology and Physiology of Photosynthetic Organisms in Highly Acid Streams*, 336 pp. Ph.D. Thesis, University of Durham.

HARGREAVES J.W., LLOYD E.J.H. & WHITTON B.A. (1975) Chemistry and vegetation of highly acidic streams. *Freshwat. Biol.* 5, 563-76.

HARGREAVES J.W. & WHITTON B.A. (1977) Effect of pH on tolerance of *Hormidium rivulare* to zinc and copper. *Oecologia* 26, 235-43.

HARPER H.J. & DANIEL H.R. (1934) Chemical composition of certain aquatic plants. *Bot. Gaz.* 96, 186-89.

HARVEY R.S. & PATRICK R. (1967) Concentration of ^{137}Cs, ^{65}Zn and ^{85}Sr by freshwater algae. *Biotech. Bioengng* 9, 449-56.

HELLMANN H. (1970) Die Absorption von Schwermetallen an den Schwebstaffen des Rheins - eine Untersuchung zur Entfigtung des Rheinwassers (ein Nachtrag). *Dt. gewasserk. Mitt.* 14, 42-47. Quoted in Wilson (1976).

HICKLING H.G.A. et al. (1931) The Geology of Northumberland and Durham. *Proc. Geol. Ass.* 42, 217-295.

HOAGLAND D.R. & DAVIS A.R. (1923) The composition of the cell sap of the plant in relation to the absorption of ions. *J. gen. Physiol.* 5, 629-46.

HOLMES N.T.H. (1975) *The Vegetation of the River Tweed,* 489 pp. Ph.D. Thesis, University of Durham.

HOLMES N.T.H. & WHITTON B.A. (1977) Macrophytes of the River Wear: 1966 - 1976. *Naturalist, Hull,* 102, 53-74.

HOLMES N.T.H., LLOYD E.J.H., POTTS M. & WHITTON B.A. (1972) Plants of the River Tyne and future water transfer scheme. *Vasculum,* 57, 56-78.

HOOD S.L., PARKS R.Q. & HURWITZ C. (1944) Mineral contamination resulting from grinding plant samples. *Ind. Eng. Chem.* 16, 2P2-205.

HUET M. (1954) Biologie, profils en long et en travars des eaux courantes. *Bull. fr. Piscic.* 175, 41-53.

HYNES H.B.N. (1960) *The Biology of Polluted Waters.* 202 pp. Liverpool University Press, Liverpool.

JOHNSON C.H. & ULRICH R. (1959) Analytical methods for use in plant analysis. *California Agricultural Experimental Station Bulletin,* 766, 24-78.

JOHNSON G.A.L. (1970) Geology. In: Dewdney J.C. (Ed) *Durham County and City with Teesside.* 522 pp., pp. 3-25. British Association, Durham.

JONES J.R.E. (1938) Antagonism between two heavy metals in their toxic action on freshwater animals. *Proc. zool. Soc. Lond. A.* 108, 481-99.

JONES J.R.E. (L940a) The fauna of the River Melindwr, a lead polluted tributary of the River Rheidol in North Cardiganshire, Wales. *J. Anim. Ecol.* 9, 188-201.

JONES J.R.E. (1940b) A study of the zinc polluted River Ystwyth in North Cardiganshire, Wales. *Ann. appl. Biol.* 27, 368-78.

KAHN H.L., PETERSON G.E. & SCHALLIS J.E. (1968) Atomic absorption microsampling with the 'sampling boat' technique. *Atomic Absorption Newsletter* , 7, 35-39.

KEENEY W.L., BRECK W.G., VANLOON G.W. & PAGE J.A. (1976) The determination of trace metals in *Cladophora glomerata* - *C. glomerata* as a potential biological monitor. *Wat. Res.* 10, 981-84.

KEULDER P.C. (1975) Influence of the clay types illite and montmorillonite on the uptake of ^{65}Zn by *Scenedesmus obliquus. J. Limnol. Soc. S. Africa,* 1, 33-35.

KOLKWITZ R. & MARSSON M. (1908) Okologie die pflanzlichen Saprobien. *Ber. dt. bot. Ges.* 26, 505-19.

LEEDER A. (1972) *Studies on Lead and Zinc Pollution in an Upland Stream,* 51 pp. M.Sc. Ecology Dissertation, University of Durham.

LIVINGSTONE D.A. (1963) *Chemical Composition of Rivers and Lakes*, 64 pp. U.S. Geo. Surv. Prof. Paper 440-G.

LORD D.A. (1974) *Trace Elements in Mussels and Seston in the Kingston Basin of Lake Ontario.* Ph.D. Thesis, Queens University, Canada. Quoted in Keeney *et al.* (1976).

MACKERETH F.J.H. (1963) *Some Methods of Water Analysis for Limnologists. Freshwat. Biol. Ass. Sci. Publ.* 21.

MAYER A.M. & GORHAM (1951) The iron and manganese content of some plants present in the natural vegetation of the English Lake District. *Ann. Bot. Lond.* 15, 247-63.

MONTGOMERY H.A.C. & DYMOCK J.F. (1962) The rapid determination of nitrate in fresh and saline waters. *Analyst, Lond.* 87, 374-78.

MOREL F. & MORGAN J.J. (1968) *A Numerical Method for Solution of Chemical Equilibria in Aqueous Systems.* California Institute of Technology, Pasadena, California. Quoted in Stumm & Morgan (1970) *Aquatic Chemistry*, 583 pp. Wiley-Interscience.

NEWTON L. (1944) Pollution of the rivers of West Wales by lead and zinc mine effluent. *Ann. appl. Biol.* 31, 1-11.

PATRICK P.H. (1973) *Bioaccumulation of Zinc and Cadmium in two Stream Systems,* 76 pp. M. Sc. Ecology Dissertation. University of Durham.

PASSOW H., ROTHSTEIN A. & CLARKSON T.W. (1961) The general pharmacology of heavy metals. *Pharmac. Rev.* 13, 185-224.

PENTELOW F.T.K. & BUTCHER R.W. (1938) Observations on the Rivers Churnet and Dove in 1938. *Rep. Trent. Fish. Distr. App I.*

PERHAC R.M. (1972) Distribution of Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn in dissolved and particulate solids from two streams in Tennessee. *J. Hydrol.* 15, 177-86.

PERKIN-ELMER (1971) *Instruction Manual for Model 403 Atomic Absorption Spectrophotometer.* Perkin-Elmer Corporation, Norwalk, Connecticut.

PICKERING D.C. & PUIA I.L. (1969) Mechanism for uptake of zinc by *Fontinalis antipyretica*. *Physiologia Pl*. 22, 653-61.

PLATTE J.A. & MARCY V.M. (1965) Atomic absorption spectrophotometry as a tool for the water chemist. *Atomic Absorption Newsletter*, 4, 289-92.

POMFRET J. (1973) *Aspects of the Acid Tolerance of Algae in the Durham Area*. M.Sc. Ecology Dissertation, University of Durham.

PRINGLE B.H., HISSONG D.E., KATZ E.L. & MULAWKA S.T. (1968) Trace metal accumulation by estuarine mollusks. *J. sanit. Engng Div. Am. Soc. civ. Engrs*, 13, 455-69.

RAMAMOORTHY S. & KUSHNER D.J. (1975) Heavy metal binding components of river water. *J. Fish. Res. Bd Can.* 32, 1755-66.

RASHID (1974) Absorption of metals on sedimentary and peat humic acids. *Chem. Geol*. 13, 115-23.

REESE M.J. (1937) The microflora of the non-calcareous streams Rheidol and Melindwr with special reference to water pollution from lead mines in Cardiganshire. *J. Ecol.* 25, 385-407.

RIEMER D.N. & TOTH J. (1969) A survey of the chemical composition of *Potamogeton* and *Myriophyllum* in New Jersey. *Weed Sci.* 17, 219-23.

ROBERTSON D.E. (1969) Role of contamination in trace element analysis of seawater. *Anal. Chem.* 40, 1067-72.

ROBINSON C. (1971) *A Preliminary Study of the Factors Affecting the Flora of an Acid Coal Mine Drainage*. M.Sc. Ecology Dissertation, University of Durham.

ROUND F.E. (1965) *The Biology of the Algae*. pp. 269. Edward Arnold, London.

SANDHOLM M., OKSANEN H.E. & PESONEN L. (1973) Uptake of selenium by aquatic organisms. *Limnol. Oceanogr.* 18, 496-99.

SAY P.J. (1977) *Microbial Ecology of High Zinc Level Streams*, 294 pp. Ph.D. Thesis, University of Durham.

SAY P.J. & WHITTON B.A. (1977) Influence of zinc on lotic plants. II. Environmental effects of toxicity of zinc to *Hormidium rivulare*. *Freshwat. Biol.* 7, 377-84.

SCHUETTE H.R. & HOFFMAN A.E. (1921) Notes on the chemical composition of some of the larger aquatic plants of Lake Mendota. I. *Cladophora* and *Myriophyllum*. *Trans. Wisc. Acad. Sci. Arts Lett.* 20, 529-31.

SCOTT G.T. (1943) The mineral composition of *Chlorella pyrenoidosa* grown in culture media containing varying concentrations of calcium, magnesium, potassium and sodium. *J. cell. comp. Phys.* 21, 327-38.

SCULTHORPE C.D. (1967) *The Biology of Aquatic Vascular Plants*, 610 pp. Edward Arnold, London.

SHACKLETTE H.T. (1967) *Copper Mosses as Indicators of Metal Concentrations*, 21 pp. *U.S. Geological Survey Bulletin* 1178-99.

SHAPIRO J. (1957) Chemical and biological studies on the yellow organic acids of lake water. *Limnol. Oceanogr.* 2, 161-78.

SHAPIRO J. (1964) Effect of yellow organic acids on iron and other metals in water. *J. Am. Wat. Wks Ass.* 56, 1062-81.

SLADECEK V. (1958) Die Abhangigkeit de Belebtschaum verfahrens von physikalischen, chemischen und biologischen Faktoren. *Verh. Int. Ver. theor. angew. Limnol.* 13, 611-616.

SNOW M. & WHITTON B.A. (1971) The River Wear: inorganic chemistry relevant to a biologist. *Vasculum*, 56, 50-54.

STUMM W. & BILINSKI H. (1972) Trace metals in natural waters: difficulties of interpretation arising from our ignorance of their speciation. In: Jenkins S.H. (Ed.) *Advances in Water Pollution Research, Proceedings 6th International Conference*, 946 pp. pp. 39-49. Pergamon Press, Oxford.

STUMM W. & MORGAN J.J. (1970) *Aquatic Chemistry. An Introduction Emphasizing Chemical Equilibria in Natural Waters*, 583 pp. Wiley;Interscience, New York, London, Sydney, Toronto.

SMITH A.E. (1973a) A study of the variation with pH of the solubility and stability of some metal ions at low concentrations in aqueous solution. Part I. *Analyst Lond.* 98, 65-68.

SMITH A.E. (1973b) A study of the variation with pH of the solubility and stability of some metal ions at low concentrations in aqueous solution. Part II. *Analyst Lond.* 98, 209-12.

SMITH K. (1970) Weather and Climate. In: Dewdney J.C. (Ed.) *Durham County and City with Teesside*, 522 pp., pp. 58-74. British Association, Durham.

TIMOFEEVA-RESOVSKAYA E.A., TIMOFEEVA-RESOVSKY N.V. & GILEVA E.A. (1961). Specific accumulation of individual radioisotopes among freshwater organisms. *Dokl. Akad. Nauk.* SSSR 140, 780-783.

WHITEHEAD N.E. & BROOKS R.R. (1969) Aquatic bryophytes as indicators of uranium mineralisation. *Bryologist*, 72, 501-07.

WHITTON B.A. (1970) Biology of *Cladophora* in freshwaters. *Wat. Res.* 4, 457-76.

WHITTON B.A. (1972) Environmental limits of plants in flowing waters. In: Edwards R.W. & Garrod D.J. (Eds) *Conservation and productivity of Natural Waters. Symp. zool. Soc. Lond.* 29, 3-19.

WHITTON B.A. & BUCKMASTER R.C. (1970) Macrophytes of the River Wear. *Naturalist, Hull* 914, 97-116.

WHITTON B.A. & SAY P.J. (1975) Heavy metals. In: Whitton B.A. (Ed.) *River Ecology*, 725 pp., pp. 286-311. Blackwell Scientific Publications, Oxford.

WILLIAMS L.G., JOYCE J.C. & MONK J.T. (1973) Stream velocity effects on the heavy metal concentrations. *J. Am. Wat. Wks. Ass.* 65, 275-79.

WILSON A.L. (1976) *Concentrations of Trace Metals in River Waters: A Review*. Technical Report 16, 60 pp. Water Research Centre, Stevenage.

ADDENDUM

p. 8.

KENNEDY V.C., ZELLWEGER W. & JONES B.F. (1974) Filter pore size effects on the analysis of Al, Fe, Mn and Ti in water. Wat. Resour. Res. 10, 785-90.

p. 11.

BOYD C.E. (1971) The limnological role of aquatic macrophytes and their relationship to reservoir management. Reservoir Fisheries and Limnology 8, 153-66.

p. 12.

PRESTON A., JEFFRIES D.F., DUTTON J.W.R., HARVEY B.R. & STEELE A.K. (1972) British Isles coastal waters: the concentrations of selected heavy metals in sea water, suspended matter and biological indicators - a pilot survey. Environ. Pollut. 3, 69-82.

p. 13.

FJERDINGSTAD E., KEMP K., FJERDINGSTAD E. & VANGGAARD L. (1974) Chemical analyses of red 'snow' from East-Greenland with remarks on Chlamydomonas nivalis (Bau.) Wille. Arch. Hydrobiol. 73, 70-83.

p. 17.

NORTHUMBRIAN RIVER AUTHORITY (1967-71) Annual Reports for the Years Ending 31st March 1967-1971. Northumbrian River Authority, Newcastle-upon-Tyne.

NORTHUMBRIAN WATER AUTHORITY (1972-76) Annual Reports for the Years Ending 31st March 1972-1976. Northumbrian Water Authority, Gosforth, Newcastle-upon-Tyne.

p. 36.

COLSON A.F. (1963) The removal of phosphate in the barium perchlorate titration of sulphate. Analyst Lond. 87, 374-78.

APPENDIX 1.

Water Chemistry

Tables A.1a - A.1i

Table A.1a River Wear - water chemistry

mean, standard deviation and coefficient of variation of 4 replicate samples

site	km	day	date	time	O.D.	cond µmhos	pH	Na	K	Mg	Ca	Zn	Cu	Mn	Fe	Al	Pb	Cd	Cl	Si	PO_4-P	NH_3-N	NO_2-N	NO_3-N
Sunderland Br. 1	58.3	Thu	16.3.73	1000	0.013	200	8.3	21.6	3.95	17.6	47.8	0.011	0.010	0.005	0.046	0.07	0.002	<0.0001	29.5	2.83	0.162	0.74	0.015	2.22
2				1000	0.014	200	8.3	22.0	3.92	17.2	48.5	0.012	0.013	0.004	0.034	0.17	0.003	<0.0001	29.0	2.84	0.160	0.74	0.013	2.10
3				1000	0.012	200	8.3	21.2	3.66	17.2	48.0	0.012	0.010	0.005	0.040	0.13	0.003	<0.0001	28.5	2.97	0.136	0.73	0.015	2.14
4				1000	0.013	200	8.3	20.9	3.99	17.3	46.9	0.013	0.010	0.007	0.064	0.10	0.003	<0.0001	29.0	2.95	0.156	0.71	0.014	2.08
mean								21.45	3.88	17.33	47.80	0.012	0.0107	0.0053	0.046	0.117	0.0025	-	29.0	2.89	0.154	0.73	0.0143	2.135
std dev.								±0.41	±0.129	±0.16	±0.58	0.0007	±0.0013	±0.0010	±0.011	±0.036	±0.0005	-	±0.35	±0.063	±0.010	±0.012	±0.0008	±0.054
coeff. var. (%)								1.93	3.32	0.92	1.20	5.83	12.15	18.86	23.9	30.7	20.0	-	1.2	2.19	6.49	1.64	5.59	2.52
Finchale Abbey 1	78.1	Thu	16.3.72	1200	0.012	290	8.3	29.6	4.26	18.0	47.9	0.010	0.012	0.007	0.035	0.03	0.002	<0.0001	43.5	3.30	0.244	0.85	0.030	3.05
2				1200	0.013	290	8.3	30.5	4.39	18.2	48.5	0.010	0.013	0.010	0.040	0.07	0.002	<0.0001	38.0	3.46	0.240	0.81	0.031	2.82
3				1200	0.013	290	8.3	31.1	4.24	18.7	49.3	0.011	0.013	0.007	0.024	0.10	0.002	<0.0001	45.0	3.36	0.245	0.80	0.031	3.16
4				1200	0.013	290	8.3	31.5	4.32	18.6	49.3	0.011	0.010	0.008	0.024	0.13	0.004	<0.0001	39.0	3.36	0.248	0.82	0.032	2.86
mean								30.6	4.302	18.38	48.75	0.0105	0.0120	0.008	0.0307	0.095	0.0025	-	41.37	3.37	0.244	0.82	0.031	2.97
std dev.								±0.71	±0.058	±0.29	±0.59	±0.0005	±0.0012	±0.0012	±0.007	±0.023	±0.0008	-	±2.94	±0.057	±0.003	±0.019	±0.0007	±0.138
coeff. var. (%)								2.3	1.3	1.6	1.2	4.8	10.0	15.0	22.0	24.7	32.0	-	7.1	1.7	1.2	2.3	2.3	4.6

site	km	day	date	time	cond µmhos	pH	Na	K	Mg	Ca	Zn	Cu	Pb	Cd	Cl	flow cumecs
Sunderland Br.	58.3	Thu	16.3.72	1000	200	8.3	21.5	3.68	17.3	47.8	0.012	0.011	0.0025	<0.0001	29.0	6.7
Finchale Abbey	78.1			1200	290	8.3	30.6	4.30	18.4	48.8	0.011	0.012	0.0025	<0.0001	41.4	
Sunderland Br.	58.3	Tue	21.3.72	1130	195	8.1	19.7	2.49	12.0	38.1	0.010	<0.01	0.002	-	27.5	7.6
Finchale Abbey	78.1			1100	285	8.1	26.3	3.20	16.0	44.1	0.011	<0.01	0.002	-	35.0	
Sunderland Br.	58.3	Thu	28.3.72	1200	205	8.2	22.5	3.03	13.2	43.2	0.012	<0.01	0.003	-	36.9	6.6
Finchale Abbey				1115	290	8.2	31.2	4.23	17.3	41.6	0.011	<0.01	0.002	-	38.6	
Sunderland Br.	58.3	Tue	28.3.72	1040	200	8.2	19.6	3.87	12.0	42.9	0.017	<0.01	0.002	-	35.7	7.7
Finchale Abbey	78.1			1000	290	8.2	35.1	5.17	10.6	48.4	0.010	<0.01	0.003	-	43.5	
Sunderland Br.	58.3		6.4.72	1145	180	7.9	11.6	3.50	7.8	27.2	0.013	<0.01	0.004	-	23.3	18.5
Finchale Abbey	78.1			1100	220	7.9	26.3	4.18	11.5	33.9	0.014	<0.01	0.004	-	30.7	
Sunderland Br.	58.3	Tue	11.4.72	1145	175	7.8	12.8	3.00	10.0	32.8	0.010	<0.01	0.001	-	22.9	10.7
Finchale Abbey	78.1			1100	265	7.8	24.2	4.15	14.2	35.6	0.010	<0.01	0.001	-	29.9	
Sunderland Br.	58.3	Thu	13.4.72	1600	220	8.0	13.3	3.42	11.3	25.5	0.018	<0.01	0.002	-	23.2	7.8
Finchale Abbey	78.1			1500	300	8.0	29.7	4.50	15.9	36.2	0.010	<0.01	0.003	-	29.0	
Sunderland Br.	58.3	Thu	20.4.72	1600	285	8.3	28.9	6.45	22.8	52.2	0.012	<0.01	0.001	-	22.9	4.9
Finchale Abbey	78.1			1500	390	8.3	52.2	8.32	25.0	51.8	0.011	<0.01	0.002	-	37.7	
Sunderland Br.	58.3	Tue	25.4.72	1600	320	8.3	31.3	6.78	22.2	58.1	<0.010	<0.01	0.001	-	32.1	4.2
Finchale Abbey	78.1			1500	455	8.3	60.5	8.38	28.3	55.8	<0.010	<0.01	0.001	-	44.3	
Sunderland Br.	58.3	Thu	27.4.72	1545	310	8.2	31.3	6.98	24.5	51.5	<0.010	<0.01	0.003	-	30.3	3.9
Finchale Abbey	78.1			1500	450	8.2	55.8	8.49	25.6	49.5	<0.010	<0.01	0.002	-	42.0	
Sunderland Br.	58.3	Tue	2.5.72	1610	340	8.2	30.4	6.56	22.6	46.6	0.013	<0.01	0.001	-	28.8	3.7
Finchale Abbey	78.1			1530	465	8.2	52.8	8.22	26.8	52.5	0.010	<0.01	0.001	-	37.0	
Sunderland Br.	58.3	Thu	4.5.72	1645	350	8.0	28.8	6.40	21.7	49.4	0.010	<0.01	0.002	-	28.2	4.6
Finchale Abbey	78.1			1600	470	8.0	55.0	10.1	25.8	49.0	0.012	<0.01	0.003	-	47.2	
Sunderland Br.	58.3	Thu	11.5.72	1630	320	8.1	20.2	4.55	15.5	36.2	0.010	<0.01	0.003	-	25.2	5.4
Finchale Abbey	78.1			1545	445	8.2	41.1	5.25	17.3	40.5	0.016	<0.01	0.003	-	31.8	
Sunderland Br.	58.3	Tue	16.5.72	1715	330	8.2	18.7	3.90	10.8	40.9	<0.010	<0.01	0.002	-	25.2	5.3
Finchale Abbey	78.1			1630	450	8.2	41.9	5.48	15.4	41.8	<0.010	<0.01	0.002	-	36.2	
Sunderland Br.	58.3	Thu	18.5.72	1645	325	8.1	19.0	4.58	14.8	42.1	<0.010	<0.01	0.002	-	24.8	4.9
Finchale Abbey	78.1			1600	440	8.0	42.3	7.79	18.9	42.1	<0.010	<0.01	0.002	-	37.6	
Sunderland Br.	58.3	Tue	23.5.72	1640	350	8.2	22.0	5.07	16.2	46.5	<0.010	<0.01	0.002	-	27.2	3.8
Finchale Abbey	78.1			1600	490	8.3	57.5	8.80	28.2	49.7	<0.010	<0.01	0.002	-	38.5	
Sunderland Br.	58.3	Thu	25.5.72	1620	360	8.2	31.4	7.58	27.1	55.8	<0.010	<0.01	0.002	-	29.2	3.8
Finchale Abbey	78.1			1530	485	8.2	46.5	7.62	21.7	47.8	<0.010	<0.01	0.002	-	37.0	
Sunderland Br.	58.3	Tue	30.5.72	1700	230	8.0	13.0	3.41	10.2	37.2	0.010	<0.01	0.005	<0.0001	20.4	6.1
Finchale Abbey	78.1			1615	315	8.0	29.5	5.50	16.2	35.8	0.011	<0.01	0.004	<0.0001	27.5	
Sunderland Br.	58.3	Thu	1.6.72	1715	190	7.7	9.3	2.76	6.8	25.5	0.013	<0.01	0.005	0.0003	14.7	11.7
Finchale Abbey	78.1			1630	230	7.9	21.0	4.08	9.6	26.3	0.015	0.05	0.007	0.0002	19.1	
Sunderland Br.	58.3	Tue	6.6.72	1530	185	7.8	11.8	3.28	10.3	30.8	<0.010	<0.01	0.004	0.0001	15.6	9.5
Finchale Abbey	78.1			1445	255	7.8	20.7	4.47	14.7	32.4	<0.010	<0.01	0.004	0.0001	18.5	
Sunderland Br.	58.3	Thu	8.6.72	1715	200	8.0	19.1	3.53	11.9	39.6	<0.010	<0.01	0.003	<0.0001	20.6	7.1
Finchale Abbey	78.1			1630	295	8.1	34.2	4.96	15.8	43.8	<0.010	<0.01	0.004	<0.0001	29.2	
Sunderland Br.	58.3	Tue	13.6.72	1720	220	8.2	17.9	3.71	11.3	40.3	0.010	<0.01	0.010	<0.0001	23.1	6.6
Finchale Abbey	78.1			1640	315	8.2	33.3	5.62	19.5	46.0	0.010	<0.01	0.010	<0.0001	32.6	
Sunderland Br.	58.3	Thu	29.6.72	1735	280	8.3	38.2	7.16	18.4	48.5	0.013	<0.01	0.010	0.0002	25.2	3.9
Finchale Abbey	78.1			1650	405	8.2	61.4	8.83	22.4	51.2	0.010	<0.01	0.010	0.0002	40.1	
Sunderland Br.	58.3	Tue	4.7.72	1715	295	8.3	39.7	8.09	21.0	47.3	<0.010	<0.01	0.011	0.0001	28.3	3.9
Finchale Abbey	78.1			1630	420	8.3	64.7	9.15	27.9	50.6	<0.010	<0.01	0.012	0.0001	45.4	
Sunderland Br.	58.3	Sat	22.7.72	1540	250	8.2	26.2	5.97	14.3	47.4	0.010	<0.01	0.011	0.0001	25.2	4.7
Finchale Abbey	78.1			1500	350	8.1	47.5	7.56	20.3	44.8	0.010	<0.01	0.011	0.0001	31.9	
Sunderland Br.	58.3	Thu	10.8.72	1645	260	8.1	25.7	5.63	18.1	40.3	<0.010	<0.01	0.004	<0.0001	23.4	5.0
Finchale Abbey	78.1			1600	380	8.1	53.8	8.17	24.9	44.3	<0.010	<0.01	0.004	<0.0001	34.4	
Sunderland Br.	58.3	Sun	24.8.72	1730	450	8.4	39.4	8.87	23.7	52.4	<0.010	<0.01	0.010	<0.0001	39.8	2.3
Finchale Abbey	78.1			1645	600	8.3	68.9	10.6	29.2	55.9	<0.010	<0.01	0.011	<0.0001	52.0	

Table A.1c   Lower Reaches of R. Wear - water chemistry 1973

Site	km	day	date	time	OD_{420}	cond µmhos	pH	Na	K	Mg	Ca	Zn	Cu	Mn	Fe	Al	Pb	Cd	Cl	Si	PO_4-P	NH_3-N	NO_2-N	NO_3-N	flow cumecs
Sunderland Br.	58.3	Tue	30.1.73	1600	0.022	180	7.8	21.3	4.2	9.9	36.2	0.015	0.005	0.033	0.18	0.05	0.007	<0.0001	36.5	2.25	0.172	0.37	0.018	1.12	7.393
above effluent	73.5			1700	0.024	280	7.9	27.5	5.0	10.4	39.8	0.025	0.006	0.052	0.21	0.10	0.007	<0.0001	45.0	3.30	0.340	0.75	0.027	3.48	
below effluent	73.9			1700	0.025	280	7.9	27.0	4.8	10.1	39.3	0.027	0.006	0.050	0.17	0.04	0.008	<0.0001	42.5	3.30	0.342	0.75	0.027	3.48	
Finchale Abbey	78.1			1730	0.026	285	7.9	28.2	4.9	10.3	39.7	0.018	0.007	0.053	0.19	0.07	0.008	<0.0001	41.0	3.32	0.355	0.78	0.030	3.47	
Sunderland Br.	58.3	Tue	27.2.73	1600	0.019	270	7.8	29.6	4.6	10.6	42.0	0.009	<0.002	0.036	0.11	<0.03	0.007	<0.0001	38.5	3.15	0.197	0.10	0.038	1.24	3.737
above effluent	73.5			1630	0.022	365	7.8	38.2	5.4	11.4	44.7	0.012	<0.002	0.039	0.10	<0.03	0.008	<0.0001	47.0	3.20	0.365	0.16	0.052	1.97	
below effluent	73.9			1630	0.020	370	7.8	40.1	5.7	11.3	43.6	0.015	<0.002	0.041	0.10	<0.03	0.009	<0.0001	47.5	3.20	0.370	0.16	0.061	1.99	
Finchale Abbey	78.1			1700	0.021	370	7.8	40.3	5.9	11.2	44.5	0.012	<0.002	0.039	0.10	<0.03	0.008	<0.0001	47.5	3.25	0.395	0.18	0.058	1.95	
Sunderland Br.	58.3	Fri	30.3.73	1630	0.009	445	8.1	58.3	7.9	22.7	57.7	0.012	0.004	0.017	0.14	<0.03	0.009	0.0006	43.2	3.90	0.387	0.21	0.033	1.93	1.951
above effluent	73.5			1700	0.010	650	8.1	72.3	9.3	24.1	62.5	0.018	0.005	0.017	0.13	<0.03	0.008	0.0005	57.5	4.10	0.530	0.30	0.043	2.82	
below effluent	73.9			1700	0.009	650	8.1	73.5	9.4	24.1	63.0	0.024	0.006	0.014	0.12	<0.03	0.010	0.0007	60.0	4.10	0.542	0.34	0.044	2.87	
Finchale Abbey	78.1			1800	0.008	700	8.2	76.2	9.7	25.6	63.5	0.014	0.006	0.015	0.12	<0.03	0.008	0.0006	59.5	4.05	0.563	0.42	0.050	2.79	
Sunderland Br.	58.3	Sun	29.4.73	1700	0.017	255	8.2	25.8	5.6	16.8	49.7	0.012	0.006	0.026	0.10	<0.03	0.009	0.0040	23.5	2.35	0.240	0.18	0.118	1.32	4.805
above effluent	73.5			1730	0.021	370	8.3	36.8	6.5	17.5	52.7	0.010	0.006	0.031	0.11	<0.03	0.025	0.0020	26.0	1.95	0.305	0.40	0.093	1.78	
below effluent	73.9			1730	0.020	375	8.3	37.3	6.5	17.2	54.3	0.011	0.008	0.030	0.12	<0.03	0.024	0.0030	26.5	2.20	0.305	0.31	0.152	2.04	
Finchale Abbey	78.1			1800	0.019	375	8.3	40.5	6.5	17.3	54.3	0.009	0.007	0.029	0.11	<0.03	0.011	0.0020	28.0	1.90	0.346	0.22	0.086	1.82	
Sunderland Br.	58.3	Fri	18.5.73	1400	0.014	235	8.2	36.2	7.9	19.4	52.5	0.009	0.004	0.018	0.15	<0.03	0.003	<0.0001	31.5	2.11	0.302	0.22	0.048	1.74	3.161
above effluent	73.5			1500	0.012	330	8.2	48.6	8.3	22.7	50.9	0.007	0.004	0.017	0.14	0.05	0.003	<0.0001	43.8	2.04	0.384	0.43	0.062	2.42	
below effluent	73.9			1500	0.013	335	8.2	50.1	8.3	23.2	51.4	0.013	0.004	0.021	0.14	0.06	0.005	<0.0001	47.2	2.08	0.389	0.41	0.066	2.58	
Finchale Abbey	78.1			1530	0.013	340	8.2	53.2	8.5	23.5	51.7	0.011	0.005	0.020	0.15	0.04	0.004	<0.0001	44.8	1.95	0.394	0.42	0.062	2.50	
Sunderland Br.	58.3	Thu	31.4.73	1200	0.027	210	8.0	20.5	4.4	14.9	45.6	0.013	0.005	0.021	0.35	0.28	0.010	<0.0001	19.5	2.90	0.160	0.49	0.022	1.90	6.118
above effluent	73.5			1300	0.022	290	8.0	20.1	5.5	13.3	46.8	0.139	0.043	0.025	0.71	1.10	0.007	<0.0001	25.3	3.35	0.280	0.63	0.043	3.16	
below effluent	73.9			1300	0.023	295	8.1	19.5	5.3	13.3	44.9	0.095	0.018	0.032	0.82	1.48	0.008	<0.0001	25.8	2.90	0.250	0.55	0.053	3.39	
Finchale Abbey	78.1			1400	0.024	295	8.1	19.6	4.7	13.3	44.8	0.014	0.009	0.028	0.56	0.66	0.005	<0.0001	26.3	3.90	0.307	0.66	0.047	3.20	
Sunderland Br.	58.3	Sat	30.6.73	1300	0.010	475	8.0	31.9	6.1	13.8	53.0	0.005	0.003	0.030	0.10	0.04	0.006	0.0002	22.7	2.30	0.556	0.43	0.170	1.96	2.002
above effluent	73.5			1500	0.015	600	8.1	60.0	10.2	21.5	62.0	0.010	0.002	0.012	0.12	0.04	0.004	0.0008	26.8	2.70	0.616	0.65	0.190	2.60	
below effluent	73.9			1500	0.022	700	8.2	58.0	9.5	21.2	61.0	0.015	0.002	0.018	0.11	0.03	0.005	0.0005	28.5	2.70	0.618	0.58	0.180	2.50	
Finchale Abbey	78.1			1600	0.012	700	8.2	54.1	8.9	21.6	62.8	0.014	0.006	0.027	0.10	0.03	0.003	0.0004	26.8	2.65	0.528	0.49	0.180	3.40	
Sunderland Br.	58.3	Mon	30.7.73	0930	0.011	335	8.2	28.7	5.4	15.1	52.9	0.009	<0.002	0.053	0.14	<0.03	0.011	<0.0001	27.5	1.55	0.304	0.34	0.057	2.00	3.153
above effluent	73.5			1000	0.013	475	8.2	45.1	6.3	16.9	52.2	0.007	<0.002	0.030	0.15	<0.03	0.007	<0.0001	36.5	6.50	0.400	0.65	0.143	3.04	
below effluent	73.9			1000	0.013	475	8.2	47.6	6.3	17.2	52.5	0.006	<0.002	0.030	0.16	<0.03	0.008	<0.0001	38.0	1.85	0.400	0.68	0.143	2.94	
Finchale Abbey	78.1			1100	0.015	480	8.2	51.6	6.7	18.4	53.8	0.007	<0.002	0.024	0.14	<0.03	0.006	<0.0001	37.0	1.95	0.422	0.59	0.232	3.32	
Sunderland Br.	58.3	Tue	14.8.73	1530	0.008	380	8.2	37.5	7.6	19.2	50.1	0.013	0.003	0.014	0.16	<0.03	0.007	0.0002	31.5	2.00	0.372	0.38	0.043	2.81	3.550
above effluent	73.5			1630	0.008	490	8.2	52.5	8.8	22.6	51.4	0.011	0.004	0.012	0.16	<0.03	0.007	<0.0001	44.6	2.21	0.442	0.59	0.071	3.45	
below effluent	73.9			1630	0.009	510	8.2	54.3	8.7	22.9	51.6	0.020	0.004	0.015	0.14	<0.03	0.009	0.0003	46.2	2.16	0.451	0.64	0.066	3.49	
Finchale Abbey	78.1			1730	0.007	520	8.2	55.7	8.6	23.5	50.8	0.010	0.003	0.015	0.15	<0.03	0.006	0.0002	45.5	2.18	0.459	0.62	0.069	3.53	
Sunderland Br.	58.3	Tue	4.9.73	1500	0.016	325	8.1	20.3	4.3	9.7	43.6	0.002	<0.002	0.002	0.05	<0.03	0.006	<0.0001	42.7	2.05	0.520	0.28	0.028	1.18	2.420
above effluent	73.5			1600	0.010	525	8.3	57.2	7.2	16.3	47.2	<0.002	<0.002	0.005	0.03	<0.03	0.005	<0.0001	65.1	0.95	0.542	0.51	0.078	1.24	
below effluent	73.9			1600	0.008	560	8.3	59.8	7.3	16.0	52.3	0.002	<0.002	0.004	0.05	<0.03	0.006	<0.0001	68.4	0.75	0.538	0.53	0.088	1.66	
Finchale Abbey	78.1			1700	0.009	660	8.2	70.3	7.9	17.6	54.3	0.002	<0.002	0.007	0.06	<0.03	0.005	<0.0001	72.3	0.58	0.556	0.36	0.043	2.16	
Sunderland Br.	58.3	Thu	10.10.73	1300	0.012	210	7.0	11.5	3.0	7.7	28.5	0.030	0.005	0.018	0.65	0.28	0.029	0.0003	37.8	3.10	0.119	0.43	0.011	0.48	9.948
above effluent	73.5			1430	0.012	340	7.2	21.0	4.6	11.1	27.3	0.015	0.003	0.028	0.64	0.52	0.020	0.0004	48.3	3.32	0.313	0.62	0.061	1.22	
below effluent	73.9			1430	0.013	340	7.1	27.4	4.5	10.8	38.0	0.023	0.003	0.014	0.50	0.37	0.022	0.0003	42.0	3.30	0.271	0.40	0.058	1.68	
Finchale Abbey	78.1			1500	0.012	345	7.1	23.1	4.7	11.7	39.4	0.018	0.002	0.018	0.51	0.36	0.020	0.0006	57.5	3.34	0.284	0.44	0.060	1.40	
Sunderland Br.	58.3	Tue	20.11.73	1000	0.009	410	8.1	28.2	5.2	15.7	54.5	0.036	0.002	0.060	0.19	0.07	0.008	<0.0001	38.4	2.70	0.410	0.35	0.032	2.46	3.600
above effluent	73.5			1100	0.008	460	8.1	36.3	6.2	17.7	54.9	0.021	0.005	0.038	0.20	0.10	0.009	<0.0001	49.2	2.95	0.446	0.46	0.042	3.28	
below effluent	73.9			1100	0.008	465	8.2	38.5	6.3	16.9	52.9	0.034	0.002	0.042	0.24	0.15	0.009	0.0002	48.3	3.10	0.452	0.47	0.046	3.38	
Finchale Abbey	78.1			1200	0.009	450	8.2	35.2	5.9	15.2	50.8	0.018	0.003	0.038	0.22	0.15	0.006	<0.0001	50.1	3.05	0.461	0.45	0.041	3.35	

Table A.1d Rookhope Burn - water chemistry 1973

no.	site	km	day	date	time	OD_{420}	cond µ mhos	pH	Na	K	Mg	Ca	Zn	Cu	Mn	Fe	Al	Pb	Cd	Cl	Si	PO_4-P	NH_3-N	NO_2-N	NO_3-N	flow cumecs
	North Grain Sike																									
115	(Rookhope Burn Head)	-0.5	Thu	1.3.73	1230	0.059	43	5.4	4.0	0.80	0.9	3.0	0.270	0.042	0.097	0.63	0.23	0.018	0.0002	2.8	2.00	<0.005	0.20	<0.002	<0.4	
012	Upper Rookhope Burn	-8.5			1230	0.050	60	6.1	6.0	1.00	1.2	6.0	0.265	0.032	0.143	0.54	0.42	0.062	0.0030	4.7	2.10	<0.005	0.20	<0.002	<0.4	
012	Lower Rookhope Burn	-3.9			1300	0.047	75	6.3	7.3	1.40	2.0	9.0	0.260	0.021	0.240	0.53	0.78	0.370	0.0035	5.1	2.25	<0.005	0.19	<0.002	<0.4	
012	Eastgate Rookhope Burn	0.6			1300	0.039	80	6.3	5.6	1.50	2.2	12.4	0.210	0.008	0.174	0.56	0.64	0.150	0.0020	5.3	2.50	<0.005	0.15	<0.002	<0.4	1.266
	North Grain Sike																									
115	(Rookhope Burn Head)	-0.5	Wed	16.5.73	1200	0.045	34	4.5	5.4	1.0	1.6	3.6	0.131	0.015	0.270	0.88	0.44	0.045	0.0058	4.5	1.75	<0.005	0.30	<0.002	<0.4	
012	Upper Rookhope Burn	-8.5			1200	0.013	150	6.9	5.9	1.7	3.9	15.5	0.100	0.017	0.012	0.31	0.06	0.090	0.0018	7.1	1.95	<0.005	0.13	<0.002	<0.4	
012	Lower Rookhope Burn	-3.9			1400	0.025	245	7.3	8.0	3.8	6.2	32.3	0.520	0.022	0.094	0.28	0.12	0.390	0.0014	8.6	3.10	0.015	0.11	0.005	<0.4	
012	Eastgate Rookhope Burn	-0.6			1500	0.039	260	7.9	8.3	3.4	5.9	37.2	0.310	0.020	0.081	0.23	0.11	0.172	0.0007	8.6	2.60	0.005	0.05	0.003	0.52	0.248
	North Grain Sike																									
115	(Rookhope Burn Head)	-0.5	Sat	30.6.73	0900	0.024	120	4.6	8.0	2.4	2.2	11.6	0.004	0.002	0.170	0.24	0.11	0.005	0.0002	7.4	2.05	<0.005	0.20	<0.002	<0.4	
012	Upper Rookhope Burn	-8.5			0900	0.010	175	6.8	4.9	2.2	4.9	23.4	0.054	<0.002	0.017	0.11	<0.03	0.013	0.0004	10.0	2.20	<0.005	0.12	<0.002	<0.4	
012	Lower Rookhope Burn	-3.9			0930	0.008	300	7.1	9.2	3.4	7.8	44.3	0.610	0.002	0.200	0.09	<0.03	0.070	0.0018	9.6	2.65	0.015	0.12	0.005	0.53	
012	Easgate Rookhope Burn	-0.6			0930	0.006	300	7.2	9.2	3.5	7.8	47.1	0.320	0.003	0.040	0.05	<0.03	0.026	0.0012	11.0	2.55	0.022	0.13	0.004	0.50	0.121
	North Grain Sike																									
115	(Rookhope Burn Head)	-0.5	Fri	27.7.73	1200	0.062	95	4.5	3.5	0.5	1.2	2.6	0.054	0.008	0.240	0.70	0.24	0.006	0.0001	3.6	2.15	<0.005	0.29	<0.002	<0.4	
012	Upper Rookhope Burn	-8.5			1200	0.016	120	6.7	4.6	1.7	3.8	16.7	0.064	0.007	0.047	0.44	0.19	0.039	0.0001	8.0	2.20	<0.005	0.10	<0.002	<0.4	
012	Lower Rookhope Burn	-3.9			1300	0.007	240	7.2	7.7	2.4	6.2	32.8	0.380	0.021	0.178	0.23	0.11	0.042	0.0009	9.9	2.85	0.032	0.08	<0.002	0.49	
012	Eastgate Rookhope Burn	-0.6			1300	0.013	255	7.5	7.7	2.3	6.3	38.3	0.230	0.018	0.072	0.20	<0.03	0.033	0.0005	9.2	2.95	0.036	0.05	<0.002	0.54	0.197
	North Grain Sike																									
115	(Rookhopeburn Head)	-0.5	Tue	4.9.73	1030	0.103	100	4.8	4.5	0.7	1.3	4.7	0.015	0.002	0.015	0.78	0.18	0.009	0.0005	5.1	2.00	0.020	0.19	<0.002	<0.4	
012	Upper Rookhope Burn	-8.5			1030	0.018	136	6.7	4.8	2.0	4.4	21.3	0.030	0.002	0.009	0.46	0.03	0.024	0.0004	7.3	2.25	0.005	0.12	<0.002	<0.4	
012	Lower Rookhope Burn	-3.9			1100	0.019	225	7.1	8.6	2.8	6.6	39.5	0.330	0.017	0.146	0.17	<0.03	0.051	0.0012	10.6	3.25	0.023	0.11	0.004	0.43	
012	Eastgate Rookhope Burn	-0.6			1100	0.013	260	7.4	8.4	2.7	6.5	42.9	0.240	0.010	0.048	0.14	<0.03	0.043	0.0008	10.2	3.90	0.005	0.06	0.002	<0.4	0.167
	North Grain Sike																									
115	(Rookhope Burn Head)	-0.5	Wed	10.10.73	1030	0.069	90	5.3	2.7	0.2	0.8	1.2	0.032	<0.002	0.104	1.48	0.28	0.026	0.0002	16.8	1.70	<0.005	0.71	<0.002	<0.4	
012	Upper Rookhope Burn	-8.5			1030	0.017	130	6.3	3.6	0.9	2.1	8.3	0.088	<0.002	0.217	1.04	0.32	0.071	0.0009	23.1	1.83	<0.005	0.16	<0.002	<0.4	
012	Lower Rookhope Burn	-3.9			1100	0.020	240	6.8	5.3	1.4	3.5	17.7	0.370	0.004	0.350	0.87	0.22	0.064	0.0009	21.0	1.85	<0.005	0.06	<0.002	<0.4	
012	Eastgate Rookhope Burn	-0.6			1100	0.020	245	7.0	5.4	1.4	3.5	20.2	0.310	0.002	0.250	0.84	0.20	0.067	0.0014	25.2	1.92	<0.005	0.06	<0.002	<0.4	1.260

Table A.1e Pithouse acid streams- water chemistry mean values July 1972-August 1974

site	km	OD_{420}	cond umhos	pH	acidity	Na	K	Mg	Ca	Zn	Cu	Mn	Fe	Al	Pb	Cd	Co	Ni	Cl	Si	PO_4-P	NH_3-N	NO_3-N	SO_4-S	flow cumecs
1 (source)	-3.6	0.022	1870	2.6	807	12.9	0.95	61.4	59.4	1.13	0.69	6.1	99.6	26.8	0.024	0.009	0.214	0.47	23.2	44.7	0.350	0.78	0.41	454	3.2×10^{-4}
2		0.024	1680	2.6	772	10.8	1.05	53.5	53.2	0.88	0.58	5.33	87.8	23.0	0.013	-	0.180	0.43	34.2	44.2	0.287	0.61	0.38	426	-
3		0.021	1550	2.6	757	13.8	1.06	52.5	55.8	0.91	0.55	5.2	86.2	28.0	0.042	-	0.197	0.42	24.2	43.9	0.280	0.50	0.34	416	-
4		0.022	1640	2.6	628	12.1	1.50	55.8	56.8	0.98	0.59	6.1	89.7	25.8	0.017	-	0.170	0.43	28.1	46.0	0.12	0.49	0.20	420	-
5		0.017	1550	2.6	598	13.2	2.2	53.3	55.8	0.93	0.52	5.9	78.7	22.1	0.039	-	0.150	0.36	18.4	41.1	0.15	0.46	0.26	338	-
6		0.013	1475	2.7	630	12.7	1.86	57.8	64.6	0.83	0.46	5.3	77.6	22.0	0.018	-	0.110	0.32	20.3	41.0	0.067	0.36	0.33	399	-
8		0.002	1670	3.5	525	157	12.5	105.0	108.0	0.84	0.27	5.5	24.0	21.2	0.009	-	0.178	0.27	29.3	25.4	0.02	0.33	0.88	508	-
after confluence with stream B																									
9		0.003	1600	3.5	366	164	14.7	104.0	106.0	0.76	0.28	5.14	12.5	18.5	0.011	-	0.138	0.25	23.8	19.2	0.023	0.42	0.98	581	-
10		0.002	1580	3.2	318	148	10.5	96.8	106.0	0.75	0.26	5.40	10.9	17.7	0.03	-	0.175	0.28	26.0	19.8	0.079	0.57	1.41	503	-
11	-1.6	0.003	1580	3.5	248	85.6	6.9	65.0	84.0	0.39	0.11	3.95	8.2	10.7	0.014	-	0.09	0.144	22.8	14.4	0.048	0.402	1.10	397	-
13		0.002	704	5.2	199	53.2	9.8	51.3	66.4	0.18	0.04	2.13	1.78	1.93	0.005	-	0.052	0.073	25.0	12.2	0.024	0.33	0.56	236	-
15		0.002	650	5.8	59.6	36.2	5.9	44.8	59.1	0.09	0.06	2.20	1.01	1.12	0.004	-	0.034	0.064	23.2	9.1	0.018	0.33	0.64	187	-
16		0.029	578	7.0	12.0	39.6	9.5	36.7	54.3	0.064	0.009	0.49	0.41	0.20	0.001	-	0.020	0.024	36.2	7.57	0.097	0.074	1.18	38.2	-
17	-0.1	0.008	616	7.2	6.0	44.2	7.5	38.2	85.1	0.053	0.008	1.34	0.57	0.09	0.001	-	0.001	0.020	36.0	6.70	0.090	0.89	0.84	42.0	-
stream B	-0.6	0.003	2000	2.78	758	157	7.6	145.0	136.0	1.23	0.33	8.7	17.5	28.7	0.010	-	0.23	0.402	25.2	46.7	0.014	0.47	0.32	616	-

Table A.1f River Wear and selected tributaries - water chemistry

Late Winter 1973

no.	site	km	day	date	time	OD_{420}	cond µmhos	pH	Na	K	Mg	Ca	Zn	Cu	Mn	Fe	Al	Pb	Cd	Cl	Si	PO_4-P	NH_3-N	NO_2-N	NO_3-N	flow cumecs
008	Wearhead	00.0	Thu	1.3.73	1200	0.050	75	6.7	5.1	1.12	1.58	9.9	0.120	<0.002	0.086	0.48	1.00	0.039	0.0002	3.6	1.56	<0.005	0.24	<0.002	<0.40	
115	Rookhope Burn (head trib.)	-0.5			1230	0.059	43	5.4	4.0	0.8	0.9	3.0	0.270	0.042	0.097	0.63	0.23	0.018	0.0002	2.8	2.00	<0.005	0.20	<0.002	<0.40	
012	Rookhope Burn (upper)	-8.5			1230	0.050	60	6.1	6.0	1.0	1.2	6.0	0.265	0.032	0.143	0.54	0.42	0.062	0.0030	4.7	2.10	<0.005	0.20	<0.002	<0.40	
012	Rookhope Burn (lower)	-3.9			1300	0.047	75	6.3	7.3	1.4	2.0	9.5	0.260	0.021	0.240	0.53	0.78	0.370	0.0035	5.1	2.25	<0.005	0.19	<0.002	<0.40	
012	Rookhope Burn (Eastgate)	-0.6			1300	0.039	80	6.3	5.6	1.5	2.2	12.4	0.210	0.008	0.174	0.56	0.64	0.150	0.0020	5.3	2.56	<0.005	0.15	<0.002	<0.40	1.266
008	Stanhope Ford	14.6			1330	0.039	100	6.7	6.5	1.6	2.5	17.4	0.068	<0.002	0.066	0.46	1.08	0.049	0.0004	9.1	2.25	<0.005	0.13	<0.002	<0.40	6.647
008	Wolsingham Br.	24.3			1400	0.014	145	7.3	8.0	1.8	3.8	28.0	0.031	<0.002	0.031	0.19	0.20	0.032	0.0003	9.8	2.25	<0.005	0.13	0.004	<0.40	
008	Witton-le-Wear Br.	35.2			1430	0.005	765	7.9	8.0	2.0	4.3	32.9	0.011	<0.002	0.017	0.09	0.06	0.010	0.0003	10.7	2.25	0.010	0.12	0.005	<0.40	
008	Bishop Auckland (below Gaunless)	44.3			1500	0.004	205	7.9	10.5	2.8	7.0	37.9	0.013	<0.002	0.025	0.10	0.05	0.010	<0.0001	13.2	2.00	0.035	0.12	0.006	0.41	
008	Willington Br.	51.1			1530	0.008	225	7.8	20.9	4.6	13.4	46.3	0.018	<0.002	0.045	0.16	0.16	0.010	<0.0001	13.8	2.25	0.164	0.10	0.011	0.70	
008	Sunderland Br.	58.3			1600	0.008	300	7.8	12.6	3.2	7.3	35.0	0.009	0.002	0.029	0.10	0.08	0.010	<0.0001	18.5	2.25	0.192	0.09	0.024	0.88	8.991
002	Pithouse Stream (source)	-3.3			1400	0.010	1750	2.6	11.0	0.24	59.0	58.6	1.08	0.75	6.0	110.0	28.0	0.009	0.0080	22.1	42.0	0.245	0.28	-	<0.40	
002	Pithouse Stream (lower)	-0.1			1400	0.007	550	6.8	40.1	9.2	38.0	65.0	0.012	<0.002	1.25	0.48	<0.03	0.004	0.0002	26.3	8.50	<0.005	0.66	0.039	1.22	
005	R. Deerness (Ushaw Moor)	-3.7			1400	0.010	540	8.2	30.0	8.8	42.7	68.9	0.003	0.005	1.121	0.30	<0.03	0.004	<0.0001	27.5	2.50	0.52	0.16	0.022	4.80	
014	R. Browney (Langley Moor)	-6.1			1430	0.012	375	8.0	41.1	8.9	13.7	39.7	0.011	<0.002	0.066	0.18	0.07	0.004	<0.0001	24.7	3.50	0.70	0.54	0.080	7.80	
008	Shincliffe Br.	65.5			1630	0.007	400	7.7	40.5	7.3	15.8	52.1	0.020	<0.002	0.060	0.11	<0.03	0.007	<0.0001	22.4	3.25	0.310	0.39	0.027	2.86	
008	above effluent	73.5			1700	0.007	400	7.7	44.6	5.8	13.7	45.8	0.010	<0.002	0.041	0.11	<0.03	0.007	<0.0001	23.7	3.35	0.410	0.78	0.033	2.12	
008	below effluent	73.9			1700	0.007	400	7.7	36.3	5.5	11.7	42.2	0.018	<0.002	0.048	0.11	<0.03	0.008	<0.0001	22.9	3.25	0.400	0.83	0.033	2.12	
008	Finchale Abbey	78.1			1730	0.007	400	7.8	35.4	5.4	11.8	42.3	0.016	<0.002	0.031	0.13	<0.03	0.007	<0.0001	21.8	5.50	0.440	0.79	0.034	2.20	
008	Lumley Br.	87.9			1730	0.008	410	7.8	46.0	5.2	13.1	46.3	0.021	0.007	0.058	0.13	<0.03	0.007	<0.0001	24.3	2.75	0.470	1.02	0.038	2.56	
008	Lambton Br.	90.0			1800	0.009	575	7.8	77.8	6.9	16.9	52.0	0.049	0.016	0.125	0.18	<0.03	0.007	<0.0001	36.2	4.00	0.540	1.80	0.049	2.64	

Table A.1g River Wear and selected tributaries - water chemistry

Summer 1973

no	site	day	date	km	time	OD_{420}	cond μmhos	pH	Na	K	Mg	Ca	Zn	Cu	Mn	Fe	Al	Pb	Cd	Cl	Si	PO_4-P	NH_3-N	NO_2-N	NO_3-N	flow cumecs
008	Wearhead	Sat	30.6.73	0.00	0830	0.018	215	6.8	4.8	2.4	4.9	34.9	0.096	0.006	0.031	0.06	0.04	0.007	0.0005	8.8	1.85	<0.005	0.14	<0.002	<0.4	
115	Rookhope Burn (head trib.)			-0.5	0900	0.027	120	4.6	8.0	2.4	2.2	11.6	0.004	0.002	0.170	0.24	0.11	0.005	0.0002	7.4	2.05	<0.005	0.20	<0.002	<0.4	
012	Rookhope Burn (upper)			-8.5	0900	0.010	175	6.8	4.9	2.2	4.9	23.4	0.054	<0.002	0.017	0.11	<0.03	0.013	0.0004	10.0	2.20	<0.005	0.12	<0.002	<0.4	
012	Rookhope Burn (lower)			-3.9	0930	0.008	300	7.1	9.2	3.4	7.8	44.3	0.610	0.002	0.200	0.09	<0.03	0.070	0.0018	9.8	2.65	0.015	0.12	0.005	<0.4	
012	Rookhope Burn (Eastgate)			-0.6	0930	0.006	300	7.2	9.2	3.5	7.8	47.1	0.320	0.003	0.040	0.05	<0.03	0.026	0.0012	11.0	2.55	0.022	0.13	0.004	<0.4	0.121
008	Stanhope Ford			14.6	1030	0.005	300	6.9	8.1	3.1	6.4	49.7	0.102	0.012	0.015	<0.03	<0.03	0.007	0.0005	11.7	2.35	0.025	0.16	0.006	0.43	
008	Wolsingham Br.			24.3	1100	0.007	300	7.1	8.9	3.1	6.4	52.6	0.016	<0.002	0.005	0.04	<0.03	0.004	0.0002	12.0	2.30	0.020	0.15	0.008	0.48	
008	Witton-le-Wear Br.			35.2	1100	0.009	300	7.6	10.3	2.8	5.7	44.2	0.008	0.002	0.012	0.03	<0.03	0.003	0.0003	15.5	2.30	0.044	0.10	0.012	0.75	
008	Bishop Auckland (below Gaunless)			44.3	1130	0.010	350	7.9	14.4	4.0	10.1	47.4	0.008	<0.002	0.023	0.10	<0.03	0.004	0.0002	17.5	2.30	0.164	0.37	0.053	0.91	
008	Willington Br.			51.1	1200	0.015	385	7.8	16.2	4.6	10.2	48.5	0.008	<0.002	0.021	0.10	0.03	0.006	0.0003	17.5	2.30	0.400	0.45	0.092	1.70	
008	Sunderland Br.			58.3	1230	0.010	475	8.0	31.9	6.1	13.8	53.0	0.005	0.003	0.030	0.10	0.04	0.006	0.0002	22.7	2.30	0.556	0.43	0.070	1.96	2.002
022	Pithouses Stream (source)			-3.3	1300	0.013	2000	2.6	11.2	0.08	61.0	57.5	1.04	0.70	6.00	98.0	30.8	0.007	0.0082	20.2	39.59	0.402	0.34	-	<0.4	
022	Pithouses Stream (lower)			-0.1	1330	0.055	330	6.7	37.7	16.1	41.3	70.0	0.014	0.007	4.47	1.63	<0.03	<0.001	0.0013	29.2	7.50	0.330	2.10	0.048	<0.4	
005	R. Deerness (Usnaw Moor)			-3.7	1330	0.010	800	8.0	38.0	10.5	45.1	77.5	0.002	0.005	0.025	0.19	0.13	0.003	0.0004	31.0	2.55	0.525	0.24	0.023	2.75	
014	R. Browney (Langley Moor)			-6.1	1400	0.015	800	8.1	65.0	11.2	24.8	58.1	0.005	<0.002	0.011	0.17	0.06	0.003	0.0004	25.8	2.95	0.592	0.56	0.125	3.34	
008	Shincliffe Br.			65.5	1430	0.015	750	8.1	50.2	9.7	16.9	55.9	0.011	0.002	0.012	0.12	0.04	0.004	0.0008	28.5	2.70	0.616	0.39	0.162	2.76	
008	above effluent			73.5	1500	0.015	600	8.2	60.0	10.2	21.5	62.0	0.010	0.002	0.018	0.11	<0.03	0.004	0.0005	26.8	2.70	0.616	0.65	0.19	2.60	
008	below effluent			73.9	1530	0.012	700	8.2	58.0	9.5	21.2	61.0	0.015	0.006	0.027	0.10	<0.03	0.005	0.0004	28.5	2.65	0.526	0.58	0.18	2.50	
008	Finchale Abbey			78.1	1600	0.022	700	8.1	54.1	8.9	21.6	62.8	0.014	0.009	0.036	0.55	<0.03	0.003	0.0003	26.0	2.65	0.540	0.58	0.18	3.40	
008	Lumley Br.			87.9	1630	0.012	900	8.1	71.1	10.3	24.1	67.3	0,003	0.003	0.058	0.13	<0.03	0.003	0.0002	29.6	2.75	0.580	0.59	0.18	2.88	
008	Lambton Br.			90.0	1700	0.011	900	8.1	106.5	11.2	26.6	73.2	0.005	0.006	0.043	0.15	<0.03	0.004	0.0002	44.7	2.90	0.680	1.60	0.20	3.40	

Table A.1h River Wear and selected tributaries - water chemistry

Autumn 1973

no.	site	km	day	date	time	OD_{420}	cond µmhos	pH	Na	K	Mg	Ca	Zn	Cu	Mn	Fe	Al	Pb	Cd	Cl	Si	PO_4-P	NH_3-N	NO_2-N	NO_3-N	flow cumecs
008	Wearhead	0.00		10.10.73	1015	0.014	125	6.8	4.2	1.00	2.90	21.40	0.153	<0.002	0.068	0.60	0.80	0.039	0.0007	31.5	1.10	<0.005	0.32	<0.002	<0.4	
115	Rookhope Burn (head trib.)	-0.5			1030	0.069	90	5.5	2.7	0.21	0.75	1.11	0.032	<0.002	0.104	1.48	0.28	0.028	0.0002	16.8	1.70	<0.005	0.71	<0.002	<0.4	
012	Rookhope Burn (upper)	-8.5			1030	0.017	130	6.3	3.6	0.95	2.10	8.32	0.088	<0.002	0.217	1.04	0.32	0.071	0.0009	23.1	1.83	<0.005	0.16	<0.002	<0.4	
012	Rookhope Burn (lower)	-3.9			1100	0.020	240	6.8	5.3	1.41	3.50	17.70	0.370	0.004	0.350	0.87	0.22	0.064	0.0009	21.0	1.85	<0.005	0.06	<0.002	<0.4	
012	Rookhope Burn (Eastgate)	-0.6			1100	0.020	245	7.0	5.4	1.42	3.50	20.20	0.310	0.002	0.250	0.84	0.20	0.067	0.0014	25.2	1.92	<0.005	0.06	<0.002	<0.4	1.260
008	Stanhope Ford	14.6			1115	0.015	130	7.2	5.0	1.46	3.20	23.50	0.098	<0.002	0.040	0.62	0.32	0.050	0.0006	21.0	1.95	<0.005	0.06	<0.002	<0.4	5.011
008	Wolsingham Br.	24.3			1130	0.014	135	7.3	5.0	1.50	3.10	24.30	0.058	0.007	0.027	0.57	0.20	0.026	0.0004	21.8	2.05	<0.005	0.06	<0.002	<0.4	
008	Witton-le-Wear Br.	35.2			1200	0.014	135	7.3	5.4	1.59	3.10	21.30	0.054	0.004	0.024	0.66	0.32	0.028	0.0005	16.8	2.10	0.040	0.05	<0.002	<0.4	
008	Bishop Auckland (below Gaunless)	44.3			1215	0.012	150	7.3	6.5	2.30	5.10	23.70	0.042	<0.002	0.018	0.68	0.37	0.031	0.0005	22.1	2.35	0.048	0.25	<0.002	0.41	
008	Willington Br.	51.1			1230	0.013	175	7.2	7.1	2.50	5.50	23.90	0.043	0.003	0.017	0.74	0.32	0.037	0.0003	29.4	2.95	0.080	<0.05	0.039	1.28	
008	Sunderland Br.	58.3			1245	0.012	210	7.0	11.5	3.00	7.70	28.50	0.030	0.005	0.018	0.65	0.28	0.029	0.0004	37.8	3.10	0.119	0.43	0.011	0.48	9.948
002	Pithouses Stream (source)	-3.3			1300	0.012	1800	2.5	11.1	0.04	76.90	68.40	1.200	0.820	7.500	126.0	36.7	0.004	0.0070	27.3	38.0	0.202	0.40	-	<0.4	
022	Pithouses Stream (lower)	-0.1			1315	0.022	560	6.9	70.9	14.50	56.00	87.20	0.013	0.004	1.530	2.46	<0.03	0.001	0.0005	44.2	6.6	0.313	0.22	0.032	0.43	
005	R. Deerness (Ushaw Moor)	-3.7			1315	0.018	490	7.0	22.9	8.80	31.50	60.50	0.005	0.004	0.029	0.53	0.37	0.002	<0.0001	82.2	2.70	0.708	0.12	0.064	4.20	
014	R. Browney (Langley Moor)	-6.1			1330	0.020	360	7.1	49.7	11.40	22.30	56.30	0.006	0.003	0.008	0.23	0.12	0.003	<0.0001	92.4	3.50	0.680	0.52	0.068	4.10	
008	Shincliffe	65.5			1400	0.010	320	7.1	17.8	4.70	9.60	33.60	0.024	0.002	0.009	0.57	0.34	0.018	0.0001	45.2	3.20	0.246	0.77	0.014	0.56	
008	above effluent	73.5			1430	0.012	340	7.2	21.0	4.60	11.10	37.30	0.015	0.003	0.028	0.64	0.52	0.020	0.0004	48.3	3.20	0.313	0.62	0.061	1.22	
008	below effluent	73.9			1430	0.013	340	7.1	27.4	4.50	10.80	38.00	0.023	0.003	0.014	0.50	0.37	0.020	0.0003	42.0	3.25	0.271	0.40	0.058	1.68	
008	Finchale Abbey	78.1			1500	0.012	345	7.1	23.1	4.70	11.70	39.40	0.018	0.002	0.018	0.51	0.36	0.020	0.0006	57.5	3.25	0.284	0.44	0.060	1.40	
008	Lumley Br.	87.9			1530	0.014	355	7.1	40.1	7.70	10.00	48.30	0.011	0.002	0.014	0.30	0.24	0.012	0.0003	65.1	3.20	0.560	0.36	0.060	1.86	
008	Lambton Br.	90.0			1545	0.015	470	7.2	57.5	8.80	11.80	50.90	0.017	<0.002	0.018	0.30	0.14	0.020	0.0002	67.5	3.30	0.560	1.70	0.128	2.80	

Table A.11 River Wear and selected tributaries - water chemistry

Winter 1974

no	site	km	day	date	time	OD_{420}	cond. µmhos	pH	Na	K	Mg	Ca	Zn	Cu	Mn	Fe	Al	Pb	Cd	Cl	Si	PO_4-P	NH_3-N	NO_2-N	NO_3-N	flow cumecs
008	Wearhead	0.0	Sat	19.1.74	1000	0.043	110	6.2	3.5	0.70	1.7	10.2	0.023	0.005	0.054	0.45	0.28	0.015	0.0007	4.5	0.85	<0.005	0.70	<0.002	0.21	
115	Rookhope Burn (head trib.)	-0.5			1030	0.060	90	4.9	4.6	0.56	0.8	1.4	0.042	0.016	0.093	0.71	0.17	0.017	0.0040	4.0	0.80	<0.005	1.00	<0.002	<0.20	
012	Rookhope Burn(upper)	-8.5			1030	0.040	95	6.3	4.7	1.07	2.1	7.6	0.157	<0.002	0.186	0.39	0.33	0.060	0.0060	5.3	1.65	<0.005	0.75	<0.002	<0.20	
012	Rookhope Burn(lower)	-3.9			1100	0.023	110	6.6	6.3	1.50	3.2	15.6	0.270	0.002	0.270	0.53	0.17	0.065	0.0070	6.4	2.25	<0.005	0.66	<0.002	0.26	
012	Rookhope Burn (Eastgate)	-0.6			1100	0.030	115	6.6	6.3	1.57	3.2	20.7	0.200	0.004	0.164	0.42	0.17	0.127	0.0050	7.1	2.20	<0.005	0.42	<0.002	0.34	0.900
008	Stanhope Ford	14.6			1100	0.030	115	7.0	6.3	1.95	3.3	28.4	0.071	<0.002	0.051	0.30	0.36	0.028	0.0009	5.8	1.85	<0.005	0.42	<0.002	0.26	5.000
008	Wolsingham Br.	24.3			1130	0.022	125	7.5	6.6	1.91	2.7	31.4	0.051	<0.002	0.024	0.23	0.25	0.025	0.0007	6.1	2.15	0.008	0.67	0.003	0.29	
008	Witton-le-Wear Br.	35.2			1130	0.024	125	7.5	7.3	1.84	3.7	28.0	0.046	0.002	0.037	0.23	0.21	0.018	0.0007	8.9	2.55	0.019	0.68	0.002	0.37	
008	Bishop Auckland (below Gaunless)	44.3			1200	0.024	160	7.9	9.5	2.5	7.0	32.4	0.033	<0.002	0.040	0.26	0.16	0.021	0.0003	9.4	2.90	0.018	0.67	0.011	0.58	
008	Willington Br.	51.1			1200	0.023	180	7.9	10.6	2.6	6.8	32.6	0.035	<0.002	0.036	0.24	0.16	0.023	0.0003	13.7	3.00	0.054	0.74	0.012	0.94	
008	Sunderland Br.	58.3			1230	0.020	200	8.0	10.0	2.7	7.3	32.2	0.065	0.002	0.032	0.30	0.24	0.020	<0.0001	24.2	2.95	0.110	0.73	0.022	1.32	19.700
022	Pithouses stream (source)	-3.3			1300	0.020	1450	2.6	11.7	0.82	52.5	53.0	1.31	0.52	5.3	82.0	25.0	0.104	0.0080	20.0	61.5	0.10	2.3	-	0.75	
022	Pithouses stream (lower)	-0.1			1300	0.018	300	7.1	32.1	7.7	29.4	60.0	0.037	0.003	0.48	0.49	0.21	0.001	<0.0001	30.0	8.00	0.011	1.0	-	0.56	
005	R. Deerness (Ushaw Moor)	-3.7			1300	0.025	450	7.8	21.2	6.2	31.7	52.6	<0.002	<0.002	0.032	0.16	0.06	0.002	<0.0001	41.1	3.8	0.153	0.74	0.024	0.61	
014	R. Browney (Langley Moor)	-6.1			1300	0.014	475	7.8	21.5	5.2	16.2	43.2	0.014	0.002	0.070	0.19	0.16	0.017	<0.0001	26.9	4.45	0.116	0.68	0.032	2.02	
008	Shincliffe Br.	65.5			1400	0.026	290	7.9	14.7	3.5	9.4	35.4	0.040	<0.002	0.049	0.34	0.30	0.094	<0.0001	28.2	3.35	0.061	0.85	0.021	2.48	
008	above effluent	73.5			1430	0.031	300	8.0	21.2	4.2	11.2	38.0	0.038	<0.002	0.058	0.40	0.36	0.040	<0.0001	30.1	3.25	0.070	0.77	0.020	2.67	
008	below effluent	73.9			1430	0.031	300	8.0	21.8	4.3	11.1	38.6	0.060	<0.002	0.068	0.37	0.30	0.230	<0.0001	31.3	3.30	0.083	0.88	0.020	2.70	
008	Finchale Abbey	78.1			1500	0.032	305	8.0	22.1	4.4	11.5	38.0	0.037	0.009	0.049	0.35	0.33	0.031	<0.0001	31.1	3.15	0.078	0.75	0.022	2.71	
008	Lumley Br.	87.9			1530	0.038	315	8.1	22.1	4.6	10.8	36.9	0.074	0.011	0.047	0.39	0.45	0.06	<0.0001	35.7	3.15	0.068	0.71	0.022	3.04	
008	Lambton Br.	90.0			1530	0.034	375	8.1	26.2	4.1	12.3	40.0	0.033	0.005	0.055	0.47	0.52	0.03	<0.0001	41.2	3.20	0.101	0.78	0.028	3.26	

APPENDIX 2.

Plant Analysis

Tables A.2A - A.2P

** A.2A SURVEY OF MACROPHYTIC COMPOSITION R.WEAR FINCHALE 1967-68. **
****

LIST OF NAMES 1 NA 2 K 3 MG 4 CA 5 ZN 6 CU 7 MN 8 FE 9 AL 10 PB 11 CD 12 CO 13 NI

NUMBER OF BLOCKS-CASES 9 NUMBER OF REPLICATES IN FIRST BLOCK 4

SIMPLE STATISTICS FOR 4 REPLICATES Cladophora glomerata 27. 7. 67

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	323.1165	8.1260	264.1250	16.2519	5.0297
K	25780.5469	256.4578	63082.6250	512.9158	1.9895
MG	2741.4248	47.2299	8922.6641	94.4599	3.4456
CA	10458.1563	230.2000	11968.0000	460.3999	4.4023
ZN	194.9933	4.9508	98.0417	9.9016	5.0779
CU	42.1078	1.3373	7.1536	2.6746	6.3519
MN	8487.8984	113.8888	51882.6641	227.7777	2.6836
FE	3454.6240	105.5778	44586.6641	211.1555	6.1123
AL	1389.2549	8.9768	322.3333	17.9536	1.2923
PB	79.6946	1.1513	5.3021	2.3026	2.8893
CD	1.6346	0.0106	0.0005	0.0212	1.2984
CO	135.7068	3.1317	39.2292	6.2633	4.6153
NI	154.5090	3.4034	46.3333	6.8069	4.4055

SIMPLE STATISTICS FOR 4 REPLICATES Enteromorpha flexuosa 13. 8. 68

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	274.6282	7.6906	236.5833	15.3813	5.6008
K	22067.2656	118.0282	55722.6641	236.0565	1.0697
MG	11005.1836	72.4431	20992.0000	144.8862	1.3165
CA	33425.3750	115.3776	53248.0000	230.7553	0.6904
ZN	48.6807	1.1908	5.6719	2.3816	4.8922
CU	7.6668	0.2682	0.2877	0.5364	6.9964
MN	778.8347	6.2450	156.0000	12.4900	1.6037
FE	442.1436	16.6305	1106.2315	33.2610	7.5227
AL	859.9563	14.4885	839.6665	28.9770	3.3696
PB	17.8466	0.6444	1.6611	1.2888	7.2216
CD	1.6226	0.0025	0.0000	0.0049	0.3049
CO	6.4931	0.6715	1.8036	1.3430	20.6829
NI	18.2556	0.7865	2.4744	1.5730	8.6168

SIMPLE STATISTICS FOR 4 REPLICATES Oedogonium sp. (9) 13. 8. 68

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	107.6663	3.8212	58.4075	7.6425	7.0983
K	20202.1875	180.9015	30901.3125	361.8030	1.7909
MG	6430.4023	56.5803	12805.3320	113.1606	1.7598
CA	11084.0703	155.7434	97024.0000	311.4868	2.8102
ZN	51.1373	0.7331	2.1497	1.4662	2.8672
CU	7.3581	0.1906	0.1454	0.3813	5.1819
MN	1177.1094	21.3053	1815.6665	42.6105	3.6199
FE	633.2317	19.5384	1527.0000	39.0768	6.1710
AL	687.4465	11.1692	499.0000	22.3383	2.5171
PB	36.0313	1.0497	4.4076	2.0994	5.8266
CD	1.6370	0.0227	0.0021	0.0454	2.7752
CO	11.4769	0.7681	2.3599	1.5362	13.3852
NI	19.2222	1.0014	4.0111	2.0028	10.4191

SIMPLE STATISTICS FOR 4 REPLICATES *Vaucheria sessilis* 13. 8. 68

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	432.7563	8.0961	262.1875	16.1972	3.7416
K	2771.9092	38.0000	5776.0000	76.0000	2.7418
MG	5229.5078	74.9222	22453.3320	149.8444	2.8654
CA	19364.0938	190.3821	44981.3125	380.7642	1.9663
ZN	536.2454	5.5151	121.6667	11.0303	2.0569
CU	33.8429	0.5416	1.1732	1.0831	3.2005
MN	7616.3750	105.4577	44485.3320	210.9155	2.7692
FE	7632.6523	161.9712	04938.6250	323.9424	4.2442
AL	2420.7793	56.2020	12634.5641	112.4040	4.6433
PB	81.4988	1.9658	15.4570	3.9315	4.8240
CD	4.0134	0.1063	0.0452	0.2126	5.2962
CO	136.1230	2.5228	25.4583	5.0456	3.7067
NI	131.1732	6.0065	144.3125	12.0130	9.1581

SIMPLE STATISTICS FOR 4 REPLICATES *Eurhynchium riparioides* 27. 7. 67

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	250.0483	6.4315	165.4583	12.8631	5.1258
K	6044.2969	60.6740	14725.3320	121.3480	2.0076
MG	3724.9668	71.6194	20517.3320	143.2387	3.8454
CA	15914.4570	116.5733	54357.3320	233.1466	1.4650
ZN	1139.0986	8.9675	321.6665	17.9351	1.5745
CU	38.2132	0.6315	1.5951	1.2630	3.3050
MN	30552.4688	78.5196	24661.3320	157.0393	0.5140
FE	7565.0781	82.6075	27296.0000	165.2150	2.1839
AL	4295.4883	242.2863	34810.6250	484.5725	11.2810
PB	183.0246	2.5238	25.4792	5.0477	2.7579
CD	3.9084	0.1047	0.0438	0.2093	5.3555
CO	289.4998	5.3716	115.4167	10.7432	3.7110
NI	1058.0605	9.5917	368.0000	19.1833	1.8131

SIMPLE STATISTICS FOR 4 REPLICATES *Fissidens crassipes* 27. 7. 67

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	441.0286	8.7265	304.6040	17.4529	3.9573
K	5338.1484	137.3123	75418.6250	274.6245	5.1446
MG	3594.4414	114.7635	52682.6641	229.5270	6.3856
CA	16434.0938	89.6809	32170.6641	179.3618	1.0914
ZN	2148.3174	26.3818	2784.0000	52.7636	2.4560
CU	57.1925	0.4239	0.7188	0.8478	1.4823
MN	48391.7500	400.1067	40341.3125	800.2134	1.6536
FE	13766.0547	106.3328	45226.5641	212.6656	1.5449
AL	5932.0781	55.2328	12202.6641	110.4657	1.8622
PB	318.3079	3.2946	43.4167	6.5891	2.0700
CD	8.1351	0.1073	0.0461	0.2146	2.6382
CO	513.9836	5.5076	121.3333	11.0151	2.1431
NI	1388.0850	19.7653	1562.6665	39.5306	2.8478

SIMPLE STATISTICS FOR 4 REPLICATES *Fontinalis antipyretica* 27. 7. 67

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	177.5449	4.3547	75.8542	8.7094	4.9055
K	4461.2500	87.1015	30346.6641	174.2029	3.9048
MG	2045.2646	9.0600	328.3333	18.1200	0.8859
CA	8836.6133	193.1631	49248.0000	386.3262	4.3719
ZN	414.1958	7.6977	237.0208	15.3955	3.7170
CU	19.8671	0.2420	0.2343	0.4840	2.4364

MN	17762.5469	234.2421	19477.3125	468.4841	2.6375
FE	4126.7422	165.4851	09541.3125	330.9702	8.0201
AL	1641.4102	36.6447	5371.3320	73.2894	4.4650
PB	245.3277	1.7425	12.1458	3.4851	1.4206
CD	1.6835	0.0086	0.0003	0.0172	1.0224
CO	149.3961	2.5475	25.9583	5.0949	3.4104
NI	363.1553	4.0965	67.1250	8.1930	2.2561

SIMPLE STATISTICS FOR 4 REPLICATES <u>*Potamogeton crispus*</u> 20. 8. 68

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	11153.5352	135.2134	73130.6250	270.4268	2.4246
K	32659.9688	328.1299	30677.3125	656.2600	2.0094
MG	2483.1738	16.5731	1098.6665	33.1461	1.3348
CA	7829.4688	125.6344	63136.0000	251.2588	3.2093
ZN	246.6512	1.3712	7.5208	2.7424	1.1119
CU	28.2484	0.4133	0.6834	0.8267	2.9265
MN	1132.1475	10.2997	424.3333	20.5993	1.8195
FE	1587.3447	45.6079	8320.3320	91.2159	5.7464
AL	740.9749	15.3921	947.6665	30.7842	4.1546
PB	43.3578	0.8909	3.1745	1.7817	4.1093
CD	1.6837	0.0104	0.0004	0.0207	1.2299
CO	19.7769	1.2332	6.0830	2.4664	12.4710
NI	83.3771	2.6694	28.5026	5.3386	6.4032

SIMPLE STATISTICS FOR 4 REPLICATES <u>*Potamogeton pectinatus*</u> 20. 8. 68

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	11117.4609	273.0176	98154.6250	546.0354	4.9115
K	33590.1250	122.5507	60074.6641	245.1013	0.7297
MG	5036.3945	94.4669	35696.0000	188.9339	3.7514
CA	10742.1094	197.4774	55989.3125	394.9548	3.6767
ZN	188.2200	3.1910	40.7292	6.3819	3.3907
CU	15.4240	0.1383	0.0765	0.2766	1.7932
MN	2604.3125	16.7332	1120.0000	33.4664	1.2850
FE	1538.3828	8.4163	283.3333	16.8325	1.0942
AL	339.9968	9.8250	386.1250	19.6501	5.7795
PB	34.4197	0.7472	2.2331	1.4943	4.3415
CD	1.6590	0.0120	0.0006	0.0239	1.4418
CO	40.2168	0.8743	3.0573	1.7485	4.3477
NI	81.2581	1.6039	10.2904	3.2079	3.9477

** A.2B CLADOPHORA MINERAL COMPOSITION FINCHALE R.WEAR 1972. **
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LIST OF NAMES 1 NA 2 K 3 MG 4 CA 5 ZN 6 CU 7 MN 8 FE 9 AL 10 PB 11 CD
12 CO 13 NI

NUMBER OF BLOCKS-CASES 5 NUMBER OF REPLICATES IN FIRST BLOCK 4

SIMPLE STATISTICS FOR 4 REPLICATES <u>Cladophora glomerata</u> 1. 4. 72

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	941.2971	52.3418	10958.5641	104.6836	11.1212
K	30875.7813	988.1428	05706.0000	1976.2859	6.4008
MG	2124.9854	88.8069	31546.6641	177.6138	8.3584
CA	8722.3594	321.6292	13781.3125	643.2583	7.3748
ZN	725.9924	17.3566	1205.0000	34.7131	4.7815
CU	21.7420	1.0017	4.0135	2.0034	9.2143
MN	262.1406	23.5502	2218.4583	47.1005	17.9676
FE	1045.1494	46.1745	8528.3320	92.3490	8.8360
AL	1030.4053	63.7116	16236.6641	127.4232	12.3663
PB	20.4591	1.1304	5.1117	2.2609	11.0508
CD	3.3027	0.5597	1.2529	1.1193	33.8923
CO	20.3481	0.7367	2.1709	1.4734	7.2409
NI	19.5940	1.9615	15.3900	3.9230	20.0214

SIMPLE STATISTICS FOR 4 REPLICATES <u>Cladophora glomerata</u> 25. 4. 72

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	328.1533	84.5154	28571.3750	169.0307	51.5097
K	33741.0156	710.5151	19328.0000	1421.0305	4.2116
MG	2133.2002	12.1106	586.6665	24.2212	1.1354
CA	5399.8711	75.6219	22874.6641	151.2437	2.8009
ZN	125.3752	4.4955	80.8398	8.9911	7.1714
CU	32.4991	0.8115	2.6341	1.6230	4.9940
MN	442.0762	6.5955	174.0000	13.1909	2.9839
FE	953.8896	59.0085	13928.0000	118.0170	12.3722
AL	875.0774	20.6922	1712.6665	41.3844	4.7292
PB	21.2221	3.0736	37.7889	6.1473	28.9663
CD	1.6668	0.0072	0.0002	0.0143	0.8604
CO	14.1619	0.4275	0.7311	0.8551	6.0377
NI	17.9190	0.8125	2.6408	1.6250	9.0689

SIMPLE STATISTICS FOR 4 REPLICATES <u>Cladophora glomerata</u> 9. 5. 72

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	479.1074	65.3427	17078.6641	130.6854	27.2768
K	40656.2281	361.5669	22922.6250	723.1338	1.7786
MG	2426.7090	7.0238	197.3333	14.0475	0.5789
CA	6881.7539	76.7072	23536.0000	153.4145	2.2293
ZN	137.8962	1.6378	10.7292	3.2755	2.3754
CU	20.1179	0.0636	0.0162	0.1273	0.6326
MN	198.2458	1.5828	10.0208	3.1656	1.5968
FE	888.6018	16.5907	1101.0000	33.1813	3.7341
AL	767.0212	9.0738	329.3333	18.1475	2.3660
PB	14.6746	0.8357	2.7939	1.6715	11.3903
CD	1.6765	0.0053	0.0001	0.0106	0.6310
CO	10.8951	0.4695	0.8816	0.9389	8.6179
NI	11.3146	0.4059	0.6591	0.8118	7.1752

SIMPLE STATISTICS FOR 4 REPLICATES <u>Cladophora glomerata</u> 24. 5. 72

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	235.8392	10.4455	436.6875	20.8971	8.8607
K	41870.8438	563.4180	69760.0000	1126.8362	2.6912
MG	1985.4189	9.4604	358.0000	18.9209	0.9530
CA	5441.5791	83.5384	27914.6641	167.0768	3.0704
ZN	60.8210	3.0213	36.5130	6.0426	9.9351
CU	14.0316	0.4302	0.7404	0.8605	6.1323
MN	161.9629	2.0817	17.3333	4.1633	2.5705
FE	555.3398	10.9962	483.6665	21.9924	3.9602
AL	352.9614	11.3539	515.6458	22.7078	6.4335
PB	16.1463	1.9915	15.8641	3.9830	24.6680
CD	1.7003	0.0085	0.0003	0.0170	0.9967
CO	8.5055	0.3639	0.5297	0.7278	8.5569
NI	9.5655	0.4005	0.6417	0.8011	8.3743

SIMPLE STATISTICS FOR 4 REPLICATES <u>Cladophora glomerata</u> 14. 7. 72

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	488.7102	16.2862	1060.9583	32.5724	6.6650
K	24473.0000	197.2612	55648.0000	394.5225	1.6121
MG	1732.9922	8.4261	284.0000	16.8523	0.9724
CA	10944.5000	134.5808	72448.0000	269.1616	2.4593
ZN	141.3234	1.5910	10.1250	3.1820	2.2516
CU	9.2458	1.0695	4.5754	2.1390	23.1349
MN	2909.1133	41.6973	6954.6641	83.3946	2.8667
FE	479.7339	10.3966	432.3540	20.7931	4.3343
AL	404.0679	9.7115	377.2500	19.4229	4.8068
PB	23.5885	1.8137	13.1573	3.6273	15.3774
CD	1.6837	0.0294	0.0035	0.0589	3.4968
CO	22.3071	0.8910	3.1758	1.7021	7.9888
NI	31.5588	0.8726	3.0459	1.7453	5.5302

** A.2C CLADOPHORA MINERAL COMPOSITION LOWER R.WEAR 29.4.73. **

LIST OF NAMES 1 NA 2 K 3 MG 4 CA 5 ZN 6 CU 7 MN 8 FE 9 AL 10 PB 11 CD 12 CO 13 NI

NUMBER OF BLOCKS-CASES 4 NUMBER OF REPLICATES IN FIRST BLOCK 4

SIMPLE STATISTICS FOR 4 REPLICATES *Cladophora glomerata* Sunderland Bridge (km 58.3) 29. 4. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	228.8133	4.3893	77.0625	8.7785	3.8365
K	12761.3867	206.1456	69984.0000	412.2913	3.2308
MG	2147.4053	35.0808	4922.6641	70.1617	3.2673
CA	6825.9805	200.5027	60805.3125	401.0054	5.8747
ZN	163.6017	2.6722	28.5625	5.3444	3.2667
CU	9.0451	0.4409	0.7774	0.8817	9.7480
MN	1509.2363	24.0243	2308.6665	48.0486	3.1836
FE	2175.5439	19.8662	1578.6665	39.7324	1.8263
AL	1470.2246	52.0928	10854.6641	104.1857	7.0864
PB	78.9258	1.4083	7.9336	2.8167	3.5687
CD	3.2716	0.0329	0.0043	0.0658	2.0098
CO	13.4859	0.3084	0.3804	0.6167	4.5732
NI	14.1142	0.4741	0.8991	0.9482	6.7181

SIMPLE STATISTICS FOR 4 REPLICATES *Cladophora glomerata* above effluent (km 73.5) 29. 4. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	192.9161	7.7285	238.9167	15.4569	8.0123
K	15343.6172	148.3059	87978.6250	296.6118	1.9331
MG	2340.9629	40.1331	6442.6641	80.2662	3.4288
CA	5717.0664	150.0621	90074.6250	300.1243	5.2496
ZN	83.5531	1.6800	11.2891	3.3599	4.0213
CU	6.4723	0.4012	0.6439	0.8025	12.3984
MN	510.3193	17.5554	1232.7708	35.1108	6.8802
FE	1884.4609	79.1323	25047.6641	158.2645	8.3984
AL	1085.1113	45.5924	8314.6641	91.1848	8.4033
PB	40.1745	0.8488	2.8815	1.6975	4.2253
CD	1.6067	0.0114	0.0005	0.0228	1.4220
CO	29.5911	19.9952	1599.2278	39.9903	135.1430
NI	9.0383	0.3943	0.6219	0.7886	8.7252

SIMPLE STATISTICS FOR 4 REPLICATES *Cladophora glomerata* below effluent (km 73.9) 29. 4. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	196.9821	4.5168	81.6042	9.0335	4.5859
K	17766.9219	455.7192	30720.0000	911.4385	5.1300
MG	2230.5244	45.0333	8112.0000	90.0667	4.0379
CA	5264.4951	218.7540	91413.3125	437.5081	8.3105
ZN	125.3846	2.1637	18.7266	4.3274	3.4513
CU	5.7073	0.1653	0.1093	0.3306	5.7926
MN	610.9419	19.6977	1552.0000	39.3954	6.4483
FE	1539.3721	41.1329	6767.6641	82.2658	5.3441
AL	843.5864	36.2687	5261.6641	72.5373	8.5987
PB	48.6387	1.4228	8.0977	2.8456	5.8506
CD	1.6078	0.0070	0.0002	0.0139	0.8668
CO	8.8391	0.4408	0.7773	0.8817	9.9747
NI	9.6468	0.0421	0.0071	0.0841	0.8722

SIMPLE STATISTICS FOR 4 REPLICATES <u>Cladophora glomerata</u> Finchale Abbey (km 78.1) 29. 4. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	370.2283	7.4400	221.4167	14.8801	4.0192
K	35640.2500	185.6736	137898.6250	371.3472	1.0419
MG	2623.1621	42.3163	7162.6641	84.6325	3.2264
CA	7038.8125	53.4914	11445.3320	106.9829	1.5199
ZN	88.7606	3.6199	52.4154	7.2398	8.1566
CU	6.1608	0.2955	0.3493	0.5910	9.5929
MN	493.4199	6.5044	169.2292	13.0088	2.6365
FE	2085.0566	20.1329	1621.3333	40.2658	1.9312
AL	675.1343	30.2737	3666.0000	60.5475	8.9682
PB	43.8370	2.8700	32.9000	5.7400	13.1050
CD	1.5923	0.0250	0.0025	0.0499	3.1355
CO	12.9444	0.3823	0.5847	0.7647	5.9073
NI	11.9328	0.2579	0.2661	0.5159	4.3230

** A.2C CONT. CLADOPHORA MIN. COMP. LWR R.WEAR 18.5.73 **

LIST OF NAMES 1 NA 2 K 3 MG 4 CA 5 ZN 6 CU 7 MN 8 FE 9 AL 10 PB 11 CD 12 CO 13 NI

NUMBER OF BLOCKS-CASES 4 NUMBER OF REPLICATES IN FIRST BLOCK 4

SIMPLE STATISTICS FOR 4 REPLICATES _Cladophora glomerata_ Sunderland Bridge (km 58.3) 18. 5. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	213.2364	5.9112	139.7708	11.8225	5.5443
K	7163.4375	144.4854	83504.0000	288.9707	4.0340
MG	1288.4609	25.3213	2564.6665	50.6425	3.9305
CA	5119.8477	92.3400	34106.6641	184.6799	3.6071
ZN	117.9415	4.2806	73.2956	8.5613	7.2589
CU	6.4097	0.3141	0.3948	0.6283	9.8024
MN	491.2019	9.3056	346.3750	18.6111	3.7889
FE	1244.7109	20.9285	1752.0000	41.8569	3.3628
AL	684.1208	37.3140	5569.3320	74.6280	10.9086
PB	22.1810	1.0597	4.4922	2.1195	9.5554
CD	1.6111	0.0208	0.0017	0.0417	2.5871
CO	7.8464	0.1094	0.0479	0.2188	2.7879
NI	8.8523	0.2679	0.2871	0.5358	6.0529

SIMPLE STATISTICS FOR 4 REPLICATES _Cladophora glomerata_ above effluent (km 73.5) 18. 5. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	317.2305	19.1763	1470.9165	38.3525	12.0898
K	25146.3906	334.4407	47402.6250	669.9816	2.6600
MG	2034.9990	13.8654	769.0000	27.7309	1.3627
CA	5437.9531	93.9432	35301.3320	187.8865	3.4551
ZN	67.0453	1.4187	8.0508	2.8374	4.2320
CU	5.5681	0.2295	0.2107	0.4590	8.2434
MN	389.9524	6.4441	166.1042	12.8881	3.3051
FE	1620.7871	14.6173	854.6665	29.2347	1.8037
AL	1097.1523	43.8625	7695.6641	87.7249	7.9957
PB	18.7141	1.6664	11.1073	3.3328	17.8088
CD	1.6250	0.0121	0.0006	0.0241	1.4855
CO	7.5238	0.4414	0.7795	0.8829	11.7343
NI	5.2861	0.2720	0.2959	0.5439	10.2899

SIMPLE STATISTICS FOR 4 REPLICATES _Cladophora glomerata_ below effluent (km 73.9) 18. 5. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	389.6672	0.5154	1.0625	1.0308	0.2645
K	28593.4219	177.3884	25866.6250	354.7769	1.2408
MG	2334.2100	24.6306	2426.6665	49.2612	2.1104
CA	6251.9473	185.5371	37696.0000	371.0742	5.9353
ZN	203.3379	2.3071	21.2017	4.6143	2.2682
CU	5.5012	0.2808	0.3155	0.5617	10.2105
MN	389.8328	6.5943	173.9375	13.1885	3.3831
FE	2487.7578	72.8926	21253.3320	145.7852	5.8601
AL	2175.7588	91.3747	33397.3320	182.7494	8.3993
PB	38.9872	0.9877	3.9023	1.9754	5.0669
CD	1.6413	0.0180	0.0013	0.0360	2.1953
CO	7.5899	0.3910	0.6114	0.7819	10.3022
NI	15.5903	0.7160	2.0505	1.4319	8.9551

SIMPLE STATISTICS FOR 4 REPLICATES <u>*Cladophora glomerata*</u> Finchale Abbey (km 78.1) 18. 5. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	273.5735	2.7557	30.3750	5.5114	2.0146
K	19197.0625	98.9545	39168.0000	197.9091	1.0309
MG	2243.3848	28.5890	3267.3333	57.1781	2.5487
CA	6178.5469	80.5812	25973.3320	161.1624	2.6084
ZN	158.3828	1.1704	5.4792	2.3408	1.4779
CU	7.5188	0.0511	0.0105	0.1022	1.2911
MN	410.4773	3.8770	60.1250	7.7540	1.8890
FE	3429.0098	34.4287	4741.3320	68.8573	2.0081
AL	1284.9336	14.3817	827.3333	28.7634	2.2385
PB	39.7825	0.8759	3.0690	1.7519	4.4036
CD	1.6537	0.0132	0.0007	0.0263	1.5886
CO	7.8823	0.4388	0.7702	0.8776	11.1341
NI	10.3593	0.3509	0.4926	0.7019	6.7751

** A.2C CONT. CLADOPHORA MIN. COMP. LWR R.WEAR 14.8.73. **
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LIST OF NAMES 1 NA 2 K 3 MG 4 CA 5 ZN 6 CU 7 MN 8 FE 9 AL 10 PB 11 CD 12 CO 13 NI

NUMBER OF BLOCKS-CASES 4 NUMBER OF REPLICATES IN FIRST BLOCK 4

SIMPLE STATISTICS FOR 4 REPLICATES <u>Cladophora glomerata</u> Sunderland Bridge (km 58.3) 14. 8. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	263.0930	5.3376	113.9583	10.6751	4.0575
K	33308.3438	332.0400	41002.6250	664.0803	1.9937
MG	2215.8701	20.5913	1696.0000	41.1825	1.8585
CA	5761.1953	76.2190	23237.3320	152.4380	2.6459
ZN	146.8304	4.1357	68.4167	8.2714	5.6333
CU	6.9077	0.1659	0.1101	0.3318	4.8027
MN	950.0581	11.7615	553.3333	23.5230	2.4760
FE	2002.6133	12.8128	656.6665	25.6255	1.2796
AL	967.2766	73.6484	21696.3320	147.2968	15.2280
PB	60.4352	0.9549	3.6471	1.9097	3.1600
CD	1.6451	0.0137	0.0007	0.0274	1.6639
CO	5.5462	0.3637	0.5290	0.7273	13.1136
NI	11.5128	0.6648	1.7681	1.3297	11.5496

SIMPLE STATISTICS FOR 4 REPLICATES <u>Cladophora glomerata</u> above effluent (km 73.5) 14. 8. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	493.4805	9.0772	329.5833	18.1544	3.6789
K	29732.2031	129.4913	67072.0000	258.9827	0.8711
MG	2529.4531	42.1900	7120.0000	84.3801	3.3359
CA	7681.2930	70.3136	19776.0000	140.6272	1.8308
ZN	128.9136	2.3728	22.5208	4.7456	3.6812
CU	8.0020	0.5314	1.1295	1.0628	13.2814
MN	1052.8281	27.8717	3107.3333	55.7435	5.2946
FE	1480.7549	16.2532	1056.6665	32.5064	2.1953
AL	631.9595	17.6375	1244.3333	35.2751	5.5819
PB	60.7972	1.2061	5.8190	2.4123	3.9677
CD	1.6318	0.0163	0.0011	0.0325	1.9927
CO	8.3613	0.1958	0.1533	0.3916	4.6830
NI	19.9956	0.5368	1.1528	1.0737	5.3697

SIMPLE STATISTICS FOR 4 REPLICATES <u>Cladophora glomerata</u> below effluent (km 73.9) 14. 8. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	567.0210	12.9647	672.3333	25.9294	4.5729
K	28515.9063	132.6650	70400.0000	265.3301	0.9305
MG	2482.4863	28.6589	3285.3333	57.3178	2.3089
CA	6419.5820	123.7632	61269.3320	247.5264	2.9399
ZN	259.7454	2.9173	34.0417	5.8345	2.2462
CU	5.3749	0.2876	0.3309	0.5752	10.7022
MN	735.6553	18.8105	1415.3333	37.6209	5.1139
FE	2148.5273	65.2380	17024.0000	130.4761	6.0728
AL	1109.1924	16.9337	1147.0000	33.8674	3.0533
PB	81.3936	1.4509	8.4206	2.9018	3.5652
CD	3.2884	0.0430	0.0074	0.0861	2.6169
CO	8.2211	0.1077	0.0464	0.2154	2.6198
NI	15.6136	0.4430	0.7849	0.8860	5.6742

SIMPLE STATISTICS FOR 4 REPLICATES *Cladophora glomerata* Finchale Abbey (km 78.1) 14. 8. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	586.3843	8.2006	269.0000	16.4012	2.7970
K	32146.3594	227.9181	07786.6250	455.8362	1.4180
MG	2449.8594	40.0666	6421.3320	80.1332	3.2709
CA	7710.5078	62.6418	15696.0000	125.2837	1.6248
ZN	81.9588	0.6427	1.6523	1.2854	1.5684
CU	5.0584	0.1245	0.0620	0.2489	4.9212
MN	369.8210	2.8229	31.8750	5.6458	1.5266
FE	1797.0664	22.2598	1982.0000	44.5197	2.4774
AL	662.7930	8.1803	267.6665	16.3605	2.4684
PB	52.5766	2.4453	23.9180	4.8906	9.3019
CD	1.6093	0.0291	0.0034	0.0582	3.6170
CO	13.0529	0.3230	0.4173	0.6460	4.9491
NI	14.8899	0.5172	1.0699	1.0344	6.9467

** A.2C CONT. CLADOPHORA MIN. COMP. LWR R.WEAR 4.9.73. **

LIST OF NAMES 1 NA 2 K 3 MG 4 CA 5 ZN 6 CU 7 MN 8 FE 9 AL 10 PB 11 CD 12 CO 13 NI

NUMBER OF BLOCKS-CASES 4 NUMBER OF REPLICATES IN FIRST BLOCK 4

SIMPLE STATISTICS FOR 4 REPLICATES <u>Cladophora glomerata</u> Sunderland Bridge (km 58.3) 4. 9. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	410.2522	3.3088	43.7917	6.6175	1.6130
K	48644.7500	265.8120	82624.0000	531.6240	1.0929
MG	3014.1797	30.8329	3802.6665	61.6658	2.0459
CA	7673.4727	127.4990	65024.0000	254.9980	3.3231
ZN	101.2849	5.1904	107.7591	10.3807	10.2490
CU	6.9311	0.4235	0.7173	0.8469	12.2189
MN	533.2239	19.0613	1453.3333	38.1226	7.1495
FE	1357.7744	9.0416	327.0000	18.0831	1.3318
AL	594.0386	35.4507	5027.0000	70.9013	11.9355
PB	35.7177	1.4820	8.7852	2.9640	8.2983
CD	3.2820	0.0265	0.0028	0.0529	1.6130
CO	23.3761	0.2663	0.2837	0.5326	2.2785
NI	23.7872	0.3797	0.5766	0.7593	3.1922

SIMPLE STATISTICS FOR 4 REPLICATES <u>Cladophora glomerata</u> above effluent (km 73.5) 4. 9. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	560.3499	13.2696	704.3333	26.5393	4.7362
K	46122.5469	243.7047	37568.0000	487.4094	1.0568
MG	3276.5908	74.1889	22016.0000	148.3779	4.5284
CA	6377.0000	124.6863	62186.6641	249.3725	3.9105
ZN	54.0002	2.0369	16.5963	4.0739	7.5442
CU	4.9148	0.3314	0.4392	0.6627	13.4846
MN	658.7869	28.5613	3263.0000	57.1227	8.6709
FE	1043.5000	44.5720	7946.6641	89.1441	8.5428
AL	367.8056	22.6517	2052.3958	45.3034	12.3172
PB	35.9793	0.9203	3.3880	1.8407	5.1159
CD	1.6357	0.0146	0.0009	0.0292	1.7858
CO	9.6146	0.2795	0.3126	0.5591	5.8150
NI	19.2133	0.3445	0.4749	0.6891	3.5866

SIMPLE STATISTICS FOR 4 REPLICATES <u>Cladophora glomerata</u> below effluent (km 73.9) 4. 9. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	739.2708	6.8313	186.6667	13.6626	1.8481
K	38083.6094	213.8660	82954.6250	427.7319	1.1231
MG	2836.6035	44.9296	8074.6641	89.8591	3.1678
CA	7561.5586	304.4995	70880.0000	608.9993	8.0539
ZN	97.5896	2.3192	21.5156	4.6385	4.7531
CU	5.6076	0.1223	0.0599	0.2447	4.3629
MN	747.5498	12.2236	597.6665	24.4472	3.2703
FE	917.9482	28.2916	3201.6665	56.5833	6.1641
AL	477.5230	20.3935	1663.5833	40.7870	8.5412
PB	36.1163	1.1023	4.8607	2.2047	6.1044
CD	1.6612	0.0071	0.0002	0.0142	0.8566
CO	9.5520	0.2429	0.2359	0.4857	5.0850
NI	22.4237	0.4450	0.7921	0.8900	3.9689

SIMPLE STATISTICS FOR 4 REPLICATES <u>Cladophora glomerata</u> Finchale Abbey (km 78.1) 4. 9. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	677.7573	28.2916	3201.6665	56.5833	8.3486
K	34298.4844	462.9873	57429.3125	925.9749	2.6998
MG	3202.4268	53.9506	11642.6641	107.9012	3.3694
CA	8036.9141	78.8247	24853.3320	157.6494	1.9616
ZN	97.5230	5.1385	105.6159	10.2770	10.5380
CU	7.2308	0.0877	0.0308	0.1755	2.4268
MN	1351.0732	28.4751	3243.3333	56.9503	4.2152
FE	1512.6104	47.6506	9082.3320	95.3013	6.3004
AL	516.5068	20.3981	1664.3333	40.7962	7.8985
PB	33.0587	2.0233	16.3750	4.0466	12.2407
CD	1.6529	0.0048	0.0001	0.0096	0.5779
CO	23.1424	0.6911	1.9102	1.3821	5.9722
NI	26.0344	0.4338	0.7527	0.8676	3.3324

** A2C CONT. CLADOPHORA MIN. COMP. LWR R.WEAR 20.11.73. **
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LIST OF NAMES 1 NA 2 K 3 MG 4 CA 5 ZN 6 CU 7 MN 8 FE 9 AL 10 PB 11 CD
12 CO 13 NI

NUMBER OF BLOCKS-CASES 4 NUMBER OF REPLICATES IN FIRST BLOCK 4

SIMPLE STATISTICS FOR 4 REPLICATES <u>Cladophora</u> <u>glomerata</u> **Sunderland Bridge (km 58.3) 20. 11. 73**

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	358.6431	42.7782	7314.7141	85.5565	23.8556
K	27444.9844	349.0481	87338.6250	698.0964	2.5436
MG	2424.4434	38.6609	5978.6641	77.3218	3.1893
CA	7418.1797	245.9539	41973.3125	491.9077	6.6311
ZN	500.7292	10.0703	405.6458	20.1407	4.0223
CU	12.1957	0.4795	0.9196	0.9590	7.8631
MN	9139.2891	207.8973	72885.3125	415.7947	4.5495
FE	2457.6260	24.6577	2432.0000	49.3153	2.0066
AL	1286.2520	32.4422	4210.0000	64.8845	5.0445
PB	106.1714	1.9988	15.9805	3.9976	3.7652
CD	1.6098	0.0211	0.0018	0.0423	2.6260
CO	98.9818	1.6997	11.5560	3.3994	3.4344
NI	34.6031	0.4760	0.9063	0.9520	2.7511

SIMPLE STATISTICS FOR 4 REPLICATES <u>Cladophora</u> <u>glomerata</u> **above effluent (km 73.5) 20. 11. 73**

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	354.0359	19.9640	1594.2500	39.9281	11.2780
K	24834.1406	203.8038	65144.0000	407.6077	1.6413
MG	2312.2441	32.6394	4261.3320	65.2789	2.8232
CA	8178.9883	188.7467	42501.3125	377.4934	4.6154
ZN	242.5106	5.9783	142.9583	11.9565	4.9303
CU	9.4580	0.4446	0.7907	0.8892	9.4016
MN	4683.4336	52.8141	11157.3320	105.6283	2.2554
FE	1246.1650	66.2307	17546.0000	132.4613	10.6295
AL	666.6814	1.8028	13.0000	3.6056	0.5408
PB	69.5931	3.2082	41.1706	6.4164	9.2199
CD	1.6667	0.0046	0.0001	0.0091	0.5465
CO	48.3260	1.4393	8.2865	2.8786	5.9567
NI	29.1645	0.4287	0.7351	0.8574	2.9398

SIMPLE STATISTICS FOR 4 REPLICATES <u>Cladophora</u> <u>glomerata</u> **below effluent (km 73.9) 20. 11. 73**

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	221.7067	14.5278	844.2290	29.0556	13.1054
K	24166.7344	365.0022	32906.6250	730.0046	3.0207
MG	2177.9590	29.9110	3578.6665	59.8220	2.7467
CA	8817.2647	342.0408	67968.0000	684.0818	7.7584
ZN	496.2930	3.8790	60.1875	7.7581	1.5632
CU	9.0885	0.4329	0.7496	0.8658	9.5262
MN	4020.2070	42.1584	7109.3320	84.3168	2.0973
FE	2482.4141	340.7363	64405.3125	681.4729	27.4520
AL	1256.2705	47.7973	9138.3320	95.5946	7.6094
PB	93.7731	5.7611	132.7604	11.5222	12.2873
CD	6.7008	0.0383	0.0059	0.0766	1.1428
CO	52.7927	1.7301	11.9727	3.4602	6.5542
NI	26.7976	0.6273	1.5739	1.2545	4.6816

SIMPLE STATISTICS FOR 4 REPLICATES <u>Cladophora</u> <u>glomerata</u> Finchale Abbey (km 78.1) 20. 11. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	403.4182	67.5735	18264.7266	135.1470	33.5005
K	22846.5625	252.1798	54378.6250	504.3596	2.2076
MG	2359.1982	28.7054	3296.0000	57.4108	2.4335
CA	9282.9688	216.8871	88160.0000	433.7742	4.6728
ZN	317.8323	4.0240	64.7708	8.0480	2.5322
CU	9.8789	0.2792	0.3118	0.5584	5.6528
MN	4522.8096	68.0784	18538.6641	136.1568	3.0104
FE	3695.6055	19.9332	1589.3333	39.8664	1.0788
AL	1148.7227	9.5699	366.3333	19.1398	1.6662
PB	59.0863	1.8172	13.2083	3.6343	6.1509
CD	1.6410	0.0136	0.0007	0.0273	1.6631
CO	67.6522	1.3367	7.1471	2.6734	3.9517
NI	29.1260	0.4305	0.7415	0.8611	2.9564

** A2D CLADOPHORA MINERAL COMPOSITION UPPER R.WEAR 26.8.73. **
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LIST OF NAMES 1 NA 2 K 3 MG 4 CA 5 ZN 6 CU 7 MN 8 FE 9 AL 10 PB 11 CD 12 CO 13 NI

NUMBER OF BLOCKS-CASES 4 NUMBER OF REPLICATES IN FIRST BLOCK 4

SIMPLE STATISTICS FOR 4 REPLICATES Cladophora glomerata Wolsingham (km 24.3) 26. 8. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	319.6416	22.5577	2035.3958	45.1154	14.1144
K	24190.2656	167.1725	11786.6250	334.3450	1.3821
MG	5532.0078	64.0625	16416.0000	128.1249	2.3161
CA	12515.1680	306.8289	76576.0000	613.6580	4.9033
ZN	1205.6289	10.0830	406.6665	20.1660	1.6727
CU	16.9755	0.3578	0.5120	0.7156	4.2153
MN	2967.3047	22.6569	2053.3333	45.3137	1.5271
FE	1921.7520	30.4302	3704.0000	60.8605	3.1669
AL	1202.9941	14.4885	839.6665	28.9770	2.4087
PB	387.1907	3.0542	37.3125	6.1084	1.5776
CD	8.3005	0.0707	0.0200	0.1415	1.7046
CO	44.3924	0.5587	1.2487	1.1175	2.5172
NI	25.7200	0.2769	0.3067	0.5538	2.1533

SIMPLE STATISTICS FOR 4 REPLICATES Cladophora glomerata Witton-le-Wear (km 35.2) 26. 6. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	644.8887	32.3870	4195.6641	64.7739	10.0442
K	39591.7188	288.0000	31776.0000	576.0000	1.4548
MG	2121.5293	82.1300	26981.3320	164.2599	7.7425
CA	10252.0449	69.5893	19370.6641	139.1785	1.3576
ZN	228.5493	4.4123	77.8750	8.8247	3.8612
CU	6.2502	0.2048	0.1678	0.4097	6.5547
MN	398.8818	2.6359	27.7917	5.2718	1.3216
FE	1945.0996	16.7655	1124.3333	33.5311	1.7239
AL	802.0308	21.7121	1885.6665	43.4243	5.4143
PB	92.5578	4.1400	68.5586	8.2800	8.9458
CD	1.6453	0.0178	0.0013	0.0357	2.1676
CO	25.8935	0.5838	1.3633	1.1676	4.5092
NI	27.5605	0.5362	1.1499	1.0723	3.8908

SIMPLE STATISTICS FOR 4 REPLICATES Cladophora glomerata Bishop Auckland (km 44.3) 26. 8. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	659.2510	23.0760	2130.0000	46.1519	7.0007
K	33189.2031	318.9314	06869.3125	637.8630	1.9219
MG	2244.8682	26.2298	2752.0000	52.4595	2.3369
CA	7641.0742	105.4324	44464.0000	210.8649	2.7596
ZN	125.1983	4.3235	74.7721	8.6471	6.9067
CU	4.6438	0.2020	0.1633	0.4041	8.7018
MN	380.9434	5.1680	106.8333	10.3360	2.7133
FE	1573.9150	7.9057	250.0000	15.8114	1.0046
AL	621.8435	26.6521	2841.3333	53.3042	8.5720
PB	50.5721	1.1942	5.7044	2.3884	4.7228
CD	1.6578	0.0207	0.0017	0.0414	2.4993
CO	24.0205	0.2073	0.1720	0.4147	1.7263
NI	39.3463	0.4341	0.7539	0.8683	2.2068

SIMPLE STATISTICS FOR 4 REPLICATES <u>Cladophora glomerata</u> Willington (km 51.1) 26. 8. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	671.1064	15.4299	952.3333	30.8599	4.5984
K	37213.2500	772.8733	89333.0000	1545.7468	4.1538
MG	2425.6133	61.2100	14986.6641	122.4200	5.0470
CA	7729.7813	323.3408	18197.3125	646.6819	8.3661
ZN	142.5808	8.2557	272.6250	16.5114	11.5803
CU	7.4674	0.6828	1.8648	1.3656	18.2872
MN	568.0608	11.5722	535.6565	23.1445	4.0743
FE	2798.7031	40.3650	6517.3320	80.7300	2.8845
AL	1297.9873	91.6651	33610.0000	183.3303	14.1242
PB	65.8716	1.5902	10.1146	3.1803	4.8281
CD	1.6467	0.0185	0.0014	0.0369	2.2413
CO	29.6369	0.6985	1.9517	1.3970	4.7138
NI	30.4757	0.7551	2.2808	1.5102	4.9556

** A.2E CLADOPHORA MINERAL COMPOSITION R.WEAR 1968. **
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LIST OF NAMES 1 NA 2 K 3 MG 4 CA 5 ZN 6 CU 7 MN 8 FE 9 AL 10 PB 11 CD 12 CO 13 NI

NUMBER OF BLOCKS-CASES 6 NUMBER OF REPLICATES IN FIRST BLOCK 4

SIMPLE STATISTICS FOR 4 REPLICATES *Cladophora glomerata* above Gaunless (km 44.0) 15. 8. 68

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	244.6609	2.3805	22.6667	4.7610	1.9459
K	35684.6563	113.8888	51882.6641	227.7777	0.6383
MG	1964.6699	17.0831	1167.3333	34.1663	1.7390
CA	7723.5508	98.0408	38448.0000	196.0816	2.5387
ZN	101.1432	1.7141	11.7526	3.4282	3.3895
CU	5.3742	0.0715	0.0204	0.1429	2.6597
MN	1741.9170	14.8324	880.0000	29.6648	1.7030
FE	2007.0752	99.5879	39671.0000	199.1758	9.9237
AL	377.6799	21.2262	1802.2083	42.4524	11.2403
PB	48.7439	1.9254	14.8294	3.8509	7.9003
CD	1.6797	0.0181	0.0013	0.0362	2.1522
CO	13.8556	1.0610	4.5028	2.1220	15.3149
NI	15.1146	0.6890	1.8990	1.3780	9.1172

SIMPLE STATISTICS FOR 4 REPLICATES *Cladophora glomerata* Willington (km 51.1) 15. 3. 68

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	246.0732	3.7673	56.7708	7.5346	3.0620
K	29886.0625	570.0618	99882.0000	1140.1238	3.8149
MG	2556.3740	77.1751	23824.0000	154.3503	6.0379
CA	10225.6250	262.2161	75029.3125	524.4324	5.1286
ZN	152.5441	1.2011	5.7708	2.4023	1.5748
CU	8.9354	0.2204	0.1943	0.4408	4.9336
MN	4551.3594	71.3582	20368.0000	142.7165	3.1357
FE	1970.1055	34.8126	4847.6641	69.6252	3.5341
AL	677.4690	13.0512	681.3333	26.1024	3.8529
PB	59.4390	0.3480	0.4844	0.6960	1.1709
CD	1.6627	0.0045	0.0001	0.0090	0.5404
CO	27.4325	1.5803	9.9889	3.1605	11.5210
NI	13.7156	0.7904	2.4992	1.5809	11.5261

SIMPLE STATISTICS FOR 4 REPLICATES *Cladophora glomerata* Durham Sands (km 70.4) 16. 8. 68

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	299.7871	3.7701	56.8542	7.5402	2.5152
K	27244.0625	286.1047	27424.0000	572.2097	2.1003
MG	1953.3193	51.2648	10512.3320	102.5297	5.2490
CA	7247.3047	2122.6855	23184.0000	4245.3711	58.5786
ZN	69.2390	1.4609	8.5365	2.9217	4.2198
CU	6.5944	0.0924	0.0341	0.1847	2.8011
MN	1401.5488	16.7655	1124.3333	33.5311	2.3924
FE	1716.8037	42.0397	7069.3320	84.0793	4.8974
AL	588.8105	21.2289	1802.6665	42.4578	7.2108
PB	48.0928	0.9684	3.7513	1.9368	4.0273
CD	1.6589	0.0069	0.0002	0.0139	0.8374
CO	9.5339	0.7784	2.4237	1.5568	16.3294
NI	21.1425	0.7203	2.0754	1.4406	6.8139

SIMPLE STATISTICS FOR 4 REPLICATES **Cladophora glomerata** **Finchale Abbey (km 78.1)** **13. 8. 68**

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	469.1772	5.1072	104.3333	10.2144	2.1771
K	30758.0781	8956.5664	80384.0000	17913.1328	58.2388
MG	2083.4043	32.6599	4266.6641	65.3197	3.1352
CA	7968.8594	157.1750	98816.0000	314.3501	3.9447
ZN	65.3468	1.1160	4.9818	2.2320	3.4156
CU	4.8881	0.2058	0.1694	0.4115	8.4193
MN	1774.7822	20.5000	1681.0000	41.0000	2.3101
FE	1023.0955	17.4093	1212.3333	34.8186	3.4033
AL	279.6855	21.3654	1825.9165	42.7307	15.2781
PB	8.2202	0.6860	1.8826	1.3721	16.6918
CD	1.6437	0.0086	0.0003	0.0172	1.0461
CO	24.6641	0.7871	2.4781	1.5742	6.3825
NI	22.1989	0.9055	3.2794	1.8109	8.1576

SIMPLE STATISTICS FOR 4 REPLICATES **Cladophora glomerata** Cocken **Bridge (km 80.6)** **13. 8. 68**

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	428.7627	3.5274	49.7708	7.0548	1.6454
K	41508.0625	263.2312	77162.6250	526.4624	1.2683
MG	1374.1377	6.9342	192.3333	13.8684	1.0092
CA	9285.6523	158.8625	00947.3125	317.7251	3.4217
ZN	65.6469	0.5962	1.4219	1.1924	1.8172
CU	13.9885	0.1522	0.0927	0.3045	2.1765
MN	1728.9932	15.3025	936.6665	30.6050	1.7701
FE	581.9346	11.8357	560.3333	23.6714	4.0677
AL	202.2474	3.7880	57.3958	7.5760	3.7459
PB	17.7442	0.4118	0.6783	0.8236	4.6415
CD	1.6507	0.0084	0.0003	0.0169	1.0213
CO	19.8038	0.6404	1.6402	1.2807	6.4670
NI	22.2907	0.5765	1.3295	1.1530	5.1728

SIMPLE STATISTICS FOR 4 REPLICATES **Cladophora glomerata** Lambton **Bridge (km 90.0)** **16. 8. 68**

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	482.5789	6.1144	149.5417	12.2287	2.5340
K	33773.7813	444.5581	90528.0000	889.1165	2.6326
MG	2134.5010	69.0217	19056.0000	138.0435	6.4672
CA	7323.7852	2131.7383	77248.0000	4263.4766	58.2141
ZN	106.2678	1.4340	8.2253	2.8680	2.6988
CU	10.0919	0.1837	0.1350	0.3674	3.6409
MN	2421.5901	77.5629	24064.0000	155.1258	6.4060
FE	2746.3242	122.8278	60346.6641	245.6556	8.9449
AL	1214.9951	44.7269	8002.0000	89.4539	7.3625
PB	25.0379	0.8636	2.9835	1.7273	6.8986
CD	1.6413	0.0080	0.0003	0.0160	0.9764
CO	16.4152	0.6938	1.9253	1.3875	8.4528
NI	27.8954	0.5708	1.3032	1.1416	4.0924

** A.2F FONTINALIS MINERAL COMPOSITION FINCHALE R.WEAR 1972. **

LIST OF NAMES 1 NA 2 K 3 MG 4 CA 5 ZN 6 CU 7 MN 8 FE 9 AL 10 PB 11 CD 12 CO 13 NI

NUMBER OF BLOCKS-CASES 3 NUMBER OF REPLICATES IN FIRST BLOCK 4

SIMPLE STATISTICS FOR 4 REPLICATES **Fontinalis antipyretica young tip Finchale Abbey (km 78.1)**

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	504.1655	15.9645	1019.4583	31.9290	6.3330
K	9256.1836	132.1815	69888.0000	264.3633	2.8561
MG	2122.3164	14.0475	789.3333	28.0951	1.3238
CA	5351.1367	90.5686	32810.6641	181.1371	3.3850
ZN	194.5076	4.4341	78.6458	8.8682	4.5593
CU	39.4150	0.3895	0.6068	0.7790	1.9763
MN	352.5571	8.9643	321.4375	17.9287	5.0853
FE	730.3748	15.8640	1006.6665	31.7280	4.3441
AL	308.3811	20.6332	1702.9165	41.2664	13.3816
PB	40.9185	1.0129	4.1042	2.0259	4.9510
CD	1.3845	0.1215	0.0590	0.2429	17.5451
CO	13.8402	1.1952	5.7136	2.3903	17.2708
NI	47.8613	1.0341	4.2773	2.0682	4.3212

SIMPLE STATISTICS FOR 4 REPLICATES **Fontinalis antipyretica mature Finchale Abbey (km 78.1)**

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	258.6814	11.8669	563.2915	23.7338	9.1749
K	5495.6445	166.4011	10757.3125	332.8022	6.0557
MG	1531.7422	12.6029	635.3333	25.2058	1.6456
CA	5065.1328	160.1000	02528.0000	320.2000	6.3216
ZN	196.4883	11.2294	504.3958	22.4588	11.4301
CU	23.9630	0.7947	2.5260	1.5894	6.6325
MN	1296.9004	18.3053	1340.3333	36.6106	2.8229
FE	1976.3613	12.5067	625.6665	25.0133	1.2656
AL	568.4583	31.4510	3956.6665	62.9020	11.0654
PB	51.2782	1.9435	15.1081	3.8869	7.5800
CD	1.3596	0.0752	0.0226	0.1503	11.0585
CO	14.2017	0.5801	1.3461	1.1602	8.1695
NI	25.3378	1.2704	6.4556	2.5408	10.0276

SIMPLE STATISTICS FOR 4 REPLICATES **Fontinalis antipyretica old part Finchale Abbey (km 78.1)**

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	271.2290	10.2584	420.9375	20.5168	7.5644
K	3753.6963	136.0686	74058.6250	272.1372	7.2498
MG	1398.0293	15.7427	991.3333	31.4854	2.2521
CA	6232.2578	134.1641	72000.0000	268.3281	4.3055
ZN	464.2256	4.3000	73.9583	8.5999	1.8525
CU	32.1391	0.4416	0.7799	0.8831	2.7479
MN	7305.1289	103.7690	43072.0000	207.5379	2.8410
FE	6034.2930	99.5858	39669.3320	199.1716	3.3007
AL	1482.4277	41.1420	6770.6641	82.2840	5.5506
PB	147.6714	4.3193	74.6250	8.6386	5.8499
CD	4.2374	0.0882	0.0311	0.1763	4.1609
CO	72.6130	0.6668	1.7786	1.3237	1.8367
NI	84.1281	1.2797	6.5506	2.5594	3.0423

** A.2G FONTINALIS MINERAL COMPOSITION (DIVIDED) LOWER R.WEAR 29.4.73. **

LIST OF NAMES 1 NA 2 K 3 MG 4 CA 5 ZN 6 CU 7 MN 8 FE 9 AL 10 PB 11 CO 12 CD 13 NI

NUMBER OF BLOCKS-CASES 16 NUMBER OF REPLICATES IN FIRST BLOCK 4

SIMPLE STATISTICS FOR 4 REPLICATES *Fontinalis antipyretica* 1st 30 mm Sunderland Bridge (km 58.3) 29. 4. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	1078.9502	156.7971	98341.3125	313.5942	29.0647
K	10347.9453	205.3160	68618.6250	410.6321	3.9682
MG	2167.7783	63.1295	15941.3320	126.2590	5.8243
CA	4967.5703	354.0432	01386.6250	708.0867	14.2542
ZN	224.4271	3.8924	60.6042	7.7849	3.4688
CU	18.9721	1.8206	13.2582	3.6412	19.1923
MN	1358.8223	21.4612	1842.3333	42.9224	3.1588
FE	1896.4951	20.3142	1650.6665	40.6284	2.1423
AL	1091.5634	15.1850	922.3333	30.3699	2.7822
PB	105.3490	2.3866	22.7825	4.7731	4.5308
CD	2.4958	0.0335	0.0045	0.0670	2.6837
CO	11.8374	0.5390	1.1619	1.0779	9.1062
NI	10.9303	0.4416	0.7799	0.8831	8.0794

SIMPLE STATISTICS FOR 4 REPLICATES *Fontinalis antipyretica* 2nd 30 mm Sunderland Bridge (km 58.3) 29. 4. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	802.1375	177.8782	26562.6250	355.7563	44.3510
K	6922.7109	47.9305	9189.3320	95.8610	1.3847
MG	1683.0996	28.5102	3251.3333	57.0205	3.3878
CA	4965.3398	97.7070	38186.6641	195.4141	3.9356
ZN	344.8254	1.6504	10.8958	3.3009	0.9573
CU	26.0918	0.8246	2.7196	1.6491	6.3205
MN	3594.5430	10.0000	400.0000	20.0000	0.5564
FE	2829.9824	23.7206	2250.6665	47.4412	1.6764
AL	1709.4658	49.6454	9858.6641	99.2908	5.8083
PB	148.2851	4.0729	66.3542	8.1458	5.4933
CD	2.4331	0.0614	0.0151	0.1227	5.0430
CO	18.8338	0.5806	1.3484	1.1612	6.1655
NI	21.3144	0.8756	3.0670	1.7513	8.2164

SIMPLE STATISTICS FOR 4 REPLICATES *Fontinalis antipyretica* 3rd 30 mm Sunderland Bridge (km 58.3) 29. 4. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	841.2356	235.2433	21357.6250	470.4866	55.9280
K	6253.0938	70.9836	20154.6641	141.9671	2.2703
MG	1664.2930	43.5622	7590.6641	87.1244	5.2349
CA	5644.7530	62.3645	15557.3320	124.7290	2.2096
ZN	578.6443	8.6506	299.3333	17.3013	2.9900
CU	28.2950	0.9764	3.8131	1.9527	6.9010
MN	8003.4922	104.7537	43893.3320	209.5074	2.6177
FE	3486.2852	43.9242	7717.3320	87.8483	2.5198
AL	2064.5928	105.1729	44245.3320	210.3457	10.1882
PB	223.6737	5.2445	110.0208	10.4891	4.6895
CD	8.0385	5.5722	124.1973	11.1444	138.6376
CO	45.6957	0.8476	2.8737	1.6952	3.7098
NI	33.1096	1.0559	4.4596	2.1118	6.3782

SIMPLE STATISTICS FOR 4 REPLICATES <u>Fontinalis</u> <u>antipyretica</u> 4th 30 mm Sunderland Bridge (km 58.3) 29. 4. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	848.2415	74.3612	22118.3320	148.7223	17.5330
K	6869.2383	310.0903	84624.0000	620.1807	9.0284
MG	1933.9004	35.5914	5067.0000	71.1829	3.6808
CA	9826.6758	347.3325	82560.0000	694.6553	7.0692
ZN	2560.4424	99.6393	39712.0000	199.2787	7.7830
CU	46.0516	1.0050	4.0404	2.0101	4.3648
MN	39105.4844	1553.7859	57002.0000	3107.5718	7.9466
FE	5206.2578	174.2756	21488.0000	348.5513	6.6948
AL	4934.7148	166.4412	10810.6250	332.8823	6.7457
PB	492.9043	29.8054	3553.4593	59.6109	12.0938
CD	8.6554	0.1549	0.0960	0.3099	3.5802
CO	210.5460	3.8911	60.5625	7.7822	3.6962
NI	173.1763	4.2811	73.3125	8.5623	4.9443

SIMPLE STATISTICS FOR 4 REPLICATES <u>Fontinalis</u> <u>antipyretica</u> 1st 30 mm above effluent (km 76.5) 29. 4. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	792.9607	32.3123	4176.3320	64.6245	8.1498
K	7621.5078	132.6399	70373.3125	265.2798	3.4807
MG	2169.0879	46.3177	8581.3320	92.6355	4.2707
CA	4993.2070	265.4177	81786.6250	530.8357	10.6312
ZN	271.0771	2.6605	28.3125	5.3209	1.9629
CU	28.7158	0.3778	0.5710	0.7556	2.6314
MN	2167.9688	31.5172	3973.3333	63.0344	2.9075
FE	3223.8477	59.7662	14288.0000	119.5324	3.7078
AL	1772.5215	23.1589	2145.3333	46.3177	2.6131
PB	151.2925	4.0723	66.3333	8.1445	5.3833
CD	2.6241	0.0779	0.0243	0.1559	5.9402
CO	18.0676	0.9356	3.5011	1.8711	10.3563
NI	7.5009	0.1509	0.0911	0.3019	4.0246

SIMPLE STATISTICS FOR 4 REPLICATES <u>Fontinalis</u> <u>antipyretica</u> 2nd 30 mm above effluent (km 76.5) 29. 4. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	1075.6230	159.1537	01319.6250	318.3074	29.5928
K	6311.6758	117.3996	55130.6641	234.7992	3.7201
MG	1995.7910	52.6783	11100.0000	105.3565	5.2789
CA	5430.5586	110.4355	48784.0000	220.8710	4.0672
ZN	317.1643	2.7367	29.9583	5.4734	1.7257
CU	28.2103	1.0464	4.3796	2.0927	7.4183
MN	3406.1914	62.8225	15786.6641	125.6450	3.6887
FE	3607.7109	41.2310	6800.0000	82.4621	2.2857
AL	1838.5664	85.1592	29008.3320	170.3183	9.2636
PB	184.9379	2.8895	33.3958	5.7789	3.1248
CD	2.5151	0.1001	0.0400	0.2001	7.9562
CO	28.2103	1.0464	4.3796	2.0927	7.4183
NI	18.4060	0.9212	3.3941	1.8423	10.0093

SIMPLE STATISTICS FOR 4 REPLICATES <u>Fontinalis</u> <u>antipyretica</u> 3rd 30 mm above effluent (km 76.5) 29. 4. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	704.1150	45.7384	8368.0000	91.4768	12.9917
K	5387.8398	220.0000	93600.0000	440.0000	8.1665
MG	1950.2930	26.2456	2755.3333	52.4913	2.6915
CA	6183.9453	67.1416	18032.0000	134.2833	2.1715
ZN	471.1316	5.3400	114.0625	10.6800	2.2669
CU	30.3936	1.4939	8.9275	2.9879	9.8306

MN	7560.1758	65.6150	17221.3320	131.2301	1.7358
FE	4071.6934	47.4974	9024.0000	94.9947	2.3331
AL	2425.4404	41.5371	6901.3320	83.0742	3.4251
PB	229.9116	3.8676	59.8333	7.7352	3.3644
CD	2.7817	0.1182	0.0559	0.2364	8.4981
CO	53.7871	0.6837	1.8698	1.3674	2.5422
NI	24.7041	1.2833	6.5873	2.5666	10.3893

SIMPLE STATISTICS FOR 4 REPLICATES <u>Fontinalis antipyretica</u> 4th 30 mm above effluent (km 76.5) 29. 4. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	511.2854	11.0990	492.7530	22.1980	4.3416
K	6233.0742	194.3159	51034.6250	388.6318	6.2350
MG	2082.4844	20.2649	1642.6665	40.5298	1.9462
CA	8170.6289	143.3644	82213.3125	286.7288	3.5093
ZN	1241.4004	9.4384	356.3333	18.8768	1.5206
CU	40.5236	1.0397	4.3242	2.0795	5.1315
MN	22507.1250	302.2051	65312.0000	604.4104	2.6854
FE	4071.8076	14.6059	853.3333	29.2119	0.7174
AL	3442.1016	35.2704	4976.0000	70.5408	2.0494
PB	286.1821	4.9566	98.2708	9.9132	3.4639
CD	4.8673	0.4823	0.9304	0.9646	19.8173
CO	102.2739	1.8022	12.9922	3.6045	3.5242
NI	96.0363	1.5230	9.2786	3.0461	3.1718

SIMPLE STATISTICS FOR 4 REPLICATES <u>Fontinalis antipyretica</u> 1st 30 mm below effluent (km 76.9) 29. 4. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	771.2759	177.7379	26363.0000	355.4758	46.0893
K	8612.5742	167.4913	12213.3125	334.9827	3.8895
MG	2359.2588	30.6594	3760.0000	61.3188	2.5991
CA	5613.1367	119.3482	56976.0000	238.6965	4.2525
ZN	395.7341	6.4145	164.5833	12.8290	3.2418
CU	25.5602	0.9891	3.9130	1.9781	7.7391
MN	2465.2373	20.8487	1738.6665	41.6973	1.6914
FE	4257.0820	49.4503	9781.3320	98.9006	2.3232
AL	2989.4365	55.3414	12250.6641	110.6827	3.7025
PB	173.5035	1.9053	14.5208	3.8106	2.1963
CD	6.6244	0.3859	0.5957	0.7718	11.6510
CO	19.9885	1.1368	5.1695	2.2737	11.3748
NI	31.2010	0.6779	1.8381	1.3557	4.3452

SIMPLE STATISTICS FOR 4 REPLICATES <u>Fontinalis antipyretica</u> 2nd 30 mm below effluent (km 76.9) 29. 4. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	459.4749	36.6740	5379.9141	73.3479	15.9634
K	6153.6406	39.7827	6330.6641	79.5655	1.2930
MG	2223.0547	9.7297	378.6665	19.4594	0.8753
CA	6168.1250	100.8497	40682.6641	201.6994	3.2700
ZN	578.1924	8.1599	266.3333	16.3197	2.8225
CU	32.6450	1.9782	15.6523	3.9563	12.1192
MN	6149.2891	80.4239	25872.0000	160.8477	2.6157
FE	5439.9805	73.0114	21322.6641	146.0228	2.6843
AL	4208.8242	87.7344	30789.3320	175.4689	4.1691
PB	232.3732	3.3393	44.6042	6.6786	2.8741
CD	5.4030	0.3394	0.4607	0.6787	12.5621
CO	27.6066	0.7607	2.3148	1.5214	5.5112
NI	33.9077	0.6384	1.6302	1.2768	3.7655

SIMPLE STATISTICS FOR 4 REPLICATES *Fontinalis antipyretica* 3rd 30 mm below effluent (km 76.9) 29. 4. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	423.8123	31.3134	3922.1250	62.6269	14.7770
K	5986.3867	63.1612	15957.3320	126.3223	2.1102
MG	2080.5615	19.3563	1498.6665	38.7126	1.8607
CA	7852.0430	182.8186	33690.6250	365.6372	4.6566
ZN	904.0012	7.9791	254.6667	15.9583	1.7653
CU	34.4258	1.5090	9.1091	3.0180	8.7665
MN	12625.6250	121.5895	59136.0000	243.1789	1.9261
FE	5473.4570	48.3046	9333.3320	96.6092	1.7650
AL	4316.5195	53.0157	11242.6641	106.0314	2.4564
PB	284.2007	6.0622	147.0000	12.1244	4.2661
CD	6.1947	0.6723	1.8077	1.3445	21.7043
CO	60.6358	2.6031	27.1042	5.2062	8.5860
NI	49.0266	1.5145	9.1745	3.0289	6.1782

SIMPLE STATISTICS FOR 4 REPLICATES *Fontinalis antipyretica* 4th 30 mm below effluent (km 76.9) 29. 4. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	429.0627	30.1456	3635.0208	60.2911	14.0518
K	6035.8359	149.8800	89856.0000	299.7600	4.9663
MG	2189.4131	37.7182	5690.6641	75.4365	3.4455
CA	10274.4336	185.2710	37301.3125	370.5420	3.6064
ZN	2055.9326	21.5097	1850.6665	43.0194	2.0925
CU	44.7456	0.6065	1.4714	1.2130	2.7109
MN	32148.2500	1263.5442	85176.0000	2527.0884	7.8607
FE	6757.5586	151.4728	91776.0000	302.9456	4.4831
AL	6367.3945	314.4858	95605.3125	628.9717	9.8780
PB	343.9290	6.1403	150.8125	12.2806	3.5707
CD	8.3945	0.2940	0.3458	0.5880	7.0050
CO	132.3479	0.9298	3.4583	1.8597	1.4051
NI	116.8644	1.3612	7.4115	2.7224	2.3295

SIMPLE STATISTICS FOR 4 REPLICATES *Fontinalis antipyretica* 1st 30 mm Finchale Abbey (km 78.1) 29. 4. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	419.4624	9.7855	383.0208	19.5709	4.6657
K	6823.3008	430.2603	40496.0000	860.5208	12.6115
MG	2121.3252	40.3485	6512.0000	80.6970	3.8041
CA	4853.3594	86.5101	29936.0000	173.0202	3.5659
ZN	238.3113	3.1647	40.0625	6.3295	2.6560
CU	22.1569	0.7320	2.1433	1.4640	6.6074
MN	1538.8545	26.3755	2782.6665	52.7510	3.4279
FE	4333.3398	88.2194	31130.6641	176.4388	4.0717
AL	1755.2285	7.4666	223.0000	14.9332	0.8508
PB	131.8344	2.9110	33.8958	5.8220	4.4162
CD	2.4674	0.0576	0.0132	0.1151	4.6651
CO	16.0173	0.6537	1.7093	1.3074	8.1625
NI	18.4847	0.6631	1.7590	1.3263	7.1750

SIMPLE STATISTICS FOR 4 REPLICATES *Fontinalis antipyretica* 2nd 30 mm Finchale Abbey (km 78.1) 29. 4. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	353.2000	6.9996	195.9792	13.9993	3.9635
K	5872.3711	160.1915	02645.3125	320.3831	5.4558
MG	1824.6943	30.8383	3804.0000	61.6766	3.3801
CA	5057.3594	116.3558	54154.6641	232.7115	4.6014
ZN	286.4319	2.3530	22.1458	4.7059	1.6430
CU	25.2177	0.7716	2.3815	1.5432	6.1196
MN	2082.7686	22.9492	2106.6665	45.8984	2.2037
FE	6168.7109	133.5165	71306.6250	267.0330	4.3288

AL	2042.8379	131.3132	68972.6250	262.6265	12.8560
PB	188.1177	3.3642	45.2708	6.7284	3.5767
CD	2.6526	0.0928	0.0344	0.1856	6.9960
CO	25.8759	0.6011	1.4451	1.2021	4.6457
NI	23.3424	0.4745	0.9006	0.9490	4.0656

SIMPLE STATISTICS FOR 4 REPLICATES <u>Fontinalis antipyretica</u> 3rd 30 mm Finchale Abbey (km 78.1) 29. 4. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	319.7063	21.7434	1891.1040	43.4868	13.6021
K	5723.1211	213.5228	82368.0000	427.0457	7.4618
MG	1942.0557	44.7828	8022.0000	89.5656	4.6119
CA	5944.8359	185.3573	37429.3125	370.7146	6.2359
ZN	344.9009	5.6693	128.5625	11.3385	3.2875
CU	25.7950	1.0941	4.7885	2.1883	8.4833
MN	3063.7422	21.4787	1845.3333	42.9573	1.4021
FE	7024.7500	48.7169	9493.3320	97.4337	1.3870
AL	2446.4316	162.9069	06154.6250	325.8137	13.3179
PB	224.9229	4.2248	71.3958	8.4496	3.7567
CD	2.7593	0.1496	0.0895	0.2991	10.8409
CO	33.9928	1.5209	9.2526	3.0418	8.9484
NI	31.4218	0.9773	3.8208	1.9547	6.2208

SIMPLE STATISTICS FOR 4 REPLICATES <u>Fontinalis antipyretica</u> 4th 30 mm Finchale Abbey (km 78.1) 29. 4. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	296.8870	9.4227	355.1458	18.8453	6.3476
K	6372.3438	117.9774	55674.6641	235.9548	3.7028
MG	1887.6787	32.1299	4129.3320	64.2599	3.4042
CA	8350.1250	78.6554	24746.6641	157.3107	1.8839
ZN	776.0125	5.5453	123.0000	11.0905	1.4292
CU	24.0923	0.8911	3.1762	1.7822	7.3973
MN	12053.1289	206.7140	70922.6250	413.4290	3.4300
FE	7308.3398	121.2985	58853.3320	242.5971	3.3195
AL	3743.3408	131.6713	69349.3125	263.3425	7.0350
PB	251.7320	4.1652	69.3958	8.3304	3.3092
CD	3.0326	0.0768	0.0236	0.1536	5.0663
CO	110.7930	2.0627	17.0182	4.1253	3.7233
NI	78.5759	1.2648	6.3984	2.5295	3.2192

** A.2H FONTINALIS MINERAL COMPOSITION LOWER R.WEAR 14.8.73 **

LIST OF NAMES 1 NA 2 K 3 MG 4 CA 5 ZN 6 CU 7 MN 8 FE 9 AL 10 PB 11 CD 12 CO 13 NI

NUMBER OF BLOCKS-CASES 4 NUMBER OF REPLICATES IN FIRST BLOCK 4

SIMPLE STATISTICS FOR 4 REPLICATES *Fontinalis antipyretica* undivided Sunderland Bridge (km 58.3) 14. 8. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	408.0098	8.6307	297.9583	17.2615	4.2307
K	7580.7148	139.4131	77744.0000	278.8262	3.6781
MG	2455.3145	13.6626	746.6665	27.3252	1.1129
CA	10262.6484	133.0664	70826.6250	266.1328	2.5932
ZN	1889.9531	2.5331	25.6667	5.0662	0.2681
CU	25.7495	0.2482	0.2465	0.4965	1.9281
MN	37646.2031	336.6575	98016.0000	773.3149	2.0542
FE	2631.1182	43.4818	7562.6641	86.9636	3.3052
AL	2845.1699	44.3471	7866.6641	88.6942	3.1174
PB	334.9053	3.8944	60.6667	7.7889	2.3257
CD	11.3902	0.4463	0.7969	0.8927	7.8372
CO	161.1553	1.1524	5.3125	2.3049	1.4302
NI	127.7944	1.9328	14.9427	3.8656	3.0248

SIMPLE STATISTICS FOR 4 REPLICATES *Fontinalis antipyretica* undivided above effluent (km 76.5) 14. 8. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	218.9553	27.9267	3119.6040	55.8534	25.5090
K	3275.0996	45.0333	8112.0000	90.0667	2.7500
MG	2061.9961	20.5589	1690.6665	41.1177	1.9941
CA	7794.6328	90.1702	32522.6641	180.3404	2.3136
ZN	907.1182	13.8924	772.0000	27.7849	3.0630
CU	27.5406	1.1975	5.7358	2.3949	8.6961
MN	24393.0625	413.4021	83605.3125	826.8042	3.3895
FE	1697.4053	24.0555	2314.6665	48.1110	2.8344
AL	1628.3115	30.7449	3781.0000	61.4898	3.7763
PB	235.7463	2.6369	27.8125	5.2738	2.2370
CD	3.5839	0.1276	0.0651	0.2551	7.1186
CO	83.5901	1.2082	5.8385	2.4163	2.8907
NI	79.8173	1.8801	14.1393	3.7602	4.7110

SIMPLE STATISTICS FOR 4 REPLICATES *Fontinalis antipyretica* undivided below effluent (km 76.9) 14. 8. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	188.1720	7.9409	252.2292	15.8817	8.4400
K	3246.0352	26.4071	2789.3333	52.8141	1.6270
MG	1862.6992	19.4401	1511.6665	38.8802	2.0873
CA	7807.7101	95.0579	36144.0000	190.1158	2.4350
ZN	661.4883	10.3441	428.0000	20.6882	3.1275
CU	32.6975	0.7844	2.4609	1.5687	4.7992
MN	16715.9844	230.3389	12224.0000	460.6777	2.7557
FE	1573.2998	53.0385	11252.3320	106.0770	6.7423
AL	1506.0820	5.8239	135.6667	11.6476	0.7734
PB	218.9590	14.3839	827.5833	28.7677	13.1384
CD	3.5099	0.5526	1.2214	1.1052	31.4875
CO	78.1735	4.5295	82.0654	9.0591	11.5884
NI	60.8696	1.5280	9.3385	3.0559	5.0204

SIMPLE STATISTICS FOR 4 REPLICATES *Fontinalis antipyretica* undivided Finchale Abbey (km 78.1) 14. 8. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	155.4172	9.4904	360.2708	18.9808	12.2128
K	3295.7617	56.5332	12784.0000	113.0663	3.4307
MG	1882.1543	30.5259	3727.3333	61.0519	3.2437
CA	7563.8477	110.8633	49162.6641	221.7265	2.9314
ZN	645.3044	20.0582	1609.3333	40.1165	6.2167
CU	19.3096	0.3811	0.5811	0.7623	3.9476
MN	16526.0000	544.6660	86645.0000	1089.3323	6.5916
FE	3587.6328	63.0238	15888.0000	126.0476	3.5134
AL	1854.2549	28.3755	3220.6665	56.7509	3.0606
PB	187.4691	1.0358	4.2917	2.0716	1.1051
CD	2.8230	0.3181	0.4047	0.6361	22.5342
CO	118.9869	4.7829	91.5039	9.5658	8.0393
NI	81.4224	3.7314	55.6927	7.4628	9.1655

** A.2H CONT. FONT. MIN. COMP. LWR R.WEAR 20.11.73. **

LIST OF NAMES 1 NA 2 K 3 MG 4 CA 5 ZN 6 CU 7 MN 8 FE 9 AL 10 PB 11 CD 12 CO 13 NI

NUMBER OF BLOCKS-CASES 4 NUMBER OF REPLICATES IN FIRST BLOCK 4

SIMPLE STATISTICS FOR 4 REPLICATES *Fontinalis antipyretica* undivided Sunderland Bridge (km 58.3) 20. 11. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	555.6470	9.3229	347.6665	18.6458	3.3557
K	9523.3164	169.7057	15200.0000	339.4114	3.5640
MG	2859.5713	13.6137	741.3333	27.2274	0.9522
CA	13690.8867	208.8700	74506.6250	417.7400	3.0512
ZN	2541.5996	24.5221	2405.3333	49.0442	1.9297
CU	43.6909	0.4094	0.6706	0.8189	1.8743
MN	36819.1875	350.5425	91520.0000	701.0850	1.9041
FE	5670.2383	93.8154	35205.3320	187.6308	3.3090
AL	4343.6281	28.8906	3338.6665	57.7812	1.3302
PB	254.7675	4.0659	66.1250	8.1317	3.1918
CD	7.8407	0.2854	0.3257	0.5707	7.2791
CO	345.4431	8.0006	256.0415	16.0013	4.6321
NI	210.8406	4.1796	69.8750	8.3591	3.9647

SIMPLE STATISTICS FOR 4 REPLICATES *Fontinalis antipyretica* undivided above effluent (km 76.5) 20. 11. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	217.3546	11.9789	573.9790	23.9579	11.0225
K	6407.4492	152.4248	92933.3125	304.8496	4.7577
MG	2387.2227	10.3280	426.6665	20.6559	0.8653
CA	5609.4414	167.6823	12469.3125	335.3645	3.4899
ZN	1080.1357	24.8998	2480.0000	49.7996	4.6105
CU	33.7254	0.5734	1.3151	1.1468	3.4003
MN	21982.4219	317.5574	03370.6250	635.1147	2.8892
FE	3209.5684	35.7025	5098.6641	71.4049	2.2248
AL	2116.2295	53.6408	11509.3320	107.2816	5.0695
PB	182.7788	3.8797	60.2083	7.7594	4.2452
CD	2.2630	0.1117	0.0499	0.2235	9.8748
CO	61.5468	1.9708	15.5365	3.9416	6.4043
NI	73.4764	1.4571	8.4922	2.9141	3.9661

SIMPLE STATISTICS FOR 4 REPLICATES *Fontinalis antipyretica* undivided below effluent (km 76.9) 20. 11. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	195.4123	8.9355	319.3750	17.8711	9.1453
K	5811.5586	74.9044	22442.6641	149.8088	2.5778
MG	2449.8477	24.7925	2458.6665	49.5849	2.0240
CA	10607.5273	270.8208	93376.0000	541.6418	5.1062
ZN	1340.6035	38.2492	5852.0000	76.4984	5.7063
CU	28.8960	0.9085	3.3012	1.8169	6.2878
MN	27055.8125	770.0664	72010.0000	1540.1331	5.6924
FE	3350.3340	77.4769	24010.6641	154.9538	4.5250
AL	2539.2139	46.2601	8560.0000	92.5203	3.6437
PB	176.3921	4.9524	98.1042	9.9048	5.6152
CD	6.0072	0.2363	0.2234	0.4727	7.8688
CO	69.6719	5.5390	122.7240	11.0781	15.9004
NI	107.4725	3.6719	53.9323	7.3439	6.8332

SIMPLE STATISTICS FOR 4 REPLICATES <u>Fontinalis</u> <u>antipyretica</u> **undivided Finchale Abbey (km 78.1) 20. 11. 73**

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	198.5124	3.1606	39.9583	6.3213	3.1843
K	5522.3672	120.1111	57706.6641	240.2221	4.3500
MG	2450.2598	29.9778	3594.6665	59.9555	2.4469
CA	10919.0195	247.8710	45760.0000	495.7419	4.5402
ZN	1182.1846	11.9757	573.6465	23.9513	2.0260
CU	22.8472	0.6605	1.7450	1.3210	5.7818
MN	20230.5781	253.7400	57536.0000	507.4800	2.5085
FE	5112.5625	22.6274	2048.0000	45.2548	0.8852
AL	2333.7100	39.8664	6357.3320	79.7329	3.4166
PB	160.6579	1.5529	9.6458	3.1058	1.9332
CD	4.6550	0.1704	0.1161	0.3407	7.3190
CO	132.7673	2.7013	29.1875	5.4025	4.0692
NI	130.2819	1.7290	11.9583	3.4581	2.6543

** A.21 FONTINALIS MINERAL COMPOSITION R.WEAR 1968. **

LIST OF NAMES 1 NA 2 K 3 MG 4 CA 5 ZN 6 CU 7 MN 8 FE 9 AL 10 PB 11 CD 12 CO 13 NI

NUMBER OF BLOCKS-CASES 6 NUMBER OF REPLICATES IN FIRST BLOCK 4

SIMPLE STATISTICS FOR 4 REPLICATES **Fontinalis antipyretica** above **Gaunless (km 40.0) 15. 8. 68**

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	374.9688	7.2021	207.4792	14.4041	3.8414
K	8456.7109	147.6572	87210.6250	295.3145	3.4921
MG	1916.4512	39.5780	6265.6641	79.1559	4.1303
CA	10788.5508	41.3118	6826.6641	82.6236	0.7658
ZN	1251.4277	9.0462	327.3333	18.0923	1.4457
CU	24.7080	0.5821	1.3555	1.1643	4.7122
MN	22914.3750	334.3770	47232.0000	668.7542	2.9185
FE	3029.4834	97.3173	37882.6641	194.6347	6.4247
AL	1879.0000	64.7045	16746.6641	129.4089	6.8871
PB	398.6685	3.2137	41.3125	6.4275	1.6122
CD	6.9155	4.8551	94.2888	9.7102	140.4131
CO	48.7417	1.7343	12.0313	3.4686	7.1163
NI	37.0570	1.5848	10.0469	3.1697	8.5535

SIMPLE STATISTICS FOR 4 REPLICATES **Fontinalis antipyretica Willington (km 51.1) 15. 8. 68**

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	376.8606	5.7911	134.1458	11.5821	3.0733
K	8173.5430	211.6979	79264.0000	423.3958	5.1801
MG	1927.8838	9.4912	360.3333	18.9825	0.9846
CA	9680.6875	90.8625	33024.0000	181.7251	1.8772
ZN	883.1045	4.2720	73.0000	8.5440	0.9675
CU	22.5136	0.6388	1.6322	1.2776	5.6746
MN	25572.9531	221.3655	96010.6250	442.7310	1.7312
FE	1827.4863	71.9606	20713.3320	143.9213	7.8754
AL	1227.7979	26.5283	2815.0000	53.0566	4.3213
PB	172.6290	3.7186	55.3125	7.4372	4.3082
CD	1.8020	0.0755	0.0228	0.1510	8.3792
CO	82.1179	1.3550	7.3438	2.7099	3.3001
NI	64.0941	1.8720	14.0169	3.7439	5.8413

SIMPLE STATISTICS FOR 4 REPLICATES **Fontinalis antipyretica** Durham **Sands (km 70.4) 16. 8. 68**

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	518.0664	11.0189	485.6665	22.0378	4.2539
K	7199.5586	265.1138	81141.3125	530.2275	7.3647
MG	2296.6574	25.4296	2586.6665	50.8593	2.2143
CA	11109.4102	152.9792	93610.6250	305.9585	2.7540
ZN	835.1272	11.7473	552.0000	23.4947	2.8133
CU	34.1614	0.3046	0.3711	0.6092	1.7832
MN	33288.1719	261.2788	73066.6250	522.5579	1.5698
FE	3395.1641	121.6498	59194.6641	243.2995	7.1661
AL	2492.4033	25.6125	2624.0000	51.2250	2.0552
PB	237.5919	2.5850	26.7292	5.1700	2.1760
CD	1.6645	0.0029	0.0000	0.0057	0.3454
CO	366.1538	9.2722	343.8956	18.5444	5.0647
NI	554.2346	10.4003	432.6665	20.8006	3.7530

SIMPLE STATISTICS FOR 4 REPLICATES <u>Fontinalis</u> <u>antipyretica</u> **Finchale Abbey (km 78.1) 13. 8. 68**

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	427.0425	6.3373	160.6458	12.6746	2.9680
K	6500.2500	216.8470	88090.6250	433.6941	6.6720
MG	1883.1738	60.1075	14451.6641	120.2151	6.3836
CA	9207.1875	211.5593	79029.3125	423.1187	4.5955
ZN	473.6833	6.9518	193.3125	13.9037	2.9352
CU	20.5424	0.7193	2.0696	1.4386	7.0031
MN	20540.4531	282.2007	18549.3125	564.4016	2.7478
FE	2412.2402	64.7971	16794.6641	129.5942	5.3724
AL	1450.0361	45.8130	8395.3320	91.6261	6.3189
PB	100.3938	1.4149	8.0065	2.8296	2.8185
CD	1.6664	0.0047	0.0001	0.0095	0.5682
CO	222.8864	4.0633	66.0417	8.1266	3.6461
NI	266.2290	4.2524	72.3333	8.5049	3.1946

SIMPLE STATISTICS FOR 4 REPLICATES <u>Fontinalis</u> <u>antipyretica</u> **Cocken Bridge (km 80.6) 13. 8. 68**

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	251.8684	8.8506	313.3333	17.7012	7.0280
K	6610.4219	121.1610	58720.0000	242.3221	3.6658
MG	2079.1738	29.2119	3413.3333	58.4237	2.8099
CA	8107.4805	118.2596	55941.3320	236.5192	2.9173
ZN	297.7102	1.7002	11.5625	3.4004	1.1422
CU	18.9155	0.6428	1.6526	1.2855	6.7962
MN	17836.2188	108.9097	47445.3320	217.8195	1.2212
FE	2357.4971	27.6887	3066.6665	55.3775	2.3490
AL	1205.6973	20.6216	1701.0000	41.2432	3.4207
PB	99.7618	1.6613	11.0391	3.3225	3.3304
CD	1.6634	0.0105	0.0004	0.0211	1.2678
CO	212.4590	3.3245	44.2083	6.6489	3.1295
NI	247.3856	2.5207	25.4167	5.0415	2.0379

SIMPLE STATISTICS FOR 4 REPLICATES <u>Fontinalis</u> <u>antipyretica</u> **Lambton Bridge (km 90.0) 16. 8. 68**

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	424.5181	6.3455	161.0625	12.6910	2.9895
K	5497.8008	157.8607	99680.0000	315.7214	5.7427
MG	3162.3652	47.9166	9184.0000	95.8332	3.0304
CA	12566.8281	167.7458	12554.6250	335.4917	2.6697
ZN	632.8655	7.5829	230.0000	15.1658	2.3964
CU	45.3457	0.5303	1.1250	1.0607	2.3391
MN	37782.3281	361.5669	22922.6250	723.1338	1.9139
FE	5026.4805	137.0887	75173.3125	274.1775	5.4547
AL	5146.6523	82.5025	27226.6641	165.0051	3.2061
PB	169.8959	5.0322	101.2917	10.0644	5.9238
CD	5.7452	0.1344	0.0722	0.2688	4.6779
CO	294.3284	3.7914	57.5000	7.5829	2.5763
NI	331.1028	6.6568	177.2500	13.3135	4.0210

** A.2JRANUNCULUS PENICILLATUS MINERAL COMPOSITION TWEED/WEAR. **

LIST OF NAMES 1 NA 2 K 3 MG 4 CA 5 ZN 6 CU 7 MN 8 FE 9 AL 10 PB 11 CD
12 CO 13 NI

NUMBER OF BLOCKS-CASES 12 NUMBER OF REPLICATES IN FIRST BLOCK 4

SIMPLE STATISTICS FOR 4 REPLICATES R.__penicillatus__ var. __calcareus__ root River Tweed Gala Ford (km 28.1) 14. 8. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	15775.6250	647.9682	78933.0000	1295.7366	8.2135
K	27587.4844	706.3598	95776.0000	1412.7195	5.1209
MG	2482.5029	20.0666	1610.6665	40.1331	1.6166
CA	5832.4648	99.6059	39685.3320	199.2118	3.4156
ZN	286.6943	14.8633	883.6665	29.7265	10.3687
CU	114.9733	2.0458	16.7409	4.0916	3.5587
MN	828.9734	9.1833	337.3333	18.3666	2.2156
FE	2242.9717	94.7136	35882.6641	189.4272	8.4454
AL	1036.6709	27.5757	3041.6665	55.1513	5.3200
PB	35.3720	1.8557	13.7747	3.7114	10.4926
CD	4.4153	0.0987	0.0390	0.1974	4.4716
CO	14.9499	2.6827	28.7869	5.3653	35.8888
NI	21.1709	3.8625	59.6766	7.7249	36.4895

SIMPLE STATISTICS FOR 4 REPLICATES R.__penicillatus__ var. __calcareus__ stem River Tweed Gala Ford (km 28.1) 14.8.73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	10159.9375	80.0000	25600.0000	160.0000	1.5748
K	59710.3281	530.3381	25034.0000	1060.6763	1.7764
MG	2080.9111	18.2209	1328.0000	36.4417	1.7512
CA	4650.6602	159.3445	01562.6250	318.6890	6.8525
ZN	81.8559	1.9769	15.6328	3.9539	4.8302
CU	51.5961	0.9034	3.2643	1.8067	3.5024
MN	139.0532	1.5943	10.1667	3.1885	2.2930
FE	258.9771	4.9276	97.1250	9.8552	3.8054
AL	187.2375	2.5729	26.4792	5.1458	2.7493
PB	10.6890	0.4159	0.6920	0.8319	7.7823
CD	1.6463	0.0261	0.0027	0.0521	3.1670
CO	5.3551	0.2882	0.3322	0.5764	10.7618
NI	10.5047	0.3647	0.5319	0.7293	6.9427

SIMPLE STATISTICS FOR 4 REPLICATES R. __penicillatus__ var. __calcareus__ leaf River Tweed Gala Ford (km 28.1) 14. 8. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	15314.9492	329.5896	34517.3125	659.1792	4.3042
K	27170.8750	659.2603	38496.0000	1318.5205	4.8527
MG	2706.1396	129.6970	67285.3125	259.3940	9.5854
CA	5930.7305	219.3536	92474.6250	438.7192	7.3974
ZN	393.8909	4.4070	77.6875	8.8141	2.2377
CU	70.3145	1.9071	14.5482	3.8142	5.4245
MN	1412.0322	37.0034	5477.0000	74.0068	5.2412
FE	674.8999	14.2770	815.3333	28.5540	4.2309
AL	432.3105	10.5761	447.4165	21.1522	4.8928
PB	19.7624	0.7497	2.2480	1.4993	7.5869
CD	6.9991	0.2374	0.2254	0.4748	6.7832
CO	13.7882	0.2296	0.2109	0.4592	3.3303
NI	19.5473	0.1515	0.0918	0.3030	1.5500

SIMPLE STATISTICS FOR 4 REPLICATES   R.<u>penicillatus</u> var. <u>calcareus</u> root River Wear above effluent (km 76.5) 14. 8. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	13895.0078	195.6323	53088.0000	391.2646	2.8159
K	40867.9375	576.2961	28469.0000	1152.5923	2.8203
MG	3001.9688	61.1773	14970.6641	122.3547	4.0758
CA	10711.1602	369.7349	46816.0000	739.4700	6.9037
ZN	1344.8301	40.6059	6595.3320	81.2117	6.0388
CU	33.6265	1.8512	13.7083	3.7025	11.0106
MN	5698.1523	61.9032	15328.0000	123.8063	2.1727
FE	1594.9434	9.1606	335.6665	18.3212	1.1487
AL	1184.5537	31.6896	4016.6665	63.3772	5.3503
PB	123.3655	4.4595	79.5495	8.9191	7.2298
CD	13.8752	0.9252	3.4241	1.8504	13.3362
CO	38.6299	0.9953	3.9622	1.9905	5.1530
NI	64.7907	1.4401	8.2956	2.8802	4.4454

SIMPLE STATISTICS FOR 4 REPLICATES   R.<u>penicillatus</u> var. <u>calcareus</u> stem River Wear above effluent (km 76.5) 14. 8. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	9915.3242	93.7514	35157.3320	187.5029	1.8910
K	48490.2656	486.0068	44810.6250	972.0137	2.0046
MG	2910.0283	20.6236	1701.3333	41.2472	1.4174
CA	9851.1172	149.3809	89258.6250	298.7617	3.0328
ZN	564.5571	12.8873	664.3333	25.7747	4.5655
CU	25.7437	1.0879	4.7343	2.1758	8.4519
MN	1842.3066	32.6165	4255.3320	65.2329	3.5408
FE	652.2659	25.3361	2567.6665	50.6721	7.7686
AL	575.0029	19.1616	1468.6665	38.3232	6.6649
PB	97.6560	9.2559	342.6887	18.5119	18.9562
CD	7.4115	0.4413	0.7790	0.8826	11.9087
CO	21.1052	0.6766	1.8310	1.3531	6.4114
NI	40.4296	1.5713	9.8763	3.1427	7.7732

SIMPLE STATISTICS FOR 4 REPLICATES   R.<u>penicillatus</u> var. <u>calcareus</u> leaf River Wear above effluent (km 76.5) 14. 8. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	14894.3086	567.9246	90154.0000	1135.8494	7.6261
K	21459.0938	829.7917	54218.0000	1659.5837	7.7337
MG	3014.9590	153.9437	94794.6250	307.8875	10.2120
CA	8578.0625	400.5596	41792.0000	801.1191	9.3392
ZN	2002.9561	44.9017	8064.6641	89.8035	4.4835
CU	35.3942	1.7103	11.7005	3.4206	9.6643
MN	5134.7266	159.6580	01962.6250	319.3159	6.2188
FE	596.3123	31.5872	3991.0000	63.1744	10.5942
AL	693.6641	48.5841	9441.6641	97.1682	14.0090
PB	24.7805	1.5263	9.3184	3.0526	12.3185
CD	8.2463	1.0685	4.5665	2.1369	25.9138
CO	41.5049	2.5308	25.6198	5.0616	12.1952
NI	70.3352	2.4976	24.9518	4.9952	7.1020

SIMPLE STATISTICS FOR 4 REPLICATES   R.<u>penicillatus</u> var. <u>calcareus</u> root River Wear below effluent (km 76.9) 14. 8. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	15358.0742	133.7062	71509.3125	267.4124	1.7412
K	35343.4531	97.7616	38229.3320	195.5232	0.5532
MG	2899.0566	22.0605	1946.6665	44.1210	1.5219
CA	10740.5664	166.9171	11445.3125	333.8342	3.1082
ZN	1319.0713	13.0480	681.0000	26.0960	1.9784
CU	23.7877	0.1944	0.1512	0.3889	1.6347

MN	4308.8633	22.6274	2048.0000	45.2548	1.0503
FE	1593.9043	45.0018	8100.6641	90.0037	5.6467
AL	1214.3564	51.0677	10431.6641	102.1355	8.4107
PB	124.6556	4.7493	90.2253	9.4987	7.6200
CD	16.0623	0.9111	3.3205	1.8222	11.3447
CO	48.5094	1.2150	5.9049	2.4300	5.0094
NI	60.0497	1.3520	7.3112	2.7039	4.5028

SIMPLE STATISTICS FOR 4 REPLICATES   R.penicillatus var. calcareus stem River Wear below effluent (km 76.9) 14. 8. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	8666.3477	294.7361	47477.3125	589.4722	6.8018
K	52569.3438	1619.7185	93952.0000	3239.4370	6.1622
MG	2571.4307	94.0921	35413.3320	188.1843	7.3183
CA	7870.1445	184.7810	36576.0000	369.5520	4.6957
ZN	376.2102	3.3080	43.7708	6.6160	1.7586
CU	33.5327	4.3469	75.5833	8.6939	25.9266
MN	1638.5400	31.1221	3874.3333	62.2441	3.7988
FE	604.4841	13.9314	776.3333	27.8629	4.6093
AL	570.0542	28.2622	3195.0000	56.5243	9.9156
PB	59.3601	3.1944	40.8177	6.3889	10.7629
CD	3.3645	0.3417	0.4670	0.6833	20.3106
CO	16.8496	1.1715	5.4900	2.3431	13.9058
NI	40.7954	2.9544	34.9141	5.9088	14.4840

SIMPLE STATISTICS FOR 4 REPLICATES   R.penicillatus var. calcareus leaf River Wear below effluent (km 76.9) 14. 8. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	16697.9688	117.3030	55040.0000	234.6060	1.4050
K	21758.0469	262.5007	275626.6250	525.0015	2.4129
MG	3263.4404	44.0454	7760.0000	88.0909	2.6993
CA	8975.5023	108.3205	46933.3320	216.6411	2.4136
ZN	2419.3779	55.3293	12245.3320	110.6586	4.5738
CU	29.9292	0.4336	0.7522	0.8673	2.8979
MN	5304.4531	23.8607	2277.3333	47.7214	0.8996
FE	613.2266	19.1790	1471.3333	38.3580	6.2551
AL	743.8958	31.8250	4051.3333	63.6501	8.5563
PB	24.8356	2.2755	20.7114	4.5510	18.3244
CD	4.4455	0.2280	0.2080	0.4561	10.2595
CO	44.6860	2.7880	31.0924	5.5761	12.4783
NI	78.0297	2.9710	35.3073	5.9420	7.6150

SIMPLE STATISTICS FOR 4 REPLICATES   R.penicillatus var. calcareus root River Wear Finchale Abbey (km 78.1) 14. 8. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	12638.0117	220.1575	193877.3125	440.3149	3.4841
K	41539.9531	258.6528	267605.3125	517.3059	1.2453
MG	3015.7633	24.4949	2400.0000	48.9898	1.6247
CA	11511.8477	35.7771	5120.0000	71.5542	0.6216
ZN	1463.8555	40.1809	6458.0000	80.3617	5.4897
CU	37.5373	0.3269	0.4271	0.6535	1.7410
MN	5317.7305	20.4939	1680.0000	40.9878	0.7708
FE	1901.7549	119.6697	57283.3320	239.3394	12.5852
AL	1664.1494	30.7571	3784.0000	61.5142	3.6964
PB	131.3855	4.3024	74.0417	8.6047	6.5492
CD	17.7680	0.2500	0.2499	0.4999	2.8136
CO	58.1754	1.0540	4.4440	2.1081	3.6237
NI	96.3580	2.5293	25.5898	5.0586	5.2498

R.penicillatus var. calcareus stem River Wear Finchale Abbey (km 78.1) 14. 8. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	14121.5703	192.5547	48309.3125	385.1024	2.7271
K	56638.5938	1498.5432	82529.0000	2997.0867	5.2916
MG	2818.0166	76.9242	23669.3320	153.8484	5.4595
CA	5786.6328	137.8695	76032.0000	275.7390	2.8175
ZN	553.2290	20.9025	1747.6665	41.8051	7.5566
CU	33.6632	1.1151	4.9740	2.2302	6.6291
MN	1754.9799	48.5026	9410.0000	97.0052	5.5277
FE	646.7083	21.8403	1908.0000	43.6807	6.7535
AL	597.5862	33.7367	4552.6641	67.4734	11.2910
PB	59.8446	5.3603	114.9297	10.7205	17.9840
CD	4.4803	0.3103	0.3850	0.6205	13.8498
CO	18.0460	1.3022	6.7807	2.6059	14.4403
NI	33.0974	2.0919	17.5039	4.1838	12.6408

SIMPLE STATISTICS FOR 4 REPLICATES **R.penicillatus var. calcareus leaf River Wear Finchale Abbey (km 78.1) 14. 8. 73**

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	19637.1563	334.8870	48597.3125	669.7742	3.4107
K	22501.4375	250.4396	50880.0000	500.8792	2.2260
MG	2394.6836	30.9623	3834.6665	61.9247	1.8242
CA	10251.4844	136.1567	74154.6250	272.3135	2.6563
ZN	2437.9434	64.3843	16581.3320	128.7595	5.2818
CU	32.0441	2.0033	16.0521	4.0065	12.5031
MN	5721.3672	60.4979	14640.0000	120.9959	2.1148
FE	758.0493	43.1142	7435.3320	86.2294	11.3750
AL	734.4563	35.7759	5119.6641	71.5518	9.7421
PB	28.5079	2.8540	32.5818	5.7080	20.0227
CD	8.8152	0.4246	0.7211	0.8492	9.6332
CO	114.3123	2.1221	18.0130	4.2442	3.7128
NI	108.3428	4.5033	81.1198	9.0067	8.3131

** A.2K ROOKHOPE ALGAE MINERAL COMPOSITION 1973. **
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LIST OF NAMES 1 NA 2 K 3 MG 4 CA 5 ZN 6 CU 7 MN 8 FE 9 AL 10 PB 11 CD
12 CO 13 NI

NUMBER OF BLOCKS-CASES 5 NUMBER OF REPLICATES IN FIRST BLOCK 4

SIMPLE STATISTICS FOR 4 REPLICATES **<u>Mougeotia</u> sp. (9μ) North Grain Sike (km -0.5) 16. 5. 73**

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	322.6409	13.0168	677.7500	26.0336	8.0689
K	6774.1602	154.3027	95237.3125	308.6055	4.5556
MG	2335.7715	80.3741	25840.0000	160.7482	6.8920
CA	3904.2500	70.2567	19744.0000	140.5134	3.5990
ZN	135.4488	7.5512	228.0523	15.1024	11.1499
CU	29.8063	0.6472	1.6755	1.2944	4.3428
MN	2331.3311	109.3130	47797.3320	218.6260	9.3777
FE	38716.7500	504.2749	17173.3125	1008.5500	2.6049
AL	6855.6758	216.9731	88309.3125	433.9463	6.3297
PB	75.9490	1.5770	9.9479	3.1540	4.1528
CD	1.6425	0.0071	0.0002	0.0141	0.8609
CO	26.2755	1.1298	5.0969	2.2576	8.5922
NI	35.7223	1.0167	4.1367	2.0339	5.6936

SIMPLE STATISTICS FOR 4 REPLICATES **<u>Spirogyra</u> sp. Upper Rookhope (km -8.5) 4. 9. 73**

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	1437.2920	11.8779	564.3333	23.7557	1.4528
K	18878.7656	353.9341	01077.3125	707.8682	3.7495
MG	2599.9238	76.1040	23216.0000	152.3680	5.8605
CA	10619.2734	214.0155	83210.6250	429.0310	4.0307
ZN	2452.3262	22.6863	2059.6665	45.3725	1.8502
CU	32.6381	0.4715	0.8893	0.9430	2.8894
MN	8162.5234	71.6100	20512.0000	143.2201	1.7546
FE	16013.9922	412.2651	79850.6250	824.5305	5.1488
AL	5839.8320	122.5833	60106.6641	245.1656	4.1982
PB	1214.2051	15.6152	975.3333	31.2303	2.5721
CD	9.7082	0.3404	0.4635	0.6808	7.0130
CO	48.1487	0.9151	2.6576	1.6302	3.3858
NI	43.5843	1.1893	5.6484	2.3766	5.4530

SIMPLE STATISTICS FOR 4 REPLICATES **<u>Stigeoclonium</u> <u>tenue</u> Lower Rookhope (km -3.9) 16. 5. 73**

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	140.7947	8.2978	275.4165	16.5957	11.7871
K	10264.4961	2531.1758	25392.0000	5062.3516	49.3190
MG	1660.4951	24.8814	2476.3333	49.7628	2.9969
CA	10175.8633	143.1084	81920.0000	286.2168	2.8127
ZN	3956.0693	59.8219	14314.6641	119.6439	3.0243
CU	50.0450	0.5505	1.2122	1.1010	2.2001
MN	1257.3340	6.4485	166.3333	12.8970	1.0257
FE	6031.4375	74.8866	22432.0000	149.7732	2.4832
AL	4304.2070	98.2514	38613.3320	196.5028	4.5654
PB	2271.7246	62.8967	15824.0000	125.7935	5.5374
CD	6.4133	0.2568	0.2638	0.5136	8.0091
CO	25.9853	0.8411	2.8301	1.6823	6.4740
NI	36.8884	1.2460	6.2096	2.4919	6.7553

SIMPLE STATISTICS FOR 4 REPLICATES ***Lemanea fluviatilis*** **young Eastgate (km -0.6) 16. 5. 73**

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	144.6043	7.3587	216.6042	14.7175	10.1778
K	17452.7344	233.6949	18453.3125	467.3899	2.6780
MG	3457.5391	106.1634	45082.6641	212.3268	6.1410
CA	1127.7949	36.2158	5246.2320	72.4316	6.4224
ZN	1309.9727	23.8240	2270.3333	47.6480	3.6373
CU	56.2427	1.1175	4.9948	2.2349	3.9737
MN	161.8300	4.5809	83.9375	9.1617	5.6613
FE	2234.3457	59.6546	14234.6641	119.3091	5.3398
AL	376.0403	17.2305	1187.5625	34.4610	9.1642
PB	553.4866	24.9700	2494.0000	49.9400	9.0228
CD	9.3745	0.2514	0.2528	0.5028	5.3639
CO	9.2869	0.4266	0.7280	0.8532	9.1876
NI	23.6460	1.0671	4.5549	2.1342	9.0257

SIMPLE STATISTICS FOR 4 REPLICATES ***Lemanea fluviatilis*** **old Eastgate (km -0.6) 4. 9. 73**

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	236.6309	7.0475	198.6667	14.0949	5.9565
K	12400.8281	123.2450	60757.3320	246.4900	1.9877
MG	7390.2383	272.9468	98000.0000	545.8938	7.3867
CA	4264.3086	59.0480	13946.6641	118.0960	2.7694
ZN	2890.2295	53.3791	11397.3320	106.7583	3.6938
CU	88.6846	3.5997	51.8307	7.1994	8.1179
MN	1047.8740	13.1624	693.0000	26.3249	2.5122
FE	3580.7520	64.9102	16853.3320	129.8204	3.6255
AL	1342.7236	27.6948	3068.0000	55.3895	4.1252
PB	1113.7588	31.5542	3982.6665	63.1084	5.6663
CD	24.5187	0.3101	0.3848	0.6203	2.5299
CO	19.6596	0.7785	2.4242	1.5570	7.9198
NI	43.4050	1.5906	10.1198	3.1812	7.3290

** A.2L ROOKHOPE BRYOPHYTES MINERAL COMPOSITION 1973. **

LIST OF NAMES 1 NA 2 K 3 MG 4 CA 5 ZN 6 CU 7 MN 8 FE 9 AL 10 PB 11 CD 12 CO 13 NI

NUMBER OF BLOCKS-CASES 10 NUMBER OF REPLICATES IN FIRST BLOCK 4

SIMPLE STATISTICS FOR 4 REPLICATES <u>Scapania</u> <u>undulata</u> **North Grain Sike (km -0.5) 16. 5. 73**

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	298.6460	10.0221	401.7709	20.0442	6.7117
K	19287.5462	453.0901	21162.6250	906.1902	4.6983
MG	1127.2910	6.2981	158.6667	12.5963	1.1174
CA	4089.5391	49.7326	9893.3320	99.4652	2.4322
ZN	150.7335	1.0557	4.4583	2.1115	1.4008
CU	33.0988	0.5395	1.1641	1.0789	3.2597
MN	666.4644	14.0890	794.0000	28.1790	4.2280
FE	32934.2656	343.1616	71040.0000	686.3235	2.0839
AL	1781.9678	37.9737	5768.0000	75.9474	4.2620
PB	281.4673	2.7176	29.5417	5.4352	1.9310
CD	2.1234	0.0743	0.0221	0.1487	7.0019
CO	18.7255	0.6758	1.8267	1.3516	7.2178
NI	14.5544	0.9531	3.6337	1.9062	13.0973

SIMPLE STATISTICS FOR 4 REPLICATES <u>Scapania</u> <u>undulata</u> **Upper Rookhope (km -8.5) 16. 5. 73**

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	256.5901	5.5570	123.5209	11.1140	4.3314
K	9641.5195	214.5134	84064.0000	429.0269	4.4498
MG	1120.9063	11.9373	570.0000	23.8747	2.1299
CA	8534.2532	135.3711	73301.3125	270.7422	3.1724
ZN	2453.6748	42.7239	7301.3320	85.4478	3.4824
CU	38.9288	0.3258	0.4245	0.6515	1.6736
MN	1615.2441	43.7159	7644.3320	87.4319	5.4129
FE	14942.7813	374.7781	61834.6250	749.5564	5.0162
AL	6675.8984	146.2829	85564.6250	292.5657	4.3824
PB	2433.7256	97.4474	37984.0000	194.8948	8.0081
CD	9.9299	0.1159	0.0537	0.2318	2.3339
CO	58.8276	1.6399	10.7565	3.2797	5.5751
NI	40.0685	0.8632	2.9805	1.7264	4.3086

SIMPLE STATISTICS FOR 4 REPLICATES <u>Scapania</u> <u>undulata</u> **North Grain Sike (km -0.5) 4. 9. 73**

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	294.7532	14.7482	870.0415	29.4965	10.0072
K	17196.3438	375.1763	63029.3125	750.3528	4.3634
MG	1809.6484	13.0863	685.0000	26.1725	1.4463
CA	6055.0820	106.5395	45402.6641	213.0790	3.5190
ZN	266.7666	8.2749	273.8958	16.5498	6.2038
CU	38.8527	0.6493	1.6862	1.2985	3.3422
MN	8129.8398	107.3871	46128.0000	214.7743	2.6418
FE	96107.4375	1242.1057	71306.0000	2484.2114	2.5850
AL	8042.1641	64.5807	16682.6641	129.1614	1.6061
PB	607.3953	12.5490	630.0000	25.0998	4.1324
CD	2.2989	0.0759	0.0230	0.1517	6.5993
CO	197.8254	2.8705	32.9583	5.7409	2.9020
NI	38.9783	0.9579	3.6706	1.9159	4.9152

SIMPLE STATISTICS FOR 4 REPLICATES **Scapania undulata** Upper Rookhope (km -8.5) 4. 9. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	431.0666	13.5545	734.8958	27.1090	6.2888
K	15477.2813	238.5735	27669.3125	477.1470	3.0829
MG	1843.7314	61.2944	15028.0000	122.5897	6.6490
CA	44560.8438	563.7202	71125.0000	1127.4419	2.5301
ZN	3896.2002	72.1757	20837.3320	144.3514	3.7049
CU	43.4494	0.3419	0.4674	0.6837	1.5736
MN	16177.0820	279.9619	13514.6250	559.9238	3.4612
FE	44576.0313	894.8564	03072.0000	1789.7129	4.0150
AL	19069.2813	390.1453	08853.3125	780.2905	4.0919
PB	3321.0771	61.8924	15322.6641	123.7847	3.7272
CD	25.5858	0.3775	0.5701	0.7550	2.9510
CO	106.4958	2.6442	27.9661	5.2883	4.9657
NI	68.1103	2.1919	19.2174	4.3838	6.4363

SIMPLE STATISTICS FOR 4 REPLICATES **Hygrohypnum ochraceum** Upper Rookhope (km -8.5) 16. 5. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	146.0052	11.2155	503.1459	22.4309	15.3631
K	5413.0934	94.7488	35900.3320	189.4976	3.5002
MG	1527.4668	14.6686	860.6665	29.3371	1.9206
CA	15431.1445	290.2505	36981.3125	580.5010	3.7619
ZN	4532.0664	53.4166	11413.3320	106.8332	2.3573
CU	32.5687	0.4456	0.7943	0.8912	2.7364
MN	14684.4922	180.9015	30901.3125	361.8030	2.4638
FE	31736.6094	363.8901	29664.0000	727.7803	2.2896
AL	10787.5313	154.9193	96000.0000	309.8386	2.8722
PB	3383.1992	124.0161	61520.0000	248.0323	7.3313
CD	12.7141	0.2397	0.2298	0.4794	3.7706
CO	80.8132	2.0301	16.4857	4.0603	5.0242
NI	61.1192	1.5087	9.1042	3.0173	4.9368

SIMPLE STATISTICS FOR 4 REPLICATES **Hygrohypnum ochraceum** Lower Rookhope (km -3.9) 16. 5. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	391.1731	15.7219	988.7093	31.4437	8.0383
K	8923.9922	170.0195	15626.6250	340.0391	3.8104
MG	1863.3164	2.3094	21.3333	4.6188	0.2479
CA	35539.4531	541.4841	72821.0000	1082.9695	3.0472
ZN	3957.6616	64.4774	16629.3320	128.9548	3.2584
CU	226.4092	2.6071	27.1875	5.2142	2.3030
MN	3263.9678	59.5539	14185.6641	119.1079	3.6492
FE	32348.3125	379.3328	75573.3125	758.6655	2.3453
AL	18052.0938	181.9597	32437.3125	363.9194	2.0159
PB	4628.2266	97.4885	38016.0000	194.9769	4.2129
CD	8.3028	0.2618	0.2743	0.5237	6.3074
CO	76.8604	2.0987	17.6185	4.1974	5.4611
NI	92.5557	1.3004	6.7643	2.6008	2.8100

SIMPLE STATISTICS FOR 4 REPLICATES **Hygrohypnum ochraceum** Eastgate (km -0.6) 16. 5. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	218.9642	18.2227	1328.2708	36.4454	16.6445
K	8129.8320	121.0509	58613.3320	242.1019	2.9779
MG	2046.8467	8.1086	263.0000	16.2173	0.7923
CA	35435.6250	243.7047	37568.0000	487.4094	1.3755
ZN	3505.9424	17.5119	1226.6665	35.0238	0.9990
CU	124.1349	35.7010	5098.2461	71.4020	57.5197

MN	3388.8242	122.2993	59819.6641	244.5795	7.2172
FE	19633.4375	440.6782	76789.3125	881.3564	4.4891
AL	11681.3398	199.1448	58634.6250	398.2896	3.4096
PB	3919.5674	184.7556	36538.6250	369.5112	9.4273
CD	9.4641	0.2277	0.2074	0.4554	5.3799
CO	67.1230	1.5063	9.0755	3.0126	4.4881
NI	112.5663	1.6611	11.0365	3.3221	2.9513

SIMPLE STATISTICS FOR 4 REPLICATES **<u>Hygrohypnum</u> <u>ochraceum</u> Upper Rookhope (km -8.5) 4. 9. 73**

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	357.4985	46.7731	8750.8945	93.5462	26.1669
K	9415.2695	241.8595	33984.0000	483.7190	5.1376
MG	2498.2344	19.1137	1461.3333	38.2274	1.5302
CA	29276.7656	425.7822	25162.6250	851.5647	2.9087
ZN	3597.2354	56.7098	12864.0000	113.4196	3.1530
CU	38.4041	1.0331	4.2695	2.0663	5.3804
MN	16437.4063	451.5571	15616.0000	903.1145	5.4943
FE	53560.9281	552.4055	20608.0000	1104.8113	2.0627
AL	12967.6797	193.2184	49333.3125	386.4368	2.9800
PB	3767.3289	157.1326	98762.6250	314.2651	8.3418
CD	19.2001	0.4792	0.9185	0.9584	4.9917
CO	2236.5869	2151.5938	17424.0000	4303.1875	192.3997
NI	79.2781	2.0141	16.2266	4.0282	5.0811

SIMPLE STATISTICS FOR 4 REPLICATES **<u>Hygrohypnum</u> <u>ochraceum</u> Lower Rookhope (km -3.9) 4. 9. 73**

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	280.1653	7.3976	218.8958	14.7951	5.2809
K	15467.8906	190.4381	45066.6250	380.8762	2.4624
MG	3036.4736	39.2768	6170.6641	78.5536	2.5870
CA	49608.7500	292.1187	41333.3125	584.2373	1.1777
ZN	16475.5156	307.5929	78453.3125	615.1855	3.7339
CU	326.0457	6.5032	169.1667	13.0064	3.9891
MN	16446.8906	516.0464	65216.0000	1032.0930	6.2753
FE	25390.3906	1171.8201	92650.0000	2343.6404	9.2304
AL	14486.5469	193.7146	50101.3125	387.4292	2.6744
PB	4300.1172	81.0843	26298.6641	162.1686	3.7713
CD	34.2227	0.5677	1.2891	1.1354	3.3166
CO	312.9304	3.6178	52.3542	7.2356	2.3122
NI	254.1382	3.5082	49.2292	7.0163	2.7608

SIMPLE STATISTICS FOR 4 REPLICATES **<u>Hygrohypnum</u> <u>ochraceum</u> Eastgate (km -0.6) 4. 9. 73**

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	257.4819	17.0072	1156.9790	34.0144	13.2104
K	13159.9922	255.2070	60522.6250	510.4141	3.8812
MG	3745.8477	24.5493	2410.6665	49.0985	1.3107
CA	40409.2188	428.1309	33184.0000	856.2617	2.1190
ZN	11793.6094	206.2490	70154.6250	412.4980	3.4976
CU	198.2201	2.3695	22.4583	4.7390	2.3907
MN	16635.4531	405.5088	57749.3125	811.0176	4.8752
FE	29550.9063	767.5554	56565.0000	1535.1108	5.1948
AL	9359.6641	153.8137	94634.6250	307.6274	3.2867
PB	3637.5197	164.8595	08714.6250	329.7190	9.0644
CD	26.5034	0.5130	1.0528	1.0261	3.8715
CO	307.5022	5.4782	120.0417	10.9564	3.5630
NI	255.0247	6.7202	180.6458	13.4405	5.2703

COMPARISON OF MEANS R2 WITH R3

** A.2M ROOKHOPE HIGHER PLANT MINERAL COMPOSITION 1973. **

LIST OF NAMES 1 NA 2 K 3 MG 4 CA 5 ZN 6 CU 7 MN 8 FE 9 AL 10 PB 11 CD 12 CO 13 NI

NUMBER OF BLOCKS-CASES 6 NUMBER OF REPLICATES IN FIRST BLOCK 4

SIMPLE STATISTICS FOR 4 REPLICATES <u>Mimulus</u> <u>guttatus</u> root Upper Rookhope (km -8.5) 4. 9. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	3287.5156	100.3261	40261.3320	200.6523	6.1035
K	42741.9531	547.0632	01403.0000	1094.1265	2.5645
MG	3063.2188	33.3666	4453.3320	66.7333	2.1785
CA	7924.4727	109.4044	47877.3320	218.8089	2.7612
ZN	1144.6289	20.5690	1692.3333	41.1390	3.5940
CU	36.5028	0.4511	0.8138	0.9021	2.4713
MN	2072.5898	46.6476	8704.0000	93.2952	4.5014
FE	4090.7422	34.6410	4800.0000	69.2820	1.6936
AL	1315.1553	21.5097	1850.6665	43.0194	3.2710
PB	474.0291	6.4129	164.5000	12.8259	2.7057
CD	17.9736	0.3663	0.5367	0.7326	4.0748
CO	18.3009	1.1202	5.0195	2.2404	12.2422
NI	48.2455	2.8626	32.7773	5.7252	11.8667

SIMPLE STATISTICS FOR 4 REPLICATES <u>Mimulus</u> <u>guttatus</u> stem Upper Rookhope (km -8.5) 4. 9. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	3667.5859	83.8252	28106.6641	167.6504	4.5711
K	69329.7500	900.3701	42666.0000	1800.7405	2.5974
MG	2946.9916	35.9629	5173.3320	71.9259	2.4407
CA	11560.7461	116.5733	54357.3320	233.1466	2.0167
ZN	769.6650	41.9772	7048.3320	83.9543	10.9079
CU	19.5332	0.1193	0.0570	0.2387	1.2216
MN	574.0554	25.0616	2512.3333	50.1232	8.7314
FE	1237.5283	26.2774	2762.0000	52.5547	4.2467
AL	374.5024	11.4830	527.4375	22.9660	6.1324
PB	115.5876	2.6026	27.0938	5.2052	4.5032
CD	2.8091	0.1049	0.0440	0.2099	7.4712
CO	7.3276	0.4714	0.8889	0.9428	12.8666
NI	11.4258	3.3419	44.6719	6.6837	58.4966

SIMPLE STATISTICS FOR 4 REPLICATES <u>Mimulus</u> <u>guttatus</u> leaf Upper Rookhope (km -8.5) 4. 9. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	2957.2461	90.2958	32613.3320	180.5916	6.1068
K	41754.6406	880.0483	97941.0000	1760.0969	4.2153
MG	5209.0352	127.2164	64735.0000	254.4327	4.8854
CA	33528.7031	251.2900	52585.6250	502.5801	1.4990
ZN	1643.7236	1161.5122	96443.0000	2323.0247	141.3269
CU	21.0970	0.2430	0.2362	0.4861	2.3039
MN	498.0713	17.6093	1240.3540	35.2187	7.0710
FE	1219.0488	20.0416	1606.6665	40.0833	3.2881
AL	372.5110	5.4112	117.1250	10.8224	2.9053
PB	83.8432	2.0235	16.3776	4.0469	4.8268
CD	2.8758	0.0840	0.0282	0.1680	5.8403
CO	7.6951	0.4095	0.6709	0.8191	10.6441
NI	20.2537	0.5398	1.1656	1.0796	5.3306

SIMPLE STATISTICS FOR 4 REPLICATES <u>Mimulus guttatus</u> root Lower Rookhope (km -3.9) 4. 9. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	5196.3203	96.4711	37226.6641	192.9421	3.7131
K	51091.2031	893.9021	96245.0000	1787.9044	3.4999
MG	3654.0547	89.5619	32085.3320	179.1238	4.9021
CA	65061.1250	993.0717	44448.0000	1986.0635	3.0526
ZN	3836.8145	85.6342	29333.3320	171.2698	4.4639
CU	222.2891	3.3048	43.6875	6.6097	2.9736
MN	3840.6230	59.7885	14298.6641	119.5770	3.1135
FE	15436.5922	329.0389	33066.6250	658.0779	4.2630
AL	16824.8906	473.2412	95822.3125	946.4827	5.6255
PB	5587.0430	105.1665	44240.0000	210.3331	3.7647
CD	31.5839	0.5600	1.2546	1.1201	3.5020
CO	117.0662	3.3460	44.7839	6.6921	5.7165
NI	77.2231	1.6768	11.2461	3.3535	4.3426

SIMPLE STATISTICS FOR 4 REPLICATES <u>Mimulus guttatus</u> stem Lower Rookhope (km -3.9) 4. 9. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	4217.7852	27.0062	2917.3333	54.0123	1.2806
K	45670.5625	577.1839	32565.0000	1154.3677	0.7713
MG	2730.5498	23.8327	2272.0000	47.6655	1.7456
CA	32838.4844	524.5134	00459.0000	1049.0271	3.1945
ZN	669.2415	16.9534	1149.6665	33.9067	5.0664
CU	40.2375	0.4118	0.6784	0.8236	2.0470
MN	239.6221	4.9032	96.1667	9.8065	4.0925
FE	920.8525	42.4235	7199.0000	84.8469	9.2139
AL	318.0483	7.0630	199.5417	14.1259	4.4414
PB	218.9104	4.9707	98.8333	9.9415	4.5414
CD	3.1815	0.1280	0.0655	0.2560	8.0462
CO	33.7111	24.3316	2368.1079	48.6632	144.3538
NI	13.6307	0.3925	0.5854	0.7651	5.6130

SIMPLE STATISTICS FOR 4 REPLICATES <u>Mimulus guttatus</u> leaf Lower Rookhope (km -3.9) 4. 9. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	3610.8242	130.0820	67685.3125	260.1641	7.2051
K	43647.7344	14360.0508	44288.0000	28720.1016	65.7997
MG	7074.3672	152.6390	93194.6250	305.2778	4.3153
CA	51198.8750	592.9360	06293.0000	1185.8723	2.3162
ZN	1347.4990	27.7905	3089.3333	55.5818	4.1248
CU	49.6411	0.4550	0.8281	0.9100	1.8332
MN	783.5700	19.7990	1568.0000	39.5980	5.0510
FE	2409.2520	54.9909	12096.0000	109.9818	4.5650
AL	1098.5840	30.4330	3704.6665	60.8660	5.5404
PB	516.9600	11.1505	497.3333	22.3010	4.3139
CD	3.8372	0.1559	0.0972	0.3118	8.1245
CO	12.6567	0.4239	0.7187	0.8477	6.6980
NI	19.3224	5.7578	132.6086	11.5156	59.5970

** A.2N PITHOUSES PLANT MINERAL COMPOSITION SURVEY 1973/74. **

LIST OF NAMES 1 NA 2 K 3 MG 4 CA 5 ZN 6 CU 7 MN 8 FE 9 AL 10 PB 11 CD 12 CO 13 NI

NUMBER OF BLOCKS-CASES 11 NUMBER OF REPLICATES IN FIRST BLOCK 4

SIMPLE STATISTICS FOR 4 REPLICATES <u>Euglena mutabilis</u> **Acid Stream A source (km -3.6) 2. 8. 74**

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	200.9348	11.7855	555.6040	23.5713	11.7309
K	2760.1787	120.3163	57904.0000	240.6325	8.7180
MG	2211.7617	224.6449	01861.3125	449.2899	20.3136
CA	1649.0089	223.4517	99722.6250	446.9033	27.1013
ZN	120.7379	7.6351	233.1797	15.2702	12.6474
CU	29.7489	1.0513	4.4210	2.1026	7.0679
MN	126.6771	6.9130	191.1602	13.8261	10.9144
FE	14472.8359	740.1475	91274.0000	1490.2952	10.2993
AL	3010.3967	109.8479	48266.6641	219.6958	7.2980
PB	8.9393	0.3221	0.4149	0.6441	7.2053
CD	4.4697	0.1610	0.1037	0.3220	7.2048
CO	6.5896	1.1061	4.8936	2.2121	33.5705
NI	8.9393	0.3221	0.4149	0.6441	7.2053

SIMPLE STATISTICS FOR 4 REPLICATES <u>Hormidium rivulare</u> **Acid Stream B source (km -0.6) 14. 6. 73**

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	1041.6143	19.9207	1587.3333	39.8414	3.8250
K	7763.7813	244.3031	38736.0000	488.6062	6.2934
MG	1642.6543	27.1324	2944.6665	54.2648	3.3035
CA	1257.6680	49.2849	9716.0000	98.5698	7.8375
ZN	59.9277	1.1773	5.5443	2.3546	3.9291
CU	42.8866	1.8294	13.3867	3.6588	8.5313
MN	131.3867	5.5589	123.6042	11.1177	8.4618
FE	6686.5273	136.5723	74609.0000	273.1445	4.0850
AL	1363.4492	55.0280	12112.2320	110.0560	8.0719
PB	5.5838	0.1347	0.0726	0.2694	4.8248
CD	2.7919	0.0673	0.0181	0.1346	4.8224
CO	5.5838	0.1347	0.0726	0.2694	4.8248
NI	5.5838	0.1347	0.0726	0.2694	4.8248

SIMPLE STATISTICS FOR 4 REPLICATES <u>Hormidium rivulare</u> **Acid Stream B source (km -0.6) 15. 4. 74**

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	851.5479	6.4679	167.3333	12.9357	1.5191
K	14809.0859	151.0143	91221.3125	302.0285	2.0395
MG	2683.3682	28.6822	3290.6665	57.3643	2.1378
CA	1160.6328	8.8223	311.3333	17.6446	1.5203
ZN	106.0899	2.6214	27.4870	5.2428	4.9414
CU	33.0735	0.8746	3.0599	1.7493	5.2890
MN	146.8753	3.3510	44.9167	6.7020	4.5630
FE	3599.0293	78.5960	24709.3320	157.1920	4.3676
AL	1235.6230	15.9557	1018.3333	31.9113	2.5826
PB	3.3281	0.0091	0.0003	0.0182	0.5463
CD	1.6641	0.0046	0.0001	0.0092	0.5505
CO	3.3281	0.0091	0.0003	0.0182	0.5463
NI	9.9816	0.6666	1.7774	1.3332	13.3565

SIMPLE STATISTICS FOR 4 REPLICATES . *Dicranella* sp. Acid Stream B source (km -0.6) 14. 6. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	890.2502	39.4631	6229.3320	78.9261	8.8646
K	10444.7852	340.3840	63445.3125	680.7681	6.5178
MG	1027.9004	8.3516	279.0000	16.7033	1.6250
CA	3937.8496	60.8057	14789.3320	121.6114	3.0883
ZN	56.8917	1.3194	6.9635	2.6389	4.6392
CU	225.2574	6.1644	152.0000	12.3288	5.4732
MN	87.2333	0.7928	2.5143	1.5857	1.8177
FE	30014.6406	371.6628	552533.3125	743.3259	2.4765
AL	1687.2900	19.0394	1450.0000	38.0789	2.2568
PB	8.9256	0.8664	3.0023	1.7327	19.4062
CD	2.5018	0.0309	0.0038	0.0617	2.4671
CO	6.5430	0.7087	2.0090	1.4174	21.5627
NI	6.8739	0.3325	0.4421	0.6649	9.6731

SIMPLE STATISTICS FOR 4 REPLICATES *Drepanocladus fluitans* Acid Stream A (km -3.6) 14. 6. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	1434.0098	35.7549	5113.6641	71.5099	4.9867
K	14659.4063	609.5093	81130.0000	1217.0168	8.2844
MG	1164.5283	13.4691	725.6665	26.9382	2.3132
CA	1955.3418	44.8386	8042.0000	89.6772	4.5963
ZN	72.2968	1.5315	9.3815	3.0629	4.2366
CU	82.5292	3.2411	42.0195	6.4822	7.8545
MN	42.8820	1.1345	5.1484	2.2690	5.2913
FE	5924.8125	170.8956	15821.3125	341.7913	3.4438
AL	772.2988	26.2869	2764.0000	52.5738	6.8074
PB	13.7807	0.5435	1.1216	1.0370	7.3981
CD	3.0509	0.5825	1.3574	1.1651	38.1982
CO	9.4960	0.2966	0.3519	0.5932	6.2468
NI	6.1017	1.1651	5.4296	2.3302	38.1884

SIMPLE STATISTICS FOR 4 REPLICATES *Drepanocladus fluitans* Acid Stream A (km -3.6) 15. 4. 74

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	1035.9473	20.6720	1709.3333	41.3441	3.9909
K	16443.5000	209.3800	175360.0000	418.7600	2.5467
MG	1312.2891	13.5277	732.0000	27.0555	2.0617
CA	1028.3232	1.8257	13.3333	3.6515	0.3551
ZN	80.0944	4.4559	79.4193	8.9117	11.1263
CU	55.7416	0.9223	3.4023	1.8445	3.3091
MN	62.9927	18.7704	1409.3149	37.5409	59.5956
FE	10882.7539	213.0665	181589.3125	426.1331	3.9157
AL	837.2227	12.8160	657.0000	25.6320	3.0616
PB	4.9266	0.0281	0.0032	0.0563	1.1426
CD	2.4633	0.0141	0.0008	0.0282	1.1435
CO	4.9266	0.0281	0.0032	0.0563	1.1426
NI	4.9266	0.0281	0.0032	0.0563	1.1426

SIMPLE STATISTICS FOR 4 REPLICATES *Drepanocladus fluitans* Acid Stream B (km -0.6) 14. 6. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	817.4221	19.2354	1480.0000	38.4708	4.7064
K	19673.4688	148.4497	88149.3125	296.8994	1.5091
MG	1367.2871	17.0612	1164.3333	34.1223	2.4956
CA	3898.1514	135.0111	72912.0000	270.0222	6.9269
ZN	50.7318	2.9467	34.7331	5.8935	11.6169
CU	78.3892	0.9689	3.7552	1.9378	2.4721

MN	35.8952	0.7522	2.2630	1.5043	4.1921
FE	10828.6516	374.0204	62261.3125	749.8408	6.9245
AL	637.1414	24.6999	2440.3333	49.3997	7.7533
PB	12.6836	0.5989	1.4348	1.1978	9.4440
CD	2.4747	0.0089	0.0003	0.0178	0.7176
CO	7.7365	0.3366	0.4532	0.6732	8.7018
NI	4.9495	0.0178	0.0013	0.0357	0.7205

SIMPLE STATISTICS FOR 4 REPLICATES <u>Juncus effusus</u> submerged root Acid Stream B (km -0.6) 2. 8. 74

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	3975.1406	109.2459	47738.6641	218.4918	5.4965
K	14718.0117	227.2068	206477.3125	454.4177	3.0889
MG	916.3860	16.4848	1087.0000	32.9697	3.5978
CA	461.4832	6.6376	176.2292	13.2751	2.8766
ZN	37.8332	1.3665	7.4688	2.7329	7.2236
CU	27.9403	0.4789	0.9173	0.9578	3.4279
MN	49.8951	1.3305	7.0807	2.6610	5.3331
FE	1234.9238	16.5806	1099.6665	33.1612	2.6853
AL	270.2981	14.3300	821.3958	28.6600	10.6031
PB	3.3265	0.0108	0.0005	0.0215	0.6467
CD	1.6633	0.0054	0.0001	0.0108	0.6467
CO	4.7832	0.2178	0.1897	0.4356	9.1059
NI	7.0667	0.2196	0.1929	0.4392	6.2147

SIMPLE STATISTICS FOR 4 REPLICATES <u>Juncus effusus</u> submerged stem Acid Stream B (km -0.6) 2. 8. 74

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	3143.6172	81.8535	26800.0000	163.7071	5.2076
K	14026.0703	194.9769	152064.0000	389.9535	2.7802
MG	603.2007	5.6936	129.6667	11.3871	1.8878
CA	535.0986	14.9416	893.0000	29.8831	5.5846
ZN	32.4369	1.0998	4.8385	2.1997	6.7814
CU	11.3324	0.2304	0.2124	0.4609	4.0668
MN	98.9849	0.6943	1.9284	1.3887	1.4029
FE	142.3743	1.7839	12.7292	3.5678	2.5059
AL	92.7033	5.1159	104.6914	10.2319	11.0372
PB	3.3698	0.0245	0.0024	0.0489	1.4525
CD	1.6849	0.0122	0.0006	0.0245	1.4532
CO	3.3698	0.0245	0.0024	0.0489	1.4525
NI	5.0547	0.0368	0.0054	0.0736	1.4561

SIMPLE STATISTICS FOR 4 REPLICATES <u>Juncus effusus</u> emergent stem Acid Stream B (km -0.6) 2. 8. 74

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	5534.9219	147.1915	86661.3125	294.3831	5.3186
K	15253.2070	89.4127	32000.0000	178.8354	1.1728
MG	1282.0176	20.0935	1615.0000	40.1871	3.1347
CA	852.5452	3.9264	61.6667	7.8529	0.9211
ZN	37.6190	1.1334	5.1390	2.2667	6.0255
CU	13.3259	0.2968	0.3524	0.5936	4.4512
MN	84.9266	1.1541	5.3281	2.3083	2.7180
FE	1099.2998	12.1655	592.0000	24.3311	2.2133
AL	334.3918	7.4631	222.7917	14.9262	4.4637
PB	3.3437	0.0191	0.0015	0.0383	1.1446
CD	2.5014	0.4717	0.8900	0.9434	37.7153
CO	3.3437	0.0191	0.0015	0.0383	1.1446
NI	7.1112	0.8213	2.6982	1.6426	23.0988

Juncus effusus emergent leaf Acid Stream B (km -0.6) 2. 8. 74

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	2867.2393	49.7326	9893.3320	99.4652	3.4690
K	14315.4563	133.6263	71424.0000	267.2527	1.8669
MG	843.1541	5.1881	107.6667	10.3763	1.2306
CA	642.4753	6.4031	164.0000	12.8062	1.9933
ZN	27.6655	1.0109	4.0879	2.0219	7.3082
CU	6.3861	0.1855	0.1391	0.3729	5.8400
MN	90.7552	1.0396	4.3229	2.0792	2.2910
FE	117.6895	7.5068	225.4063	15.0135	12.7353
AL	56.9778	4.8351	93.5143	9.6703	16.9720
PB	3.2541	0.0226	0.0020	0.0452	1.3878
CD	1.6270	0.0113	0.0005	0.0226	1.3900
CO	3.2541	0.0226	0.0020	0.0452	1.3878
NI	3.4563	0.2000	0.1601	0.4001	11.5744

** A.20 PITHOUSES/BROOKHOPE DREPANOCLADUS MINERAL COMPOSITION 1973. **

LIST OF NAMES 1 NA 2 K 3 MG 4 CA 5 ZN 6 CU 7 MN 8 FE 9 AL 10 PB 11 CD 12 CO 13 NI

NUMBER OF BLOCKS-CASES 9 NUMBER OF REPLICATES IN FIRST BLOCK 4

SIMPLE STATISTICS FOR 4 REPLICATES <u>Drepanocladus fluitans</u> **Acid Stream A site 1 14. 6. 73**

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	1424.0098	35.7549	5113.6641	71.5099	4.9867
K	14690.4063	608.5083	81130.0000	1217.0168	8.2844
MG	1164.5293	13.4491	725.6665	26.9392	2.3132
CA	1955.3418	44.8386	8042.0000	89.6772	4.5863
ZN	72.2968	1.5315	9.3815	3.0629	4.2366
CU	82.1693	3.5805	51.2786	7.1609	8.7148
MN	42.8820	1.1345	5.1486	2.2690	5.2913
FE	9924.3125	170.8956	16821.3125	341.7913	3.4438
AL	772.2988	26.2869	2764.0000	52.5738	6.8074
PB	13.7807	0.5435	1.1816	1.0870	7.8881
CD	3.0509	0.5825	1.3574	1.1651	38.1882
CO	9.4960	0.2966	0.3519	0.5932	6.2468
NI	6.1017	1.1651	5.4296	2.3302	38.1984

SIMPLE STATISTICS FOR 4 REPLICATES <u>Drepanocladus fluitans</u> **Acid Stream A site 3 14. 6. 73**

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	1615.9502	87.3794	30540.6641	174.7539	10.8146
K	23946.1250	236.6432	24000.0000	473.2864	1.9765
MG	1332.6006	30.6974	3769.3333	61.3949	4.6071
CA	1617.1377	19.7990	1568.0000	39.5980	2.4486
ZN	76.3451	3.0906	38.2083	6.1813	8.0965
CU	57.4699	1.0701	4.5807	2.1403	3.7241
MN	56.8283	1.6677	11.1250	3.3354	5.8693
FE	16336.0977	60.3987	14592.0000	120.7973	0.7395
AL	1074.5771	18.2003	1325.0000	36.4005	3.3874
PB	19.2825	0.6626	1.7559	1.3251	6.8721
CD	2.5289	0.0352	0.0049	0.0703	2.7803
CO	9.1432	0.5153	1.0622	1.0306	11.2658
NI	5.0579	0.0703	0.0198	0.1407	2.7810

SIMPLE STATISTICS FOR 4 REPLICATES <u>Drepanocladus fluitans</u> **Acid Stream A site 5 14. 6. 73**

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	2332.7305	102.9822	42421.3320	205.9644	8.8293
K	25211.5781	436.8360	63477.3125	873.7720	3.4658
MG	1416.5742	19.3249	1495.3333	38.6695	2.7298
CA	2301.0273	52.5864	11061.3320	105.1729	4.5707
ZN	79.2327	3.1334	39.2721	6.2667	7.9093
CU	75.1935	1.0973	4.8164	2.1946	2.9186
MN	41.4925	0.6870	1.8880	1.3741	3.3116
FE	16228.0078	143.1094	81920.0000	286.2168	1.7637
AL	749.2131	19.5213	1524.3333	39.0427	5.2181
PB	6.9193	0.3847	0.5920	0.7694	11.1197
CD	2.5149	0.0084	0.0003	0.0167	0.6651
CO	8.4935	0.6307	1.5911	1.2614	14.8511
NI	5.0297	0.0170	0.0012	0.0341	0.6771

SIMPLE STATISTICS FOR 4 REPLICATES **Drepanocladus fluitans** Acid Stream site 8 14. 6. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	1459.0098	90.3876	32679.6641	180.7752	12.3903
K	20688.2500	507.3750	29717.3125	1014.7500	4.9050
MG	1275.1738	12.2984	605.0000	24.5967	1.9289
CA	2533.1465	44.3471	7866.6641	88.6942	3.5013
ZN	56.8609	3.0778	37.8919	6.1556	10.8258
CU	69.1265	1.1718	5.4922	2.3435	3.3902
MN	38.5228	1.6076	10.3372	3.2152	8.3461
FE	51462.8281	187.5029	40629.3125	375.0059	0.7287
AL	997.5059	15.3813	946.3333	30.7625	3.0839
PB	38.8736	1.2028	5.7865	2.4055	6.1880
CD	2.4491	0.0178	0.0013	0.0355	1.4508
CO	12.2377	0.4911	0.9647	0.9822	8.0258
NI	4.8961	0.0357	0.0051	0.0713	1.4566

SIMPLE STATISTICS FOR 4 REPLICATES **Drepanocladus fluitans** Acid Stream site 9 14. 6. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	459.1609	46.0518	8483.0820	92.1037	20.0591
K	13632.4648	353.3608	99456.0000	706.7219	5.1841
MG	982.0938	12.7997	655.3333	25.5995	2.6066
CA	1862.8867	32.5960	4250.0000	65.1920	3.4995
ZN	51.2019	2.5291	25.5846	5.0581	9.8788
CU	44.3541	0.4289	0.7357	0.8577	1.9338
MN	41.3328	0.6192	1.5339	1.2385	2.9964
FE	40406.3125	593.5115	09024.0000	1187.0232	2.9377
AL	777.2632	11.4819	527.3333	22.9637	2.9544
PB	17.4745	4.6956	88.1932	9.3911	53.7420
CD	2.4676	0.0042	0.0001	0.0084	0.3420
CO	6.1680	0.4987	0.9947	0.9973	16.1694
NI	4.9353	0.0086	0.0003	0.0172	0.3480

SIMPLE STATISTICS FOR 4 REPLICATES **Drepanocladus fluitans** Acid Stream site 10 14. 6. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	744.6321	17.0563	1163.6665	34.1125	4.5811
K	22819.9375	359.5256	17034.6250	719.0513	3.1510
MG	1372.1592	23.4005	2190.3333	46.8010	3.4108
CA	2642.0186	61.0683	14917.3320	122.1365	4.6228
ZN	41.0002	1.4888	8.8659	2.9776	7.2623
CU	53.4162	1.5875	10.0807	3.1750	5.9439
MN	34.0564	0.9693	3.7578	1.9385	5.6921
FE	14191.2344	356.6660	08842.6250	713.3320	5.0266
AL	497.7947	9.1646	335.9583	18.3292	3.6821
PB	18.3586	5.2372	109.7126	10.4744	57.0545
CD	2.5220	0.0324	0.0042	0.0647	2.5669
CO	5.0440	0.0648	0.0168	0.1296	2.5700
NI	5.0440	0.0648	0.0168	0.1296	2.5700

SIMPLE STATISTICS FOR 4 REPLICATES **Drepanocladus fluitans** Acid Stream site 12 14. 6. 73

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	514.5212	60.3876	14586.6641	120.7753	23.4733
K	13443.3789	266.9331	85013.3125	533.8665	3.9712
MG	998.3291	7.8793	248.3333	15.7586	1.5785
CA	1753.0518	36.1063	5214.6641	72.2126	4.1193
ZN	50.9167	2.0020	16.0325	4.0041	7.8640
CU	57.1454	0.0699	0.0195	0.1398	0.2446

MN	26.3625	0.4826	0.9318	0.9653	3.6616
FE	33799.0313	584.5696	76256.0000	1173.1304	3.4709
AL	496.7202	25.2372	2547.6665	50.4744	10.1615
PB	38.6422	1.1398	5.1966	2.2796	5.8993
CD	2.5127	0.0248	0.0025	0.0496	1.9746
CO	5.0253	0.0497	0.0099	0.0995	1.9792
NI	5.0253	0.0497	0.0099	0.0995	1.9792

SIMPLE STATISTICS FOR 4 REPLICATES <u>*Drepanocladus fluitans*</u> **Acid Stream B site 1 14. 6. 73**

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	839.3294	17.9025	1282.0000	35.8050	4.2659
K	19835.7031	348.9871	87168.0000	697.9741	3.5152
MG	1366.9404	16.7207	1118.3333	33.4415	2.4464
CA	3897.1172	134.2087	72049.0000	268.4175	6.8976
ZN	50.7166	2.9294	34.3255	5.8588	11.5520
CU	78.3705	0.9803	3.8438	1.9605	2.5016
MN	35.8759	0.7441	2.2148	1.4882	4.1483
FE	10826.6758	379.1921	75146.6250	758.3843	7.0048
AL	636.9587	24.4608	2393.3333	48.9217	7.6805
PB	12.6900	0.5954	1.4182	1.1909	9.3919
CD	2.4741	0.0096	0.0004	0.0191	0.7735
CO	7.7347	0.3373	0.4552	0.6747	8.7224
NI	4.9483	0.0194	0.0015	0.0388	0.7841

SIMPLE STATISTICS FOR 4 REPLICATES **Drepanocladus fluitans North Grain Sike (km -0.5) 16. 5. 75**

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	262.0132	17.2621	1191.9165	34.5241	13.1765
K	11713.9844	275.1194	302762.6250	550.2388	4.6973
MG	1203.3447	16.8251	1132.3333	33.6502	2.7966
CA	3860.1729	58.1951	13546.6641	116.3901	3.0152
ZN	121.6865	3.6351	52.8568	7.2703	5.9746
CU	42.6427	0.5714	1.3060	1.1428	2.6799
MN	301.4175	3.1667	40.0625	6.3295	2.0999
FE	25319.7656	376.7935	567893.3125	753.5869	2.9763
AL	1599.9740	23.1661	2146.6665	46.3321	2.8960
PB	297.2779	3.2500	42.2500	6.5000	2.1865
CD	1.6475	0.0084	0.0003	0.0168	1.0186
CO	13.5667	0.2429	0.2359	0.4857	3.5802
NI	21.6463	0.4827	0.9321	0.9655	4.4602

** A.2P PITHOUSES DREPANOCLADUS MINERAL COMPOSITION (DIVIDED) **

LIST OF NAMES 1 NA 2 K 3 MG 4 CA 5 ZN 6 CU 7 MN 8 FE 9 AL 10 PB 11 CD 12 CO 13 NI

NUMBER OF BLOCKS-CASES 4 NUMBER OF REPLICATES IN FIRST BLOCK 4

SIMPLE STATISTICS FOR 4 REPLICATES <u>Drepanocladus</u> <u>fluitans</u> **1st 30 mm Acid Stream A source 2. 8. 74**

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	529.0315	46.9193	8805.6641	93.8395	17.7378
K	14834.2852	360.2666	19168.0000	720.5332	4.8572
MG	1656.5215	55.7270	12422.0000	111.4540	6.7282
CA	1197.2217	61.5339	15145.6641	123.0677	10.2794
ZN	94.4124	5.9774	142.9180	11.9548	12.6623
CU	47.8427	2.0736	17.1992	4.1472	8.6684
MN	72.6521	5.2005	108.1797	10.4009	14.3161
FE	5198.2148	87.8483	30869.3320	175.6967	3.3799
AL	461.6970	23.4173	2193.4790	46.8346	10.1221
PB	9.6626	0.3544	0.5024	0.7088	7.3358
CD	4.8313	0.1772	0.1256	0.3544	7.3351
CO	9.6626	0.3544	0.5024	0.7088	7.3358
NI	9.6626	0.3544	0.5024	0.7088	7.3358

SIMPLE STATISTICS FOR 4 REPLICATES **Drepanocladus fluitans 2nd 30 mm Acid Stream A source 2. 8. 74**

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	881.4321	31.3953	3942.6665	62.7906	7.1237
K	20428.0156	613.2229	04170.0000	1226.4460	6.0037
MG	1628.2197	41.3985	6855.3320	82.7969	5.0851
CA	996.8982	31.4285	3951.0000	62.8570	6.3053
ZN	72.9672	2.6920	28.9870	5.3840	7.3786
CU	58.6048	1.5067	9.0807	3.0134	5.1419
MN	84.0481	6.1383	153.1794	12.3765	14.7220
FE	9271.7422	379.1921	75146.6250	758.3843	8.1795
AL	754.1746	32.2232	4153.3320	64.4464	8.5453
PB	9.7243	0.1647	0.1085	0.3294	3.3870
CD	4.8622	0.0823	0.0271	0.1647	3.3866
CO	9.7243	0.1647	0.1085	0.3294	3.3870
NI	9.7243	0.1647	0.1085	0.3294	3.3870

SIMPLE STATISTICS FOR 4 REPLICATES **Drepanocladus fluitans 3rd 30 mm Acid Stream A source 2. 8. 74**

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	2152.6357	65.0026	16901.3320	130.0051	6.0393
K	20077.5000	345.2070	76672.0000	690.4143	3.4387
MG	1402.9219	37.1909	5532.6641	74.3819	5.3019
CA	1111.5146	34.4650	4751.3320	68.9299	6.2014
ZN	73.2902	1.7857	12.7552	3.5714	4.8730
CU	49.9122	2.4515	24.0404	4.9031	9.8234
MN	84.4854	3.8716	59.9557	7.7431	9.1650
FE	13053.2891	372.2078	54154.6250	744.4155	5.7029
AL	1024.1973	45.0555	8120.0000	90.1110	8.7982
PB	10.1115	0.1859	0.1382	0.3717	3.6763
CD	5.0557	0.0929	0.0345	0.1859	3.6763
CO	10.1115	0.1859	0.1382	0.3717	3.6763
NI	10.1115	0.1859	0.1382	0.3717	3.6763

SIMPLE STATISTICS FOR 4 REPLICATES . **Drepanocladus fluitans 4th 30 mm Acid Stream A source 2. 8. 74**

ELEMENT	MEAN	STANDARD ERROR	VARIANCE	STANDARD DEVIATION	COEFFICIENT OF VARIANCE
NA	2903.3105	149.6395	89568.0000	299.2791	10.3082
K	15096.5078	997.9924	83957.0000	1995.9851	13.2215
MG	882.0925	64.2969	16536.3320	120.5937	14.5782
CA	777.1140	34.3220	4712.0000	68.6440	8.8332
ZN	106.4734	2.8374	32.2031	5.6748	5.3298
CU	64.3899	4.5786	83.8542	9.1572	14.2215
MN	115.4592	7.6307	232.9075	15.2613	13.2179
FE	23486.1406	1510.9836	32288.0000	3021.9675	12.8659
AL	2038.5928	149.5991	89519.6250	299.1982	14.6767
PB	13.5481	0.5884	1.3850	1.1769	8.6866
CD	6.7740	0.2942	0.3462	0.5884	8.6864
CO	13.5481	0.5884	1.3850	1.1769	8.6866
NI	13.5481	0.5884	1.3850	1.1769	8.6866